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THE MOVEMENT OF PESTICIDES WITHIN A MIXED LAND USE CATCHMENT

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ABSTRACT

Although the application of UK non-agricultural pesticides (mainly herbicides) comprises only 3% of the total amount used, similar concentrations of agriculturally and non-agriculturally derived pesticides are routinely detected in surface waters. This has led to concern regarding the contamination of drinking water resources at concentrations above the statutory limits of the EC Drinking Water Directive (ECDWD), and the consequent risk to human health. Before the risks to drinking water resources can be fully assessed, it is important to understand and subsequently predict the chronic and transient levels of herbicide occurrence in receiving surface waters as a result of their normal application. The factors which influence herbicide transport to the aquatic environment from sites of application, particularly from the wide variety of application substrates, are not fully understood. This project addresses this lack of knowledge through an eighteen-month programme (January 1992–March 1993) of storm event herbicide monitoring on a mixed land use catchment at North Weald (Essex) which periodically received applications of common agricultural and non-agricultural herbicides including chlorotoluron, isoproturon, diuron, simazine and atrazine.

To support the field monitoring programme a robust multi-residue pesticide method was developed for the simultaneous determination of the previously mentioned compounds from stormwater. This was based on liquid-liquid extraction into dichloromethane and high-performance liquid chromatography using photo diode array detection.

The pesticide runoff data from agricultural land agreed with similar experiments carried out in the UK. The ECDWD was frequently exceeded in baseflow conditions and more frequently during storm event periods. The extent of the exceedance was found to be related to the period which had elapsed between the herbicide application and the timing of the surface water sampling. The range of application losses for the agricultural data-set was 4.0×10^{-4}*–0.204% (median;* 4.6×10^{-2}*%). The range of peak storm event concentrations was 0.03–10.0μg/l (median; 0.34μg/l). Similar exceedances of the ECDWD were observed during storm and non-storm conditions for discharged waters from the urban land area of the catchment. For the urban runoff data-set, the range of application losses was 0.01–45.1% (median; 0.28%) and the range of peak storm event concentrations was 0.2–238.4μg/l (median; 0.7μg/l).*

The results of the monitoring programme show that the underlying factor that differentiated between the fates of herbicides applied to the North Weald catchment was the difference in the application substrate properties. Specifically, the hard surfaces, where low infiltration capacity promotes the generation of relatively high volumes of surface runoff and where poor retention behaviour exists, allow applied herbicides to be readily transported in storm event runoff to receiving surface waters.

The simazine, isoproturon, chlorotoluron and diuron runoff data produced during the monitoring programme were successfully modelled using the fugacity-based Soilfug model. In the case of chlorotoluron, this model's performance was compared with a statistical model produced using multiple linear regression analysis, which showed the former approach to be superior since it required less input data and was not site specific.

For Cathi

Heuldro'r Haf

Ar doriad gwawr yr Heuldro
A 'nghalon yn 'hedfan ar gan yr ehedydd

Y natur o'm hamgylch..... yn effro o gwsg y gaeaf
Sibrydodd yr hesg a'r brwyn mewn disgwyliad..... yn awyr mwyn Heuldro'r mor
Yn symyd yn agos, cawsom gysgod clyd ymysg sisial y tonnau

Roedd amser yn ddi-amser; ein gwefysau a'n eneidiau yn gymysg
Ein angerdd yn ddi-derfyn, yn heintrydd I erwinderau y lon oleu-leuad
Dawnsiodd ein calonau a'n hysbrydion .....yn gyflym dan wres Haul yr Heuldro

Mae Haul yr Heuldro yn bell wedi machlud
Ond mae'r galon a'r ysbryd yn dawnsio byth
A phob dydd yn gynnes o'r Heuldro o hyd.

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At Birmingham University, I'd like to thank Alan Turnbull for many useful discussions.

At Epping Forest District Council, I wish to thank Mike Hobbs, Kate Cook and Tony Gibbons.

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Finally the greatest thanks goes to my wife Cathi, for her unquestioning belief in me despite numerous broken promises and deadlines, and for her patience and understanding during the many occasions over the past few years when I've been unable to share her life.

DEDICATION

This work is dedicated to my parents and family, including the Davisses, for all their patience and support.

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1. Research rationale and thesis framework

1.1 Introduction

In the UK, the use of pesticides in agriculture, as the principal means of controlling pests, disease and weed infestation, has led to concern about the possible contamination of both groundwater (Foster *et al*, 1991) and surface water (Gomme *et al*, 1991) environments. In non-agricultural situations, herbicides have become an integral part of vegetation management by local and county authorities, rail operators and airport authorities (Ellis *et al*, 1997; Revitt *et al*, 1999).

There is significant evidence associating surface runoff derived pesticides with the contamination of receiving surface water at concentrations above the statutory limits of the EC Drinking Water Directive (80/778/EEC)[1] (Stangroom *et al*, 1998). Since the UK derives much of its drinking water from surface water resources (Fawell and Miller, 1994), of particular concern is the risk associated with pesticide residues therein (Williams *et al*, 1991). Before such risks can be fully assessed, it is important to understand and subsequently predict the chronic and transient levels of pesticide occurrence in receiving surface waters as a result of the normal application of agricultural and non-agricultural pesticides (Department of the Environment, 1996; Wauchope, 1996).

However, the full range of factors which influence herbicide release from sites of application and the mechanisms which govern the transport of herbicides in the aquatic environment are not fully understood (Williams *et al*, 1995; Johnson *et al*, 1994). This is particularly true in the case of the wash-off of herbicides from urban surfaces (Davies *et al*, 1995; Heather and Carter, 1996). Whilst a review of the literature shows an abundance of research dealing with the transport of agricultural pesticides in surface runoff, with the majority being in the United States, the amount focusing on the transport of pesticides applied within the urban environment is negligible. In view of this situation, a pesticide monitoring programme was initiated in collaboration with the ADAS Land

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[1] The EC Drinking Water Directive (80/778/EEC) permits a maximum admissible concentration (MAC) of 0.1μg/l for individual pesticides and 0.5μg/l for total pesticides.

Research Centre (LRC) Cambridge, to address this lack of knowledge by investigating the seasonal removal of commonly used pesticides, in the runoff from a catchment at North Weald (Essex) composed of agricultural and non-agricultural land.

1.2 Research objectives

The objectives of the research programme were as follows:

- To develop an analytical method for the simultaneous determination of common agricultural and non-agricultural pesticides.

- To equip the main watercourse of the North Weald catchment to allow the determination of the surface hydrology of the catchment and to sample elevated levels of surface runoff during rainfall events.

- To determine the application details of pesticides applied within the catchment between Autumn 1991 and Spring 1993.

- To determine the contributions of pesticide losses, to the main watercourse, resulting from normal applications to the agricultural and non-agricultural land between January 1992 and March 1993.

- To examine and compare the underlying factors that promote the transport of pesticides to the main watercourse with particular attention to the nature of the application substrate.

- To consider options for reducing the impact on receiving surface waters of pesticides used for agricultural and non-agricultural purposes.

- To investigate the use of fugacity and statistical modelling approaches for the prediction of pesticide concentrations and losses to the main watercourse from applications to agricultural and non-agricultural areas.

1.3 Implementation strategy

Building on information supplied by the Ministry of Agriculture Fisheries and Food (MAFF) Central Science Laboratory (CSL) Cambridge, a sensitive and efficient analytical method was developed for the simultaneous determination of eight commonly used agricultural and non-agricultural pesticides. Within the constraints of available laboratory resources, this enabled the reasonably efficient processing of runoff samples collected from the catchment during the monitoring period.

In collaboration with ADAS, the mixed land use catchment at North Weald was instrumented to allow the automatic collection of runoff samples during rainfall events and for the continuous measurement of catchment rainfall and runoff. This enabled the determination of the variation of pesticide concentrations and loads transported, from each land type, during a number of monitored rainfall events between January 1992 and March 1993. Further, it allowed the temporal surface hydrology of each land area to be determined and its affect on seasonal pesticide transport assessed. To aid the interpretation of the data collected during rainfall events, manual samples were collected during non-storm conditions.

Pesticide application data were collected through liaison with the major users within the catchment. These included two cereal farmers, London Underground Limited, and the Parks and Recreation and Roads and Highways Departments of Epping Forest District Council. Data were collated for the period between Autumn 1991 and Spring 1993. Together with the pesticide event-load data, this enabled the determination of a mass balance for each monitored rainfall event, and therefore allowed the temporal loss characteristics for each pesticide to be assessed.

Once complete, the pesticide runoff data set for each pesticide was compared and interpreted in terms of pesticide properties, application details and the nature of the application substrate. To investigate, in isolation, the runoff behaviour of pesticides applied to the railway line by London Underground, an artificial rainfall-runoff test was carried out on a sample of railway line ballast. These experiments enabled the transport and loss characteristics of each pesticide to be described in terms of individual physico-chemical properties, application data and the nature of the substrate to which the pesticide was applied.

To identify measures for reducing the impacts on receiving waters of agricultural and non-agricultural pesticide use, a literature review was carried out. For the two types of land use, the review describes the various options for (i) reducing pesticide use, (ii) minimising pesticide loss and (iii) treating pesticide contaminated runoff.

Where applicable, fugacity and statistical modelling techniques were applied to the agricultural and non-agricultural pesticide runoff data sets. For the fugacity approach, the SoilFug model written by Antonio Di Guardo whilst at Milan University (Di Guardo *et al*, 1994) was used. For the statistical approach, models were developed from the data sets using multiple linear regression analysis. The exercise allowed the comparison of the accuracy and usefulness of each modelling approach for the prediction of pesticide concentrations and losses during rainfall events.

1.4 Thesis framework

The thesis is composed of eight chapters. Chapters Two and Three describe the historical development of pesticides, their use and occurrence in the environment and relevant legislation and standards. Also described are the factors affecting the environmental fate and the current approaches to modelling pesticide loss to the aquatic environment. Chapter Four describes the North Weald catchment and the field and laboratory methodologies. Chapter Five separately discusses the surface hydrology of the catchment for the agricultural and non-agricultural areas. Chapters Six and Seven present and discuss the pesticide runoff data obtained from the monitored rainfall events sampled at the two stations, including inter-event manual sample data, between January 1992 and March 1993.

Finally, Chapter Eight compares the pesticide runoff data obtained from the agricultural and non-agricultural monitoring sites and discusses their occurrence in terms of their seasonal application and the nature of the substrates to which they were applied. This chapter continues with an investigation of fugacity and statistical modelling techniques for the prediction of pesticide runoff data from the agricultural and non-agricultural monitoring sites. Chapter Eight finishes with the final conclusions drawn from the monitoring data and recommendations for further work.

1.5 Details of published papers and meetings attended during the course of the research programme

1.5.1 Published papers, conference proceedings and poster presentations

Llewellyn, N. R., and Revitt, D. M.. Monitoring and control of pesticides in runoff. *Proceedings of. Environmental Protection and Control*, Valencia, UIMP, 7-11 September 1992.

Llewellyn, N. R., Revitt, D. M., Harris, G. L., and Ellis, J. B. The determination of pesticide losses in runoff from a mixed land use catchment. Poster presentation. *Environmental fate of chemicals: Prediction and measurement.* University of Lancaster, September 1992.

Rose, S. C., Harris, G. L., Catt, J. A., Nicholls, P. H., Llewellyn, N., and Mason, D. J. The Leaching of Agrochemicals under different agricultural systems. Poster presentation. *Proceedings of. Chemistry, Agriculture, and the Environment*, Robens Institute October 1992

Llewellyn, N. R., Revitt, D. M., Harris, G. L., and Ellis, J. B. The determination of pesticide losses in runoff. Poster presentation. *Proceedings of Chemical Research in Britain.* The Royal Society, London, June 1993.

Harris, G. L., Bailey, S. W., Rose, S. C., Mason, D. J., and Llewellyn, N. R. (1993). The Transport of Pesticide Residues to Surface Waters in Small Clay Catchments. *Proceeding of the Brighton Crop Protection Conference* **Weeds**, 815-820.

Ellis, J. B., Revitt, D. M., and Llewellyn, N. (1997). Transport and the environment: effects of organic pollutants on water quality. *Journal of the Chartered Institution of Water and Environmental Management* **11**, 170-177.

Revitt, D. M., Ellis, J. B., and Llewellyn, N. R. (2000). Herbicide behaviour in the runoff from an urban catchment. *The Science of the Total Environment.* Accepted for publication.

1.5.2 Meetings attended

- Pesticides in Soils and Water: Current Perspectives. British Crop Protection Council, Warwick University, 25-27/3/ 1991.

- 3rd Workshop on the Chemistry and Fate of Modern Pesticides. RIVM, Bilthoven Netherlands, 4-6/9/1991.

- Postgraduate Workshop on Urban Runoff. University Val de Marne, Paris, 11-15/5/1992.

- Fate and Prediction of Chemicals in the Environment. Royal Society of Chemistry, Lancaster University 7/9/1992.

- The Modelling of Chemicals in the Environment. Society of the Chemical Industry, Belgravia, London, 16/12/1992.

- Chemical Research in Britain. The Royal Society, London, 11/6/1993.

CHAPTER TWO

2. The Occurrence of Pesticides in the Environment

2.1 Introduction

During the latter half of the twentieth century, the quantity and number of uses of pesticides have increased significantly both in agricultural and non-agricultural situations (Llewellyn & Revitt, 1992). Within agriculture, the growth in pesticide use is associated with intensive and mechanistic farming practices which have been adopted to meet the growing demands for economic and efficient food production (Cheng, 1990). Pesticide use in non-agricultural situations has risen mainly as a result of the changing economic climate in the UK which has increased the unit labour costs of more traditional pestilence control practices. Also, industrial and amenity weed control has increased in order to satisfy society's demand for an aesthetically pleasing environment (Garnett, 1995).

The use of pesticides in agriculture as the principal weapon against pests, disease, and weed infestation has led to concern about possible contamination of the environment (Department of the Environment, 1979; National Rivers Authority, 1995; White & Pinkstone, 1995). This conçern also applies to the use of pesticides in non-agricultural areas especially herbicide use for total vegetation control on roads, hard surfaces and railways (National Rivers Authority, 1995; Garnett, 1995; Heather & Carter, 1996). Of particular concern is the detection of pesticide residues in surface and ground waters (Lees & McVeigh, 1988; Headworth, 1989), which are used for drinking water abstraction. For surface waters, research has shown that in many cases the principal source of pesticide contamination is from surface runoff entering receiving waters from sites of pesticide application (Clarke *et. al*, 1991; Croll, 1991). The factors affecting pesticide release from application sites and the mechanisms which govern the pathways and fate of pesticides in the agricultural and urban aquatic environment are presently not completely understood (Tooby & Marsden, 1991; Heather & Carter, 1996). Relevant institutions and organisations are currently engaged in research programmes in order to address the phenomenon of aquatic pesticide pollution (Heather & Carter, 1996; Beck *et al*, 1995; Brown *et al*, 1995; Harris *et al*, 1994; Gomme *et al*, 1991; this study).

Pesticide concentrations are routinely monitored in surface and groundwaters by the National Rivers Authority (from April 1996 known as the Environment Agency) and where deemed necessary, pollution control measures are implemented (National Rivers Authority, 1995). Pesticide concentrations in drinking water are routinely monitored by water service companies and the results reported annually by the Drinking Water Inspectorate (HMSO, 1995). However, research has shown that the sampling strategies employed in routine monitoring programmes are inadequate and misrepresent the episodic nature and extent of aquatic pesticide pollution (Williams *et al*, 1991).

Water service companies are currently introducing advanced water treatment systems which should enable full compliance with the EC Drinking Water Directive (Anon, 1980; White & Pinkstone, 1993; Court *et al*, 1995).

2.2 *What are pesticides ?*

2.2.1 Definition

A pesticide is defined under section sixteen of the UK 1985 Food and Environmental Protection Act as 'any substance, preparation or organism prepared or used for destroying any pest'. Pesticides are also categorised under this section as 'substances, preparations and organisms, which are used for the following purposes: (a) protecting plants or wood or other plant products from harmful organisms; (b) regulating the growth of plants; (c) giving protection against harmful creatures; (d) rendering such creatures harmless; (e) controlling organisms with harmful or unwanted effects on water systems, buildings or other structures, or on manufactured products; (f) protecting animals against ectoparasites'.

Therefore the term 'pesticides' includes insecticides, acaricides and nematicides (which respectively control insects, mites, and some types of worm), fungicides (for the control of diseases caused by moulds), rodenticides (to control rats and mice etc.), molluscicides (which control slugs and snails), herbicides (to control weeds) and growth regulators (for example to inhibit cereal straw length and induce branching in ornamentals).

The market for pesticidal products is large and diverse ranging from relatively minor use in the home with products such as fly spray to the major use in agriculture of herbicidal products for the production of cereal crops.

2.2.2 Historical development

The use of chemicals in pest, weed, and disease control is not particularly new as for centuries farmers have used remedies involving naturally occurring chemicals. The ancient Greek philosopher, *Homer,* mentions the use of sulphur as a fumigant as long ago as 1000 B.C. In 100 B.C. the Romans used the plant *hellebore* to control rats and mice, and by A.D. 900 the Chinese were using arsenic to control garden pests.

It is only in the early to mid-twentieth century that chemical control methods have become more widespread. Until the 1940s, the chemical control of pestilence relied on the use of very few substances. These were mainly inorganic compounds such as copper and mercury salts, elemental sulphur as a fumigant, and general poisons, such as arsenical compounds and cyanide for the control of insects. Common preparations included *Bordeaux mixture*, prepared by mixing copper sulphate, lime and water, which was used to protect vines in Europe from fungal attack. Also, *Paris green*, an insecticide prepared from copper arsenite was used against caterpillars and beetles. Sodium chlorate was commonly used as a 'total weed-killer'; it was effective for many months but was easily washed away by rain to nearby watercourses. It had the disadvantage that under dry conditions it readily exploded, and could cause serious fires when used around buildings. Organic compounds included various by-products, for example, tar distillates, and plant extracts such as nicotine, derris and pyrethrum. Few of the available pesticides acted specifically against particular pests and selectivity was usually a matter of application timing. Their use was mainly confined to high value crops such as fruit, hops, market garden and glass-house crops.

The modern agrochemical industry has largely developed and grown from the early 1930s (Turnbull, 1996). In 1932, the translocated chlorinated phenoxyacid herbicide, 2,4-D, was discovered and used mainly to control broad-leafed weeds in cereal crops, but was found to have limited use due to its rapid breakdown in the environment. In 1942 it was replaced to a larger extent by MCPA, which was found to be more effective due to its greater persistence. The term 'translocated' refers to a herbicide which is absorbed by the roots or leaves of a plant before killing it. Certain insecticides also move within the plant and may, for example, pass from the roots to kill insects feeding on the leaves; these are termed 'systemic' insecticides. Alternatively, insects and plants can be poisoned directly by 'contact' insecticides and / or herbicides.

During the 1939-45 war, two groups of new insecticides and fungicides came into use. The first consisted of the organochlorines, of which DDT is the most familiar but also included hexachlorobenzene (HCB) and the structurally similar insecticide hexachlorocyclohexane, or HCH (historically known as benzenehexachloride–BHC and commonly known as lindane). The second group was discovered during research on allied compounds. These were the organophosphates, like mustard gas which was being tested for chemical warfare. Parathion (a deadly poison to man) was the first member of this group to be widely used. The great virtue of these synthetic chemicals was that industry could produce them in unlimited quantities. DDT was synthesised in the laboratory in 1874, but its insecticidal properties were only discovered in 1939. It was first widely used to control the Colorado beetle, which threatened to destroy the Swiss potato crop, in 1941. DDT was used extensively towards the end of the war to control typhus epidemics; the disease was spread through civilian and military populations by the body louse *Pediculus humanus*.

With the end of the Second World War the UK government recognised the importance of self-sufficiency in food production, and began to develop UK agriculture and increase efficiency through the use of intensive and mechanistic methods. This involved an increasing reliance on pesticides and chemical fertilisers, the introduction of more complex machinery and the removal of hedgerows to create larger, more manageable fields. By 1953, the insecticidal seed dressings, dieldrin and aldrin, were being introduced into the UK. Great gains were seen to be had through the use of organochlorine pesticides, and from the mid 1950s to the mid 1970s they were used extensively to boost the UK's agricultural output.

Due to their hydrophobic properties and greater persistence, organochlorine pesticides were seen to bio-accumulate and bio-magnify within the fatty tissue of mammals such as predatory birds that either ingested the compounds directly, from treated targets, or from species lower down in the food chain (Turnbull, 1996). In the UK, this effect was most manifest amongst populations of seed-eating birds which were found dead in the fields in the spring. Also there were disturbing reports of a fall in the numbers of breeding peregrines and sparrowhawks, possible damage to golden eagles and buzzards, and deaths of foxes and badgers. Eventually this was found to be caused by seed corn dressed with aldrin or dieldrin to protect the young seedlings from attack by the larvae of the wheat bulbfly, *Leptophylemyia coarctata.* As a result, the use of the aldrin and dieldrin as seed treatments was restricted in 1961. Their use was to some extent replaced by DDT which also went on to have a serious ecological effect on some species of predatory birds. At first this was difficult to understand as although the birds were picking up DDT the levels in their tissues were generally well below those known to be harmful. This was largely because the DDT was considered to be 'detoxified' by being transformed by metabolism to DDE, a compound of much lower toxicity. However, eventually it was found that DDE, particularly among birds, has other properties. It is responsible for causing the birds to lay eggs with thin shells which are easily broken in the nest and which reduce breeding success (Mellanby, 1992).

Further problems were caused through the over-use of organochlorine pesticides. In some instances this led to the development of biological resistance within target organisms. One historical example of this can be seen from the 1961 cotton harvest in Egypt. Despite increasing the recommended dose by 100%, 10,000 tonnes of toxaphene could do nothing to prevent a 50% loss of yield during 1961 (El Sebae *et al,* 1993). Due to the environmental impact of most organochlorine pesticides, their general use had been significantly restricted by the 1990s by the relevant regulators in the developed world. However, they are still widely used in the third world.

During the 1960s, public concern for the ecological impacts on the environment of the widespread use of organochlorine pesticides began to grow. This concern was brought to the forefront of the general public's attention by Rachel Carson and her book 'Silent Spring', in which she highlighted the rapid bio-accumulation and acute toxic effects of organochlorine pesticides on American and

European rural wildlife (Carson, 1962). Subsequently, use of organochlorine pesticides has decreased, growth in availability of new chemicals has occurred and recent growth in the number of active ingredients used within herbicide formulations has been rapid. Active ingredients are from a number of chemical groups including phenoxyacids, benzoic and acetic acids, phthalic compounds and triazine compounds. Recent developments have led to the introduction of phenylurea and sulphonylurea compounds. Application rates of pesticides are variable, and are generally higher when used for non-agricultural purposes. Typical rates of agricultural and non-agricultural pesticide application in the UK are in the range 0.2-5.0 kg(a.i.)/ha/annum and 2.0-35.0 kg(a.i.)/ha/annum, respectively. (a.i.: active ingredient.)

Since the 1940s the world agrochemical market has developed rapidly, and in the late 1970s it continued to expand at an average rate of above 6% per annum. The 1980s and 1990s have seen a decrease in the growth rate as the overall agrochemical market now approaches maturity. This international market behaviour is typified by the UK agrochemical industry. With the general expansion of the agrochemical industry, both the number of chemicals (active ingredients) approved for formulation into products, and the number of registered pesticide products have increased significantly (see Table 2-1).

Table 2-1 Growth in number of active ingredients (1950-1992) and products (1944-1992)

Year	Number of active ingredients	Number of products
1944	n/a	63
1948	n/a	216
1950	15	n/a
1952	n/a	352
1955	27	n/a
1956	n/a	446
1960	47	n/a
1964	n/a	540
1965	83	n/a
1968	n/a	783
1970	163	n/a
1972	n/a	810
1975	200	n/a
1976	n/a	819
1992	450*	3000*

Source: *Sly S.M.A. in Ecological Effects of Pesticides. Academic Press. London. 1977.*

** MAFF Pesticide Handbook. 1992.*

n/a = not available

2.3 Pesticide use: Legislation and regulation

Comprehensive legislation governs the use of pesticides in the UK (National Rivers Authority, 1995). These controls are set out and implemented through Part III of the Food and Environmental Protection Act (1985) (FEPA), the Control of Pesticides Regulations (1986) (COPR) and the Medicines Act (1968), which from the 1st January 1995 was replaced by the Marketing Authorisations for Veterinary Medicinal Products Regulations (1994).

The primary aims of FEPA are to:

- protect the health of human beings, creatures and plants;
- safeguard the environment;
- secure safe, efficient and humane methods of controlling pests;
- make information about pesticides available to the public;

These aims are achieved by ensuring that prospective pesticidal chemicals and subsequent formulated products are subject to rigorous registration procedures prior to approval of successful chemicals and products by government ministers.

2.3.1 Approval of the use of pesticides

Under the provisions of COPR, to obtain approval to use a new pesticide, manufacturers must submit data with respect to aquatic toxicity; studies on bioaccumulation; and mobility and persistence in the environment, to the relevant Government organisation (see below). However, it has been suggested that the data generated are not always scientifically the most useful, and the fundamental principles involved with pesticide fate are not sufficiently well understood to enable a satisfactorily quantitative risk assessment to be undertaken (Tooby and Marsden, 1991).

The Government organisations are:

- Ministry of Agriculture, Fisheries and Food (MAFF), **Pesticide Safety Directorate (PSD)** for pesticides used in agriculture, horticulture, amenity, forestry and gardens.

- Health and Safety Executive (HSE), **Pesticide Registration Section (PRS)** for non-agricultural pesticides, including wood preservatives, surface biocides, antifouling paints and pest control products.

Approval for veterinary medicines involves two stages of environmental risk assessment. The first phase assesses likely exposure to the environment resulting from use, excretion and disposal. If this exposure is significant, then the second phase is carried out, where data on fate and ecotoxicology are required according to the level of environmental exposure. The data are submitted to:

- Ministry of Agriculture, Fisheries and Food (MAFF), **Veterinary Medicines Directorate (VMD),** for pesticides used as veterinary medicines such as sheep dips.

Approval for the use of pesticides and most biocides requires clearance by six Government Departments following recommendations made by a panel of experts known as the **Advisory Committee on Pesticides (ACP).** The three mentioned government organisations process and disseminate data received from manufacturers and then pass it on to the ACP, which assesses the evidence for the potential impact of the pesticide.

2.4 Use of pesticides

The use of pesticides is divided between agricultural and non-agricultural purposes. Agricultural uses are mainly confined to crop and livestock protection, whereas non-agricultural uses are considerably more diverse, ranging from industrial weed control to domestic fly spray.

2.4.1 Agricultural use of pesticides

During the past twenty to thirty years, the use of pesticides has become an integral part of most crop production systems and a vast array of insecticides, fungicides and herbicides are now available to farmers and growers (Walker, 1991). Since the 1940s many changes have occurred within British agriculture. What was once regarded as a way of life has in many cases become an industry bound by market economic principles. In the UK, the need to produce high yields and increase self-sufficiency was initially encouraged by post-war government policy, but more recently in some quarters, the expansion of agriculture has been artificially sustained through the effect of EEC legislation via The Common Agricultural Policy (CAP), where farmers have a guaranteed price for their produce.

During the past half-century, the output per head employed in UK agriculture has increased at about double the rate of productivity improvement in the rest of the economy. Since the war the average milk yield from the nation's dairy herd has more than doubled; average sugar-beet yields have nearly doubled and those of wheat have increased by more than 150 per cent (Malcome, 1989). This expansion, fundamentally driven by economic forces, required farmers to seek more efficient and more cost effective techniques of production. This has been achieved through the application of industrial, biological and chemical technology to traditional farming practices. Farms have increased in size and developed intensive farming practices with a reduced range of farming activity, sometimes to levels referred to as 'monocultures'.

The revolution in farming production was brought about through adoption of new techniques and practices that covered every aspect of crop production, some of which were researched on MAFF Experimental Husbandry Farms such as Rothamstead (Stevenson, 1994). These included the use of specialist machinery and methods to improve field management by installing field drainage systems to either increase or allow crop production on previously seasonally water logged soils; the education and training for those engaged in the industry; and the planting of improved crop varieties.

An important factor which brought about higher crop yields was the development of agrochemicals such as fertilisers, pesticides and growth regulators. Modern cereal varieties rely on a high nitrogen input to reach their full yield potential, and to stop unwanted stem length, growth regulators are often applied. In some cases high nitrogen usage increases the susceptibility of the crop to pests and diseases, thus requiring a pesticide spray programme. Prior to sowing, seeds are treated with a pesticidal dressing to minimise pest damage during the early part of the growing cycle. Immediately before harvest, the crop is sprayed with a chemical desiccant which induces rapid drying of the plants, enabling more efficient harvesting. Thus by utilising modern agrochemicals the farmers of the late twentieth century can to some extent remove the elements of chance traditionally associated with farming and operate an intensive, mechanistic and pre-programmed approach to crop production.

In comparison with the varied and diverse applications of pesticides used for non-agricultural situations, the number of agricultural uses is relatively limited; however, the extent of use is significantly higher. Herbicides constitute the major proportion of all pesticides used agriculturally. Within agriculture the main use of pesticides is for the protection and subsequent high yield production of arable cereal crops such as barley and wheat etc.. Other uses include the protection of: (i) arable root crops (potatoes and sugar beet etc.); (ii) animal fodder, forage and seed crops; (iii) vegetables; (iv)orchards and (v) hops.

The Ministry of Agriculture, Fisheries and Food's Pesticide Survey provides current and historical usage of pesticides in agriculture in England and Wales. The quantity of active ingredients applied has increased considerably from the early 1970s to the 1980s for almost all groups of pesticide. The changes for cereals, the largest group of arable crops, are summarised in Table 2-2. Since the 1980s the introduction of new active ingredients such as sulphonylureas, effective at lower quantities per area, has led to a steady decline in the total quantity of active ingredients applied. This is currently in the region of 23,000 tonnes per annum, of which 37.8% are herbicides and 23.6% are fungicides. Listed and classified in Table 2-3 are the main agricultural and horticultural pesticides in current use in the UK; tonnes used per annum are shown along with pesticide type.

Table 2-2 Pesticide usage in agriculture and horticulture in England and Wales, 1977-1994

Year	Herbicides [1] (tonnes a.i.)	Fungicides (tonnes a.i.)	Insecticides [2] (tonnes a.i.)	Others [3] (tonnes a.i.)	All pesticides (tonnes a.i.)	Area grown (hectares)
1977	11,145	2,773	2,026	1,039	16,984	9,337,351
1982	18,858	4,635	1,324	3,686	28,502	10,499,759
1988	13,556	6,110	1,463	2,395	23,525	10,500,235
1990	10,888	5,990	1,225	2,927	21,030	10,303,048
1992	9,879	5,946	1,124	2,984	19,933	10,221,219
1994	8,891	5,390	1,416	2,879	18,576	10,368,825

[1] excludes sulphuric acid used as a crop desiccant, [2] includes acaricides, molluscicdes & tar oil, [3] includes plant growth regulators

Information courtesy of MAFF Pesticide Usage Survey Group, Harpenden

Table 2-3 Annual usage of pesticides in agriculture and horticulture in England and Wales in 1992.

Active ingredient	Type	tonnes/year	% of total	Active ingredient	Type	tonnes/year	% of total
Sulphuric acid	D	6,023	*	Diquat	H	159	0.96
Isoproturon	H	2,750	16.63	Propiconazole	F	153	0.93
Chlormequat	PGR	2,214	13.39	Simazine	H	151	0.91
Mancozeb	F	1,208	7.30	Flusilazole	H	128	0.77
Chorothalonil	F	936	5..66	Fluroxypyr	H	127	0.77
Mecoprop	H	607	3.67	Chloridazon	H	117	0.71
MCPA	H	590	3.57	Dimethoate	I	114	0.69
Chlorotoluron	H	579	3.50	MCPB	H	101	0.61
Sulphur	F	535	3.24	Atrazine	H	100	0.60
Fenpropimorph	F	516	3.12	Phenmedipham	H	99	0.60
Mecoprop P	H	513	3.10	Terbutryn	H	97	0.59
Pendimethalin	H	498	3.01	Ethofumesate	H	93	0.56
Maneb	F	466	2.82	Mepiquat	PGR	91	0.55
Trifluralin	H	347	2.10	Flutriafol	F	91	0.55
Glyphosate	H	288	1.74	Bentazone	H	90	0.54
Tri-allate	H	262	1.58	Bromoxynil	H	89	0.54
Fenpropidin	F	259	1.57	Linuron	H	88	0.53
Carbendizim	F	255	1.54	2,4 DB	H	86	0.52
Metamitron	H	247	1.49	Paraquat	H	83	0.50
Tridemorph	F	195	1.18	Metaldehyde	M	82	0.50
Prochloraz	F	190	1.15	1,3-Dichloropropene	N	81	0.49
Formaldehyde	F	186	1.13	Methabenxthiazuron	H	78	0.47
Tar oil	I,F	181	1.09	2,4 D	H	75	0.45
Propachlor	H	177	1.07	Propyzamide	H	72	0.44
Methyl Bromide	F	175	1.06	Cynazine	H	72	0.44

(*) % of total calculations omit sulphuric acid desiccant

H - Herbicide, I - Insecticide, F - Fungicide, N - Nematicide, M - Molluscicide

Information courtesy of MAFF Pesticide Usage Survey Group, Harpenden.

2.4.2 Non-agricultural use of pesticides

Over the past fifty years pesticides, especially herbicides, have become an integral part of the management of weeds in non-agricultural areas (Garnett, 1995). Their adoption has been encouraged by the advantages of practicality and cost effectiveness, especially in respect of the changing UK economic climate. During the latter half of the century it gradually became more cost effective to replace traditional methods of weed control with chemical methods. The first widely used total weed control, or non-selective, herbicide products were based on sodium chlorate and boric acid (Woodford & Evans, 1963). They were used at very high application rates 56-448 kg/ha and 1180-5020 kg/ha respectively, up until the mid 1960s when they were gradually replaced by the introduction of herbicides based on synthetic organic chemicals (see Table 2-4). A single application of these residual herbicides was found to be effective over the weed growing season at much lower application rates, typically 3.5-35 kg/ha depending on the level of weed control required. They were originally developed for agricultural use but the active ingredients were later reformulated for non-agricultural uses.

Table 2-4 The introduction of the major non-agricultural herbicides

Active ingredient	Year introduced
Simazine	1956
Monuron	1957
Dalapon	1957
Atrazine	1958
Amitrole	1960
Diuron	1960
Paraquat	1962
Dichlobenil	1965
Bromacil	1965
Picloram	1967
Glyphosate	1976
Imazypyr	1985

At the beginning of the 1970s, atrazine and simazine came off patent and rapidly became the most widely used of the active ingredients registered for use as non-agricultural herbicides. They were formulated in products on their own or blended with amitrole or translocated herbicides such as mecoprop, MCPA and 2,4-D. During the 1970s and early 1980s considerable quantities of triazine-based products were used; they were found to be very effective and eventually dominated the weed control programmes of many users who used them exclusively in place of non-chemical methods.

Heavy reliance on triazine based products continued up until the late 1980s when the routine monitoring of water authorities began to regularly report their occurrence in drinking water at significant levels. In May 1992, after advice from the Advisory Committee on Pesticides, MAFF revoked the use of the triazines for non-agricultural purposes; triazine users were given until September 1993 to deplete their stock-piles. With the removal of the triazines some users totally reappraised their use of herbicides as part of their weed control programmes and went on to use lower quantities of other products, generally based on diuron and glyphosate, to supplement programmes based on more traditional non-chemical means of weed control. Other users simply continued with their existing programme strategy but used diuron- and glyphosate-based products in place of the triazines.

Non-agricultural areas can generally be divided on the basis of their substrate, known as either hard or soft surfaces. The majority of pesticide application are made to hard surfaces to control annual and perennial weeds. Hard surfaces are characterised by the absence of soil and are typically constructed of concrete, asphalt, rock ballast, rock chippings, gravel or some other mineral-based material. Areas falling into this category include roads, railways, non-soil sports grounds, airport pavements, paths and general surfaces in municipal urban areas such as shopping centres and industrial estates. Such areas are now officially called 'land not intended to bear vegetation' by the Pesticide Safety Directorate. Soft surfaces are described as areas of soil generally bearing some kind of plant cover which is usually grass. This covers very diverse situations ranging from forestry fire breaks to municipal parks, recreational areas, private and public gardens, and golf courses.

The main reasons for controlling weeds in non-agricultural areas are engineering safety and aesthetics.

- **Prevention of structural engineering damage:**

  Plant growth, especially root ingress, opens up the surface layers to water and freeze-thaw damage, impairs drainage and results in the rapid decay of the surface and general structural integrity.

- **Safety considerations:**
  (i). The establishment of weeds can produce uneven surfaces, particularly where surfaces are made up of concrete paving slabs or blocks.
  (ii). Road surface grip can be affected which is particularly important at junctions and crossings.
  (iii). The proliferation of weeds at road junctions can seriously affect the visibility of car drivers and other road users. Also the visibility of signalling equipment on railway lines can be impaired.
  (iv). On railway tracks, sun-dried weeds can cause a serious fire hazard to electrically operated signal equipment and the associated control wires.
- **Aesthetics:**

  Aesthetics' or the visual impact of the local urban environment is perceived to be a significant public concern. It is considered that the general public expect urbanised areas such as towns and city centres to be free of weeds and have an ordered and cleansed appearance. Often weed populations that may be tolerated in some circumstances are likely to be unacceptable in amenity situations, particularly large paved areas such as shopping centres, pavements and car parks.

A report on the non-agricultural use of pesticides in Great Britain (Department of the Environment, 1974) has identified many diverse applications. These range from the domestic use of pesticides, mainly for insect control, wood preservation, and garden pest control, to extensive industrial use including the manufacture of pesticidal products (fly spray etc.), pesticides added to products for protection and preservation before and after sale (mothproofing of carpets etc.), and finally pesticides used for the protection of raw materials in store and during shipment (raw wool etc.). The report also identified the use of pesticides, especially herbicides, by public and local authorities. Public authorities included British Rail (since 1994 referred to as Rail Operating Companies) and British Airports Authorities which use herbicides for total vegetation control on hard surfaces. Local authorities chiefly use herbicides for the total control of vegetation on municipal roads and paved areas and selective weed control in parks, public gardens, sports grounds and golf courses. Insecticides and rodenticides are also used to control the pestilence associated with rubbish tips.

The total quantity of pesticides used in areas covered within the DoE report (Department of the Environment, 1974) was 57,000 tonnes of active ingredient, although at least 53,000 tonnes were accounted for by wood preservatives. A high proportion of the remaining 4,000 tonnes consisted of herbicide use for total vegetation control on land not intended for cropping, principally hard surfaces. The largest users of herbicides were local authorities (1,870 tonnes active ingredient) followed by British Rail (1,000 tonnes, formulated product). It was noted that British Rail considered that information on the quantities of individual herbicide used was commercially valuable and should not be published. The herbicides used included atrazine and simazine. The DoE report concluded that in general the uses dealt with involved only a small quantity of pesticide compared with that used in agriculture. However, some of the non-agricultural uses represent a large share of the market for certain pesticides, either because the pesticides have never been widely used in agriculture or because use has been restricted such as in the case of certain organochlorine pesticides.

In a more recent survey (Department of the Environment, 1991), the use of herbicides in non-agricultural situations in England and Wales was reported for 1989. Data was collected from the following user groups.

- **Local Authorities**

  County Councils, Metropolitan Councils, District Councils and Health Authorities:- road and highway maintenance, maintenance of parks, recreational areas and municipal paved areas.
- **Power and Industry**

  Maintenance of industrial sites and storage facilities, gas, electricity and coal boards, manufacturing industry and defence industry.

- **Transport**

  Railway operators, airport and port authorities. (Road maintenance comes under local authorities).

- **Water Companies**

  Water service companies and statutory water companies.

- **Golf and leisure**

  Golf clubs, leisure and recreational facilities (not covered by local authorities), theme parks and race courses.

The data collected shows that in 1989, 550 tonnes of active ingredient (a.i.) was used in England and Wales. Industry was shown to be the largest consumer, using 34% of the total, followed by local authorities (33%) and transport (21%). Of the 550 tonnes of active ingredients used, the triazines (atrazine and simazine) accounted for 39%, followed by phenoxyacid compounds (2,4-D and mecoprop) at 21%, and urea compounds (diuron) which constituted 13% of the total. The data was also classified by surface of application and showed that 43% was applied to hard surfaces, 16% to grassed surfaces, 7% to 'other' surfaces and 31% of the survey respondents did not know the nature of the application surface. Under the classification system used, urban road verges were classed as grassed surfaces. Given that these areas are generally constructed of concrete kerbstones and asphalt or concrete paving slab pavements, they would have been more accurately classed as hard surfaces. It was therefore likely that the quantity of herbicide applied to hard surfaces would be significantly higher than 43%. The report was constructed from the replies of 350 respondents and has recently been criticised for its limited scope and significant lack of understanding of the subject area (Thomas, 1996 pers comms).

The total figure of herbicide use in 1989 is surprisingly low compared with that previously reported (Department of the Environment, 1974). The recent survey (Department of the Environment, 1991), reports that 137.5 tonnes (a.i.) of atrazine was used during 1989 for non-agricultural purposes. In an account of chemical pollution of the aquatic environment, Crathorne & Dobbs (1990), estimated that in 1987, 5000 tonnes (a.i.) of atrazine were applied non-agriculturally and 50-200 tonnes (a.i.) were used agriculturally on minor UK crops such as maize and sweetcorn. More recently, from a study of pesticide levels in the surface and ground waters within the region covered by the Anglian Water Company, Croll (1991) has suggested that the national use of triazines may be in the region of 1,000 tonnes (a.i.). The actual annual level of triazine application for non-agricultural uses during the 1989-90 period appears to vary according to the source of reference. However, given the extent and widespread nature of the triazine contamination reported for surface and ground waters at that time (Lees & McVeigh, 1988) it can be suggested that quantities of triazines used for non-agricultural purposes may be somewhat higher than that reported in the 1991 DoE report. This may also have been the situation for other non-agricultural pesticides used at that time.

The most recent information regarding the levels of pesticide used non-agriculturally has been compiled by the MAFF Pesticide Usage Survey Group (PUSG) for Wales, Scotland and England. Unfortunately the full report was only available at considerable cost, however PUSG released a brief document summarising the data collected from UK local authorities in which it described details of the most important user group (Wardman and Goodwin, 1994). Of the pesticides used by local authorities, 94% were herbicides used in the weed control programmes of roads and highways, parks, amenity grass and municipal paved areas. The document stated that pesticide usage by local authorities represented less than 1% of all agricultural and horticultural inputs. This equates to less than 186 tonnes (a.i.) per annum which is in the same order as the quantity reported by the 1991 DoE report of 181.5 tonnes (a.i.) per annum . Herbicide usage was dominated by glyphosate-based products used to control both annual and perennial weeds in amenity situations whereas diuron-based products were widely used for general weed control. Seasonal usage showed that most applications (42%) were made in the spring. Patterns of usage with respect to application surface showed greatest use on hard surfaces.

2.5 Water quality in the UK

In the UK, the quality of water is controlled and monitored by two major bodies and relevant Acts of Parliament and Regulations. The National Rivers Authority (NRA), or from April 1st 1996, The Environment Agency (EA), is responsible for all controlled waters while the quality of drinking water is the responsibility of the Water Supply and Service companies.

2.5.1 Surface and groundwater quality

At present, data reflecting levels of pesticide contamination in the UK's surface and groundwaters are available from the EA's routine statutory monitoring programmes and from other research-based monitoring surveys. The latter are usually carried out on a collaborative basis involving the Agricultural Development Advisory Service (ADAS), the Water Research Centre (WRc), the EA, the Institute of Hydrology (IH), and academia. The provision of these data sources is relatively recent, driven by the requirements of the EA, created from the Water Act 1989, and the subsequent statutory monitoring duties contained in the Water Resources Act 1991.

From the early 1980s onward, concerns were expressed regarding the relatively unchecked presence of pesticides in the UK's surface, groundwater, and drinking water resources and also at the limitations of water suppliers' pesticide monitoring programmes. This concern was earlier expressed by the 1979 Royal Commission on Environmental Pollution in its statement *'the use of pesticides as the principal weapon against pests, disease, and weed infestation has led to concern about possible contamination of the environment'* (Department of the Environment, 1979). The EC Drinking Water Directive (80/778/EEC) was drafted in 1980 and became EC law in July 1985, and UK law in September 1989 with its incorporation into the Water Supply (Water Quality) Regulations. The Directive specifies a maximum admissible limit (MAC value) of 0.1μg/l for individual pesticides and 0.5μg/l for total pesticides. Prior to 1989, Water Authorities and Water Companies were provided with non-statutory advice and urged to follow guidelines in establishing their own codes of practice and operational procedures to minimise pesticide contamination (Water Authorities Association, 1984 & 1988). Upon the drafting of the Directive, a number of the then Water Authorities initiated monitoring surveys of their drinking water resources in order to construct basic databases of pesticide concentrations and trends on which to make decisions regarding the monitoring programmes and clean-up processes. These were required in order to comply with the Directive which in time would become incorporated into UK law.

2.5.1.1 *The Anglian Water Authority survey*

The first major research-based survey to be carried out on the level of pesticide contamination in surface and groundwater was initiated in 1982 by the then Anglian Water Authority (Croll, 1986). The Anglian region contains a substantial amount of the productive arable land (approximately 34% of the total land area), and the region is characterised by the intensive production of crops and the associated widespread use of pesticides. Between 1982 and 1984, approximately 600 samples were taken as part of a survey of all its drinking water sources, including surface water and bore-hole groundwater abstraction points. With the completion of the initial monitoring programme, the results were assessed and fed into the design of a second monitoring programme, carried out between 1985 and 1989. Particular attention was paid to: (a) positive results, (b) catchment considerations, (c) the properties of the pesticides, and (d) the requirements of EC Directives. During this second survey approximately 700 samples from rivers, reservoirs and groundwaters were analysed (Croll, 1991). The sampling frequencies that were used are shown in Table 2-5 and the subsequent results are summarised in Table 2-6.

Table 2-5 Sampling frequencies used in the second Anglian Water pesticide monitoring survey (1984-1989)

Type of water	Sampling frequency	
	A Pesticides detected or considered to be potential pollutants	B Pesticides undetected and thought unlikely to be pollutants
Surface waters	Surface water Directive (A2 II), 2 or 4 per annum	1 per annum
Groundwater - fast response (e.g. gravels)	1 per annum	1 per 2 years
Groundwater - slow response	1 per 2 years	1 per 4 years

After Croll, 1991

The data contained in Table 2-6 shows that there is close agreement between the concentrations of compounds that were determined in both monitoring programmes. The results show that isoproturon was the most frequently detected pesticide in surface waters followed by atrazine, simazine, chlorotoluron and mecoprop. In groundwaters pesticides were detected relatively infrequently with atrazine most commonly detected followed by simazine, isoproturon, chlorotoluron, and mecoprop. Excluding atrazine and simazine, the level of individual pesticide occurrence corresponded reasonably well with national pesticide usage. The ubiquitous presence of atrazine and simazine in surface and groundwaters was attributed to high runoff losses from non-agricultural applications to roadside verges, railways, and industrial estates (Croll, 1991).

Table 2-6 The concentration of pesticides in surface and groundwaters; Anglia water Surveys 1982-1984 and 1985-1989

Pesticide	Initial Survey 1982 - 84		Second Survey 1985 - 89			
	Surface water	Groundwater	Surface water		Groundwater	
	Range	Range	Range	Occurrence (% samples)	Range	Occurrence (% samples)
Lindane	nd	nd	<0.01 - 0.055	16	nd	
Dimethoate	nd	nd	<0.02 - 0.94	14	nd	
Diazinon	nd	nd	<0.01 - 0.23	1	nd	
Mecoprop	nd	0.1 - 0.38	<0.1 - 5.1	35	0.1 - 0.38	3
MCPA	0.02 - 2.3	0.12	<0.1 - 16	1	0.12	0.5
2,4-D	0.2 - 2.5	0.11 - 0.2	<0.2 - 2.1	1	0.11 - 0.2	1
Dichloroprop	nd	nd	<0.1 - 0.5	1	nd	
Dicamba	nd	nd	<0.1 - 0.3	1	nd	
Atrazine	0.2 - 1.4	0.2 - 0.5	<0.02 - 9	58	0.02 - 0.43	28
Simazine	nd	nd	<0.02 - 7.1	42	0.02 - 0.26	9
Ioxynil	nd	nd	<0.04 - 0.1	2	nd	
Bromoxynil	nd	nd	<0.02 - 0.1	4	nd	
Chlorotoluron	nd	nd	<0.1 - 2.6	38	0.1 - 0.12	3
Isoproturon	nd	nd	<0.05 - 11.5	84	0.1 - 0.41	6
Linuron	nd	nd	<0.2	0	nd	
Propyzamide	nd	nd	<0.1 -2.23	2	nd	

Modified from Croll, 1986 & 1991; nd = not determined

In order to obtain information on the temporal variation of pesticide levels in surface waters, weekly sampling of atrazine, simazine, and isoproturon was carried out at a river site in 1988; the results are shown in Figures 2-1 and 2-2. The isoproturon and atrazine data were reported to show similar variation to the less frequent routine monitoring survey, however no suggestions were proposed to explain the seasonal pattern of the temporal variation.

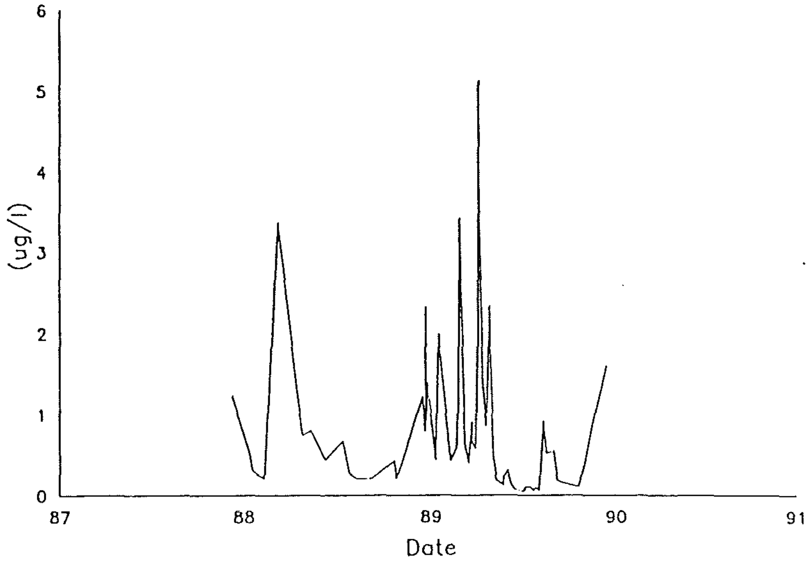

Figure 2-1 Temporal variation of isoproturon concentration in river water over a two year period, 1988-1990. (*After Croll, 1991*)

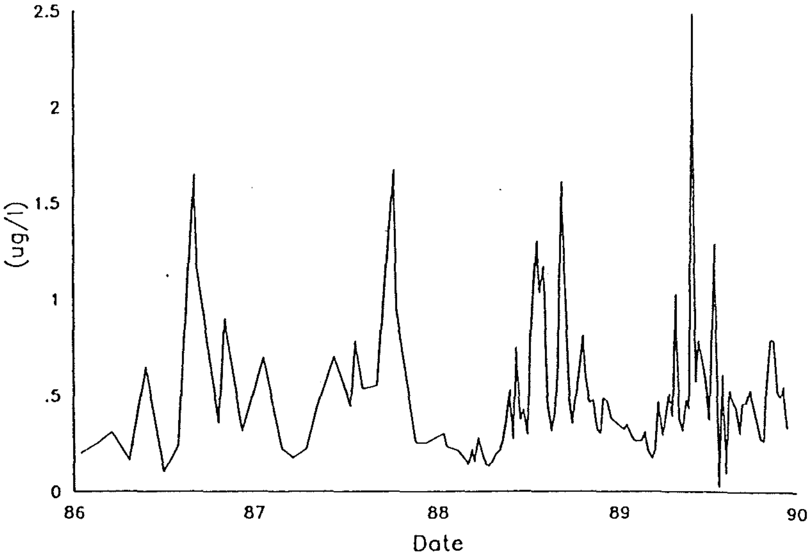

Figure 2-2 Temporal variation of atrazine concentration in river water over a two year period, 1988-1990 (*After Croll, 1991*)

2.5.1.2 The Granta catchment study

The monitoring survey of the chalk-based Granta catchment was more comprehensive than the Anglia Water survey in a number of ways. Between March 1987 and December 1988 surface water was taken from the River Granta at three locations and analysed for twenty pesticides on a monthly basis. At each sampling location the river flow was continuously gauged. The twenty pesticides reflected those most heavily used within the catchment as identified by a detailed survey of land and pesticide use (Fisher *et al*, 1991). Also, a detailed groundwater sampling survey was carried out between October 1987 and January 1990, in which four drinking water supply bore-holes and ten observational bore-holes were sampled (Gomme *et al,* 1992). The results of the river and groundwater survey and usage of individual pesticides within the catchment are shown in Table 2-7. Of the twenty pesticides in the analysis suite, fourteen were detected at least once in river water during the eighteen-month monitoring period. Apart from the most heavily used pesticides (isoproturon, mecoprop, and tri-allate) there was no obvious relationship between pesticide usage and occurrence. In particular, simazine and atrazine were frequently detected, while several more heavily used pesticides (chlorothalonil, ioxynil, bromoxynil, and captafol) were not detected at all.

The monthly river monitoring showed a significant relationship between elevated pesticide concentration and high river flow which mainly occurred in the winter and early spring months. Also it was observed that periods of high flow were associated with major inputs of surface runoff which mainly occurred during the major season of pesticide application to winter cereal crops.

As in the Anglia Water study, pesticides occurred less frequently in groundwater, with atrazine and simazine detected in 70% of all groundwater samples taken from supply and observational bore-holes. The presence of isoproturon and chlorotoluron in two of the observational bore-holes was explained as localised groundwater recharge with contaminated surface runoff from an area of the catchment capped with boulder clay

Table 2-7 Pesticide loading applications and concentrations of pesticides in surface and groundwaters 1987-90, Granta catchment survey

Pesticide	Usage 1986-87 (kg a.i) and (cumulative %)	River Water		Groundwater	
		Range (µg/l)	Number of Detections	Supply (µg/l)	Observational (µg/l)
Isoproturon	9694 (27.99)	<0.06 - 0.23	46 (28.75)	nd	0.49 - 0.61
Mecoprop	9452 (27.29)	<0.03 - 2.7	36 (22.5)	nd	nd
Tri-allate	4030 (11.63)	<0.02 - 0.13	12 (7.5)	nd	nd
Chlorotoluron	3180 (9.18)	<0.13 - 0.23	5 (3.1)	nd	<0.13 - 0.35
Chlorothalonil	1912 (5.52)	nd	0 (0)	nd	nd
Captafol	1513 (4.37)	nd	0 (0)	nd	nd
Bromoxynil	1307 (3.77)	nd	0 (0)	nd	nd
Ioxynil	1151 (3.32)	nd	0 (0)	nd	nd
Simazine	572 (1.52)	<0.04 - 0.94	23 (14.38)	<0.04 - 0.07	<0.04 - 0.4
MCPA	537 (1.55)	<0.04 - 8.9	2 (1.25)	nd	nd
Propyzamide	384 (1.11)	<0.03 - 0.43	7 (4.38)	nd	nd
Lindane	363 (1.05)	<0.03 - 0.8	7 (4.38)	nd	nd
Atrazine	180 (0.52)	<0.05 - 0.1	17 (10.62)	<0.05 - 0.13	<0.05 - 0.31
Triadimefon	146 (0.42)	<0.1	1 (0.63)	nd	nd
Dichlorprop	108 (0.31)	<0.02 - 0.19	3 (1.88)	nd	nd
2,4-D	56 (0.16)	<0.05 - 0.08	1 (0.63)	nd	nd
MCPB	54 (0.15)	<0.03	0 (0)	nd	nd
Carbetamide	-	<0.11	0 (0)	nd	nd
2,4-DB	-	<0.05	0 (0)	nd	nd

Modified from Gomme et al, 91 & 92

Overall, compared to isoproturon and chlorotoluron the occurrence of the triazines in groundwater appeared to be anomalously high considering their level of usage within the catchment (see Table 2-7). Gomme *et al* (1992) have suggested three possible explanations for this anomalous behaviour.

- The cereal herbicides may have degraded and/or be adsorbed during transport, leaving only the more persistent triazines in solution.

- Due to the travel time delay between application and occurrence in groundwater, the presence of the triazines may have reflected the fact that they were in common use long before cereal herbicides such as isoproturon, and chlorotoluron were available. At the time of groundwater sampling the latter group of compounds may only have been present in the unsaturated zone of the aquifer and in transit to the bulk of the aquifer supplying the bore-hole.

- Cereal herbicides were attenuated by various processes in the soil profile such as microbial degradation. However, the triazines were thought to be mainly used for non-agricultural weed control on hard surfaces employing relatively efficient drainage systems that by-passed the attenuation processes within the soil profile. Hence the triazines were rapidly removed in surface runoff into the unsaturated zone with the minimum of degradation.

None of these theories were proved during the Granta catchment study due to the requirement of more data. It was noted that during the initial land and pesticide use survey, non-agricultural pesticide uses were investigated but the records of weed control on a former railway line and of the main road network were not available. As discussed in Section 2.4.2, triazine use in these areas was likely to represent the largest fraction of non-agricultural use within the catchment.

2.5.1.3 The Rosemaund pesticide study

The research programmes reviewed so far have dealt with pesticide concentrations in major rivers and aquifers. The Rosemaund pesticide study (Williams *et al*, 1995) was carried out to investigate the fate of pesticides in a small scale agricultural catchment, with particular emphasis on the movement of pesticides during rainfall events from agricultural land to surface water. The pesticides investigated in the study were isoproturon, simazine, atrazine, dimethoate, MCPA, carbofuran, and aldicarb. The 150ha Rosemaund catchment lies with the Rosemaund Experimental Husbandry Farm near Hereford which is owned and managed by ADAS Rosemaund. The aim of the study was to understand the factors that influence pesticide concentrations in agricultural surface runoff and to provide data to calibrate simple predictive models.

The soils of the catchment are characterised by heavy clay which, during rainfall events, led to relatively high volumes of surface runoff feeding the main drainage stream of the catchment which is a tributary of the River Lugg. During the course of the study from autumn 1990 to spring 1992 the farm was operated following normal agricultural practices. Field management, soil tillage, seeding, and agrochemical applications were recorded, and the stream flow and rainfall were continuously logged at the outlet (Site 1) and approximately halfway up the catchment (Site 0). At the same locations, elevated stream flow was sampled during rainfall events. A summary of the results relating to the outlet of the catchment, collected over the course of the study is shown in Table 2-8 and Figure 2-3 shows an example of the data collected from a single storm event, illustrating the variation of simazine concentration in elevated stream flow at Site 0, following the onset of a rainfall event.

The variation in pesticide concentration shown in Figure 2-3 shows similarities to that found by Croll (1991) and Gomme *et al*, (1991) in their studies of pesticide concentrations in surface waters in the Anglian region and the Granta catchment respectively. Both show increased pesticide concentrations with the onset of a rainfall event which is considered to rapidly transport pesticides from sites of application to receiving waters in surface runoff.

Table 2-8 Summary of runoff data collected for pesticides at Site 1 as a result of rainfall events between autumn 1990 and spring 1992 at ADAS Rosemaund

Chemical	Event date	Rainfall (mm)	Days after application	Max conc (µg/l)	Event mean concentration (µg/l)	Mass out (g)	Mass as % of applied
Isoproturon	25.12.90	10.5	27	17.2	10.6	0.9	$4.4\text{x}10^{-3}$
	8.1.91	15.0	41	2.62	0.96	0.52	$2.5\text{x}10^{-3}$
	21.2.91	11.5	85	2.10	0.92	0.4	$1.9\text{x}10^{-3}$
Dimethoate	25.12.90	10.5	27	3.05	1.20	1.77	$3.9\text{x}10^{-4}$
	8.1.91	15.0	41	0.22	0.90	1.6	$2.9\text{x}10^{-4}$
Atrazine	8.1.92	72.5	42	5.7	2.00	9.9	$6.8\text{x}10^{-2}$
	25.1.92	9.0	59	49.4	1.9	0.15	$1.0\text{x}10^{-3}$
	14.4.92	17.5	139	2.4	0.11	0.009	$6.2\text{x}10^{-5}$
	28.5.92	14.5	183	0.02	0.06	0.004	$2.7\text{x}10^{-5}$
Carbofuran	8.1.92	72.5	36	26.8	10.40	52.6	$5.8\text{x}10^{-1}$
	25.1.92	9	53	49.4	6.20	0.49	$6.5\text{x}10^{-3}$
	14.4.92	17.5	133	2.4	0.46	0.038	$4.2\text{x}10^{-4}$
	28.5.92	28.0	177	0.02	0.01	0.0001	$4.4\text{x}10^{-6}$

Modified from Williams *et al*, 1995

In perspective, the stream pesticide data presented by Williams *et al*, (1995) from the Rosemaund small scale catchment study, represents one of numerous sources of relatively short term pesticide pulses, measured in hours, which combine on a complete catchment basis to produce a prolonged pulse at the catchment outlet. At this point it can be measured in days albeit at lower peak concentrations, as shown in the Anglian and Granta studies. Similar behaviour of pesticides in a small-scale stream catchment were found during the course of this study

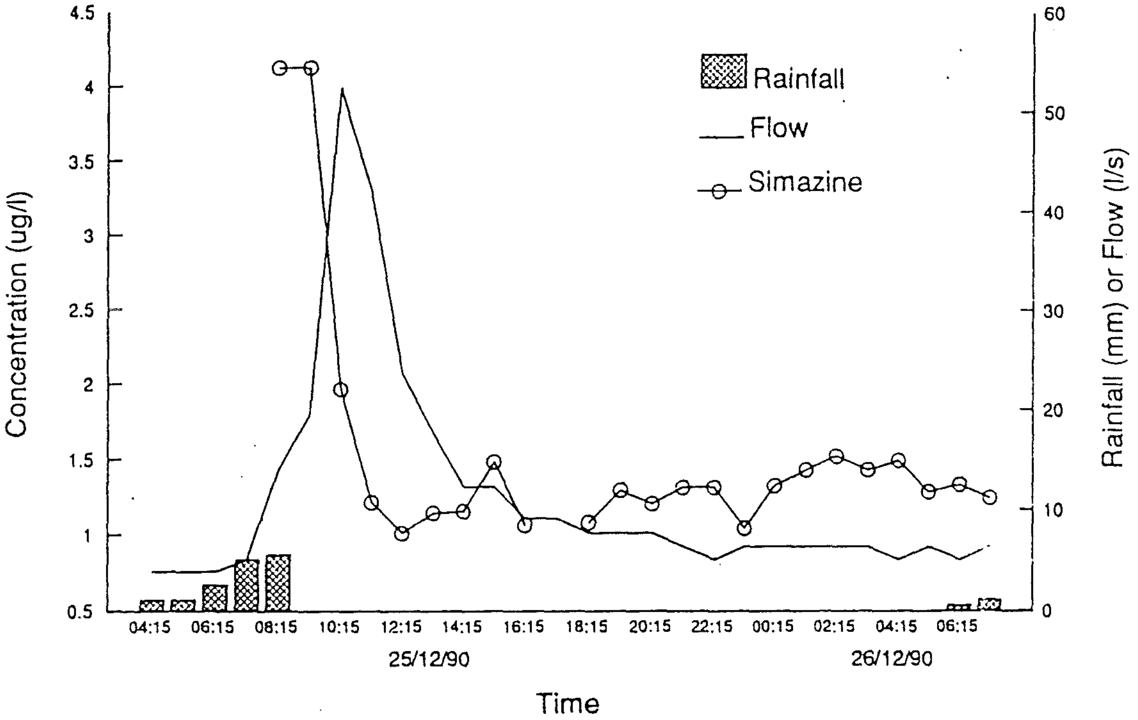

Figure 2-3 **Flow rate and simazine concentrations measured within the Rosemaund catchment (site 0) following a rainfall event after a recent application**

2.5.1.4 Environment Agency surface and groundwater monitoring

In an earlier report of the Rosemaund study it was concluded that the investigation of pesticide runoff problems using routine monitoring programmes was woefully inadequate as annual and monthly load estimates often understated the severity of pesticide pollution problems in streams and rivers; further it suggested that monitoring programmes should be strategically designed to cover peak application periods and storm events following application (Williams *et al*, 1991). Indeed in 1992 the EA stated 'Although some pesticides are widespread in surface and groundwaters, limitations to the extent of the EA's monitoring programmes preclude a comprehensive assessment of the scale and extent of the problem', (National Rivers Authority, 1992).

The EA's pesticide monitoring programme is essentially governed by the statutory monitoring requirements of the Water Resources Act 1991, to monitor pesticide concentrations in water, sediment, and biota. The EA is also statutorily required to monitor and where necessary control pollution problems, especially those from pollution incidents. Non-statutory monitoring of pesticides is also carried out and is designed according to the requirements of known or foreseen local problems. The monitoring is carried out to assess water quality, detect any changes and check that the water is suitable for its recognised uses; for example water bodies used for amenity purpose, water bodies supporting fragile aquatic ecosystems, and resources used for drinking water abstraction. Assessing whether the water is suitable for its designated use is achieved by comparing the water quality with the appropriate standards (NRA, 1995). Consents to discharge are issued under the Water Resources Act (1991) and are used to control point source inputs of effluents into watercourses. Consent conditions are set to avoid any environmental impact and where an Environmental Quality Standard (EQS) is available, conditions are calculated to ensure the EQS is met in the receiving water.

Although the EA is not responsible for the quality of drinking water, it must take appropriate action to safeguard drinking water resources following notification by water companies. Therefore the EA routinely monitors water abstraction points and where necessary investigates sources of pollution and takes action to prevent further exceedances using appropriate legislation (NRA, 1995). Also the EA monitors rivers at a number of locations which are considered to be representative of general river quality and undertakes monitoring as part of the Harmonised Monitoring Programme. This programme was set up by the DoE in 1974 to provide a network of sites at which river quality data at the lower end of the catchment could be collected and analysed in a nationally consistent manner.

Over 200,000 pesticide measurements are recorded each year by the EA at approximately 3,500 sites (National Rivers Authority, 1995). The data shown below (Table 2-9 and Table 2-10) represents the monitoring results for environmental waters for 1992 and 1993 and excludes data from discharges or pollution incidents. The results therefore reflect background concentrations in controlled waters. Since many environmental waters are used for drinking water abstraction the 1992 and 1993 data have been compared to the EC Drinking Water Directive (0.1 μg/l for a single pesticide).

Table 2-9 A summary of pesticides most frequently exceeding 0.1μg/l in freshwaters in 1992 and 1993

1992			1993		
Pesticide	Total number of samples	% samples >0.1μg/l	Pesticide	Total number of samples	% samples >0.1μg/l
Atrazine	3965	17	Chlorpropham	28	43
Mecoprop	1358	17	Diuron	1598	18
2,4D	363	15	Mecoprop	2089	18
Diuron	963	14	Atrazine	4100	14
Simazine	4065	13	Carbendazim	40	10
Isoproturon	2041	10	Simazine	4094	9
Permethrin	816	6	Bentazone	196	9
Pentachlorophenol	6299	6	2,4 DCPA	646	9
Dicamba	369	5	MCPA	2085	8
Sulcofuron	363	5	PCSD/eulan	1396	6
-	-	-	2,4D	1615	6
-	-	-	Pentachlorophenol	5478	6
-	-	-	Isoproturon	2977	6
-	-	-	Trietazine	310	6
-	-	-	Chlorotoluron	2389	5
-	-	-	Propyzamide	197	5

Table 2-10 shows the pesticides most frequently exceeding 0.1μg/l in groundwaters in 1992 and 1993 (NRA, 1995). The non-agricultural herbicides diuron and atrazine and the agricultural herbicide mecoprop exceeded 0.1 μg/l most frequently in 1992 and 1993. The number of exceedances for diuron increased from 14% of samples in 1992 to 18% in 1993. Atrazine exceedances fell from 17% to 14% in the same period. These differences may be associated with the ban on the non-agricultural use of atrazine and simazine which came into force in September 1993. It appears that users foresaw the ban and began to use alternative products, such as diuron, before the ban was implemented, thus reducing atrazine levels and increasing those of diuron. Chorpropham, an anti-sprouting agent for potatoes in store, was also detected regularly in 1993. However, the data were a result of a local monitoring survey immediately downstream of potato washing sites and therefore are not representative of concentrations in freshwaters on a national basis.

Table 2-10 Pesticides most frequently exceeding 0.1µg/l in groundwaters in 1992 and 1993.

1992			1993		
Pesticide	Total number of samples	% samples >0.1µg/l	Pesticide	Total number of samples	% samples >0.1µg/l
Atrazine	531	9	Bentazone	34	15
Terbutryn	106	4	Atrazine	603	11
Trietazine	106	3	Trietazine	42	5
Isoproturon	178	2	Diuron	129	5
Mecoprop	147	1	Pentachlorophenol	78	4
Bromoxynil	102	1	2,3,6, TBA	27	4
2,3,6 TBA	112	1	Linuron	172	3
Dicamba	112	1	Clopyralid	30	3
Simazine	523	1	Ethofumesate	31	3
Linuron	137	1	Isoproturon	181	3
Chlorotoluron	177	1	chlorotoluron	178	2
			Terbutryn	134	2
			Simazine	603	2
			Mecoprop	138	1

2.5.2 Drinking water quality

In England and Wales, drinking water quality is the responsibility of the Drinking Water Inspectorate (DWI). The DWI periodically carries out technical audits to ensure that water companies are carrying out their statutory responsibilities for monitoring the quality of drinking water as described by the 1989 Water Act and the 1991 Water Industry Act (Drinking Water Inspectorate, 1991). The technical audit comprises of three elements: annual assessments of water samples from treatment works, service reservoirs and water supply zones taken by the water company, to check compliance with sampling and other requirements; inspection of individual companies including a general check at the time of inspection and an assessment of the quality of information collected by the company; and interim checks made on aspects of compliance-based information provided periodically by companies. Annually the DWI issues a report to the Secretary of State for the Environment compiled from summarised water company performance data and performance appraisals. Water companies are required to monitor for 57 parameters as defined in the Water Supply (Water Quality) Regulations 1989 which incorporate the relevant requirements of the EC Drinking Water Directive including the standards for pesticides in drinking water. Monitoring of the quality of public drinking water supplies is carried out within designated water supply zones, often served by a single source, in which not more than 50,000 people reside. Table 2-11 shows the number of failures due to different water quality parameters during the period 1990-93. Pesticides account for the majority of failures to meet drinking water standards. The types of pesticide found and the frequency depends on a number of factors which include the type of water source, the nature of pesticide use in the catchment area and the nature of water treatment. The vast majority of pesticides found in drinking water are herbicides. This is almost certainly because large quantities are used and their application is in situations with a high probability of runoff or leaching (White and Pinkstone, 1995).

Table 2-11 Contraventions of standards in water supply zones in England and Wales 1990-1993 (values in brackets are % of total contraventions)

Parameter	1990	1991	1992	1993
Pesticides	13209 (51)	27585 (66)	35679 (75)	25531 (73)
Coliforms	3835 (15)	2709 (6)	2318 (5)	1575 (5)
Iron	2226 (9)	2515 (6)	2033 (4)	1593 (5)
Nitrite	1743 (7)	2228 (5)	2086 (4)	1876 (5)
Lead	1598 (6)	1736 (4)	1354 (3)	1263 (4)
Nitrate	1117 (4)	1170 (3)	852 (2)	364 (1)
Others	2204 (8)	3781 (9)	3317 (7)	2582 (7)
Total	25932	41724	47639	34784

Table 2-12 shows the number of contraventions for different pesticides in five water company areas during 1993. As can be seen from the data, the type of pesticide and number of contraventions found vary with the type of water resource in each area. For example, 65% of North West Water's resources are from agricultural upland catchments where pesticide use is limited. Conversely, for Thames Water, 75% of its raw water comes from lowland rivers draining large catchments with intensive pesticide use in both urban and agricultural situations. The remaining 25% comes from groundwater sources, many of which are in urban areas or close to railway lines and roads. House *et al* (1997) found a similar pattern of occurrence in a pesticide survey of the Humber rivers. The results of this work showed a high frequency of occurrence of many compounds including the triazine, phenoxyacid and phenylurea herbicides, in the southern Humber rivers Aire, Calder, Trent and Don compared with more occasional detections found in the upland rivers with catchments dominated by low intensity agriculture and non-agricultural pesticide use.

In an attempt to comply with the statutory requirements to meet the EC Drinking Water Standard many water companies have installed water treatment systems based on granular activated carbon (GAC) and ozone treatment (White and Pinkstone, 1993). In 1993 due to the ubiquitous presence of atrazine and simazine in surface and groundwaters, the registration for their non-agricultural use was revoked by the Advisory Committee on Pesticides.

Table 2-12 Numbers of samples >0.1µg/l for selected pesticides in drinking water reported by five water companies in 1993 (White and Pinkstone, 1995)

Pesticide	Anglian	North West	Severn-Trent	South West	Thames
Atrazine	80	33	45	2	5263
Simazine	32	1	7	0	3652
Diuron	0	1	32	0	3242
Isoproturon	33	1	12	0	2860
Mecoprop	13	5	157	0	44

In an exercise to prevent the contamination of drinking water resources through the setting up of catchment protection schemes, discussions have taken place between pesticide manufacturers, pesticide users, water companies, the EA, and the DoE. Discussions have focused on the development of best practice procedures to be adopted by major pesticide users, especially non-agricultural users (Department of the Environment, 1994). For non-agricultural users this has meant the revision of vegetation control procedures whereby the use of pesticide is minimised and where practicable non-chemical methods are used (Court *et al*, 1995).

The development of catchment protection plans or on the broader scale sustainable catchment development, is also empathetic to the principles behind Agenda 21 which was one of the documents resulting from the United Nations Conference on Environment and Development (the 'Earth Summit') held in Rio de Janeiro in 1992 (Gardiner, 1994). The UK Local Government

Management Board has produced a simplified guide to Agenda 21, and the following text is taken from Chapter 18 of this document:

> *Water resources must be planned and managed in an integrated and holistic way to prevent shortage of water, or pollution of water sources, from impeding development. Satisfaction of basic human needs and preservation of ecosystems must be the priorities; after these, water users should be charged appropriately.*

This statement embodies the need to consider the full implications of land use and development planning to ensure that present day and long term pollution risks are either avoided or minimised. Ultimately sustainable catchment development will only be a success if all the stakeholding (i.e. all those with legitimate interests in the outcome) bodies involved with land use and development planning communicate and, whilst appreciating each others' occasionally diverging needs, work together towards a common aim as set out in Agenda 21.

CHAPTER THREE

3. The Behaviour of Pesticides in the Environment

The fate of pesticides in the environment is governed by retention, transformation and transport processes, and the interaction of these processes (Cheng, 1990). The interrelationship between processes is illustrated in Figure 3-1.

Within the soil environment, retention results from the interaction between the pesticide molecule and the surface of a soil particle or soil components such as organic matter. The nature of retention processes within the hard-surface environment are less well understood than those operating in the soil environment and has only recently become an area of active research (Heather and Carter, 1995).

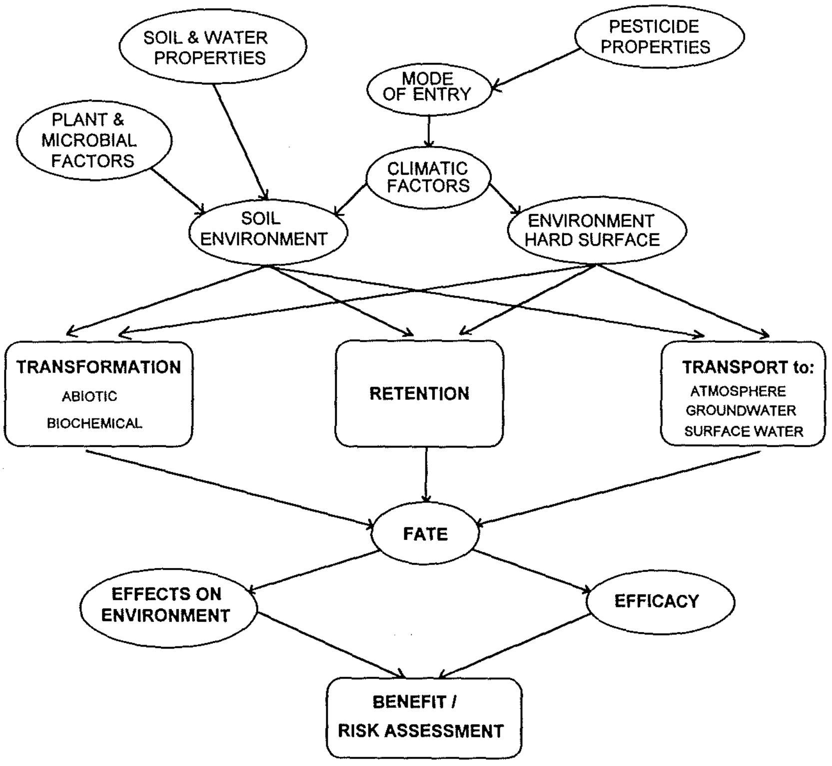

Figure 3-1 A conceptual framework illustrating the factors and processes that govern the fate of pesticides in the soil and hard-surface environment

The retention processes are described as adsorption or simply as sorption and may be reversible or irreversible; they can retard or prevent the pesticide movement and affect its availability for plant or microbial uptake or for biotic or abiotic transformation.

Whereas retention is mainly considered to be a physical process, transformation is characterised by a change in the chemical structure of the pesticide molecule, although the division between a physical and chemical process of transformation is not always readily discernible. The transformation processes may be purely chemical in nature and may be catalysed by soil constituents or brought about photochemically. Most pesticides are, however, transformed predominantly through biochemical means, such as soil microorganisms and their biotic transformation generally results in the degradation of their molecular structure into simpler forms. Degradation tends to decrease a chemical's toxicity although occasionally the metabolic products could be more toxic than the parent compound.

As the transformation processes determine persistence or *how long* a pesticide may be present in an environment, the transport processes dictate *where* the pesticide may occur. Volatilisation leads to the transfer of a pesticide from the soil or hard-surface environment to the atmosphere; surface runoff transports pesticides into surface waters, and leaching leads to the vertical movement of pesticides into groundwaters. The persistence of a pesticide at its site of application is a balance between the amount degraded in-situ and that removed by off-site transport processes.

3.1 Factors affecting environmental fate

In order to assess the fate of a pesticide, once applied to the soil or hard-surface environment, it is essential to appreciate the kinetics of the individual processes including the underlying factors that affect each process as well as the combined effects of all the processes. The following sub-sections are arranged in a sequential order so as to describe the environmental pathways as shown in Figure 3-1. The text describes the pathway of a pesticide from its entry into the environment, through its progression within the various retention, transformation and transport processes to its eventual fate within one or many environmental compartments, assuming it is not fully degraded en route. The fate of a pesticide governs its availability and efficacy for pest control as well as its potential for producing undesirable effects upon non-target organisms and other environmental compartments such as surface waters used for drinking water abstraction.

3.1.1 Indirect entry of pesticide to the soil and hard-surface environment

As well as pesticides entering the soil and hard-surface environment through direct application, they can also enter via a number of indirect pathways either during or between rainfall events. These include wet and dry atmospheric deposition, foliar wash-off, or accidental spills.

Wet deposition comes about through the incorporation into precipitation of:

- Pesticide-bearing dust particles generated by wind pickup and atmospheric transport.
- Pesticides dissolved in atmospheric water vapour generated by wind pickup and atmospheric transport of fine spray drift droplets.
- Dissolution of foliar resident pesticide and subsequent surface deposition.

A number of studies in Europe and the US have reported the presence of pesticides in wet and dry atmospheric deposition. Siebers *et al* (1994) found a number of pesticides including atrazine, isoproturon, and lindane present in rainfall at concentrations ranging from 10 to 710 ng/l; apart from lindane, occurrence in rainfall correlated with seasonal applications. The use of wet only and wet and dry atmospheric deposition samplers showed that the majority of pesticide deposition was associated with rainfall. Similar results have been obtained elsewhere as shown in Table 3-1 (Richards *et al* 1987; Buser, 1990; Trevisan *et al*, 1993; Turnbull, 1995), however differing sampling and reporting procedures as well as regional and seasonal influences make data comparison difficult.

Table 3-1 The occurrence of pesticides in rainfall sampled in Europe and the United States

	Reference				
Compound	Turnbull, 1995 (S.W. England)	Siebers *et al*, 1994 (N. Germany)	Trevisan *et al*, 1993 (Italy)	Buser, 1993 (Switzerland)	Richards *et al*, 1987 (US)
	Mean, Range (ng/l)	Max, Mean (ng/l)	Range (ng/l)	Range (ng/l)	Range (ng/l)
Atrazine	15, nd - 69	430, 76	150 - 1990	nd - 600	nd - > 1000
Simazine	31, nd - 280	na	na	nd - 121	nd - > 100
Propazine	na	na	na	na	na
Isoproturon	60, nd - 1550	367, 58	na	na	na
Trifluralin	2.3, nd - 24	na	3400	na	na
Dichlorbenil	na	na	nd - 3120	na	na
Alachlor	na	na	110 - 810	na	nd - > 1000
Metolachlor	na	na	na	na	nd - > 1000
Parathion	na	569, 164	nd - 170	na	na
2,4-D	na	na	nd	na	na
Dichlorprop	na	na	nd - 1810	na	na
Linuron	na	na	na	na	nd
Lindane	55, 1 - 400	710, 139	na	na	na
α HCH	nd - 7	12, 12	na	na	na

na :- data not available

Dry deposition comes about through:

- Short or long range spray drift, depending on droplet size and the prevailing air currents. Deposition of particles emanating from the pesticide drift process and from pesticide-bearing dust particles generated by wind pickup and atmospheric transport.

- Accidental spillages are normally referred to as point sources of pollution. Point sources of contamination usually occur as a consequence of some form of mismanagement either in production, application or surplus disposal. Usually, effects upon water quality are relatively short term, but may be acute, resulting in fish kills and serious impacts on macroinvertebrate populations. In recent years the number of minor incidents in the UK has increased, currently being approximately 1.8% of the total number of farm pollution incidents (NRA, 1992). With the exception of major incidents in Essex (1977) and Woodkirk (1986), few such incidents have seriously affected water supplies and they are most often dealt with by the Environment Agency under the provisions of the Water Act 1989. Point sources are relatively straightforward to identify and are controlled by means of pollutant discharge consents and the 'polluter pays' principle, implemented by the EA.

Typical causes of point source inputs are described below:

- Leakage from industrial production plants: Occasionally, as a result of mismanagement and poor planning, illegal discharges occur which either runoff directly to watercourses or enter sewer systems. Such discharges although occurring infrequently can have major environmental impacts.

- Accidental spillage: Lack of care and attention, inadequate precautions, use of incorrect procedures and equipment combined with inexperienced staff may result in accidental spillages of pesticides.

- Leakage from incorrect storage: Pesticide storage facilities should be designed such that accidental spillage and leakage from containers is safely contained and not lost to the environment.

- Incorrect disposal and illegal dumping: The use of unsatisfactory facilities when rinsing and cleaning sprayer tanks in farm yards, can often result in direct runoff to water courses or entry into sewer systems (Kreuger, 1998). Also disposal of small amounts of unused or surplus pesticides to foul sewers is a serious concern. The pesticide may pass through the sewer treatment process unaltered and enter a river as a point contamination source. In addition the toxicity of some compounds is such that a relatively small amount can impair or incapacitate the biological sewage treatment process resulting in a highly polluting discharge of inadequately treated sewage to a receiving water. An incident in the Northumbria Environmental Agency region, seems to confirm this concern (NRA, 1992). Urban applications of pesticides to impervious surfaces, such as roads and public grassed areas, may eventually enter the combined storm sewer system and pass untreated through a sewer treatment plant before being discharged to a river as a point source.

- The improper disposal of or leakage of sheep dip resulting from poorly designed dipper stations. Disposal procedures of spent dip often involve application to land susceptible to surface run-off and/or leaching.

3.1.2 Direct pesticide application to the soil and hard-surface environment

For the control of vegetation, pesticides can be applied directly to the plant once grown, where efficiency is achieved through translocated or systemic action. Alternatively, residual-acting herbicides can be applied to soil or hard surface areas prior to plant growth; pesticides can be directly applied to the soil to act as preplanting, premergence, or post-emergence treatments. The techniques required for the direct application of pesticides to soil or hard surfaces are dependent upon pesticide formulation. Formulations include solutions, suspensions, powders and granules. The physical and chemical properties of the formulation and its resultant spray characteristics, as indicated by particle size and surface properties, (surface tension, spreading coefficient, and contact angles), dictate whether the pesticide will adhere to the plant surface and penetrate the lipid barrier of the leaf cuticle and exert metabolic efficacy. Common pesticide formulation types are wettable powder (WP), emulsifiable concentrate (EC), water miscible concentrate (WMC), and flowables (F).

Within agriculture, the traditional approach to pesticide application has relied on the use of high-volume dilute sprays, with applications in the range of 400 to 3000 l/ha. This approach was seen as inefficient, and labour- and energy-intensive whether carried out using tractor-mounted or aerial spraying units. The method, which relies upon foliar saturation often leads to large losses to soil and spray drift.

Riley (1976) estimated that, in some circumstances, less than 10% of pesticide application reached the target area. Recent advances in pesticide application technology have led to reductions in spray drift and increased the proportion of applied pesticide that reaches and remains on the target plant or in the vicinity of its root. Such techniques are referred to as low volume (LV), ultra low volume (ULV) and controlled droplet application (CDA) (Himel *et al*, 1990). Developments in pesticide formulation have enabled the use of more concentrated spray mixtures. Whereas conventional formulations and application techniques apply between 400 and 3,000 litres of spray mixture per hectare, ULV involves spraying at a rate of less than 2l/ha using a spray mixture in a more concentrated form but still maintaining active ingredient application rates. The associated CDA technique enables this more concentrated form of pesticide to be projected from a spinning disc in droplets of more uniform size which can itself be regulated (for example, by adjusting the type and speed of disc). Through the application of pesticides using optimum droplet size, application efficiency can also be optimised, reducing active ingredient wastage and thereby allowing a reduction in active ingredient application rates. For agricultural purposes, the use of ULV/CDA techniques is currently increasing in popularity since such techniques significantly improve the efficiency of spraying operations through reduction of the frequency of sprayer tank refilling thus lowering unit labour costs.

In hard-surface or non-agricultural situations, use of ULV/CDA methods is more recent, but has rapidly become widely adopted by industry for weed control purposes (De'Ath and Collins, 1991). Excluding the use of railway rolling stock modified to apply pesticides to railway lines and embankments, the majority of non-agricultural pesticide applications in urban areas are performed using hand-held rotary atomisers incorporating ULV/CDA application systems. These applicators are often designed such that the operator only needs to load a container holding pre-mixed pesticide, thus eliminating need for the dilution and premixing of pesticide concentrates and therefore minimising the risk of spillage. Also with reduced liquid volumes, the weight of the applicator is lower than conventional knapsack sprayers hence reducing operator fatigue which might otherwise lead to erroneous applications to non-target areas.

Due to the scale of operation, applications to roads and railways are made using self-propelled application units. The tracks and embankments of the main railway network are sprayed periodically using two modified trains which operate throughout the UK from April to August (see Plate 3-1). The need to fit in with the complex timetables requires the spray train to travel at speeds of up to 80 km/hr. Therefore, to prevent excessive spray drift due to air turbulence, large-bore spray nozzles are used in conjunction with large spray volumes to produce relatively large droplets (~600μm).

Plate 3-1 Modified rolling stock used for herbicide application to railway lines

For the control of vegetation on the surface railway lines of the London Transport underground system, similar modified rolling stock is used on a periodical basis, as shown in Plate 3-2.

Plate 3-2 The spray train of the London Underground making a herbicide application to an above ground section of the Central Line.

3.1.3 The retention of pesticides in the soil environment

Once applied to the soil environment, pesticide fate is affected by a number of processes. The most fundamental process being the retention of the pesticide within the soil-water environment which prevents movement either within or outside of the soil matrix (Koskinen and Harper, 1990). Retention within the soil matrix plays a pivotal role in determining whether a pesticide is mainly lost from the soil environment through transport to groundwater, surface water or to the atmosphere; or whether the compound remains present within the soil matrix and is subject to loss through biochemical and chemical degradation. Retention refers mainly to the adsorption process but also takes into account absorption into and precipitation onto surfaces of the soil matrix. Adsorption refers to a reversible process involving the attraction of a chemical to the surface of a soil particle. However, in practice, the distinction between true adsorption, absorption, and precipitation is difficult to make and therefore adsorption is usually replaced by the general term 'sorption'.

Due to the heterogeneity of soils, the retention process is complex and often difficult to define. In reality the process is the combined result of a number of individual mechanisms which depend on specific soil composition and the physico-chemical properties of individual pesticides.

3.1.3.1 The nature of soil

The structure of the soil profile is a product both of the underlying parent rock material and of the flora and fauna living in and on the soil surface. A soil may be the direct product of underlying weathered rocks or may be formed from unconsolidated non-indigenous rocks unrelated to the underlying geology. Soil depths and their composition can therefore vary considerably. A simplified section through a soil profile is shown in Figure 3-2.. The top layer of the soil profile, termed the 'A' horizon is generally characterised by the presence of organic matter derived from the decomposition of plant debris.

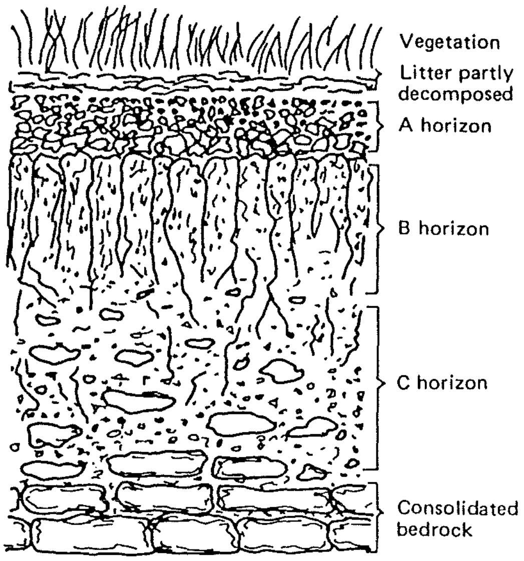

Figure 3-2 Simplified section through the soil profile showing the soil horizons

The 'B' horizon is mainly composed of well-weathered parent material with its structure modified by roots and living creatures such as earth worms. The 'C' horizon is unconsolidated rock material containing a wide range of particle and stone sizes. The thickness of the soil layers depends upon their location relative to the geological structure and the geomorphology of surface features.

In general, soil is composed of three phases, a solid phase (~50%) made up of both inorganic and organic solids, a liquid phase (~25%), and a gas phase (~25%). The liquid and gas phases provide the primary modes of transport for soluble and volatile pesticides in the soil. The solid phase is the primary site for pesticide retention. The adsorption affinity between pesticides and solid particles is a function of the physico-chemical properties of the pesticide and the number, nature and accessibility of functional groups on the surface of the solid soil particles. The inorganic solids are composed of a variety of alumino-silicate clay minerals of various particle size. Those particles less than 2μm in diameter are termed clay particles, those between 2μm and 50μm are termed silt, those between 50μm and 2mm are termed sand, and those greater than 2mm are termed gravel.

The mineral surface has an abundance of hydroxyl groups which are considered to be the most significant functional group on soil clays with respect to the retention of neutral organic compounds. The organic matter components of the solid phase include polymeric organic solids, decomposing plant and animal residues (characterised by the presence of humic and fluvic acids), and soil organisms. The variety of functional groups in soil organic matter leads to a wide range of retention affinities and therefore pesticide adsorption to organic matter generally tends to dominate soil retention mechanisms. However, in sub-soils characterised by low organic matter content, pesticide retention onto soil clay will become increasingly significant with depth (Roy and Krapac, 1994). With respect to retention mechanisms, the soil organic components are grouped together and referred to as soil organic matter content (%OM) or organic carbon content (%OC).

As well as serving as the primary means of chemical transport within the soil matrix, soil water has a dual role in the retention of pesticides in that it acts as both a solvent for the pesticide and also competes with the pesticide, acting as a solute, for adsorption sites. Soil water also contains a number of dissolved components such as inorganic salts and dissolved organic matter or carbon (DOC) that may also compete for and block adsorption sites.

A number of different intermolecular forces are involved in the overall retention process; these include Van der Waal forces, hydrogen bonding, dipole-dipole interactions, ion exchange, covalent bonding, protonation, ligand exchange, cation bridging, and water bridging. A concise explanation of each bonding process is beyond the scope of this work but is well described by Koskinen and Harper (1990). For any given pesticide and soil combination there is likely to be a continuum of mechanisms responsible for sorption to the soil matrix.

3.1.3.2 Soil retention and sorption mechanisms

Once applied to the soil environment, the distribution of a pesticide within the soil matrix between soil solids and soil water will determine the leaching potential of the pesticide from the soil environment. Generally it is assumed that once applied to the soil, a pesticide will equilibrate between soil water and soil particle surfaces. The equilibrium is normally expressed as:

$$C_e \rightleftharpoons C_s$$

where C_e is the concentration of pesticide in solution (µg/l) and C_s is the concentration of pesticide adsorbed (µg/kg) to soil particles. The relationship between soil adsorbed pesticide and that in solution, if linear, can be expressed by the soil partition coefficient, K_d:

$$K_d = [C_s] / [C_e]$$

Adsorption isotherms for pesticides are usually not linear and can be described by the Freundlich equation:

$$K_f = [C_s] / [C_e]^{1/n} \qquad \text{where 'n' equals an empirical constant}$$

However, Rao and Davidson (1980) suggested that for many modelling purposes for neutral organic compounds, a linear isotherm (n=1) can be used with acceptable error.

The soil partition coefficient K_d can be determined by direct or indirect measurement (Green and Karickoff, 1990). For direct measurement, adsorption isotherms are determined by shaking various concentrations of a pesticide solution with dilute soil slurries from one hour up to twenty-four hours to facilitate equilibration between the solid and liquid phases. Desorption coefficients are measured by replacing the equilibrium solution with water and re-equilibrating (Riley and Eagle, 1990). After centrifugation, equilibrium solution concentration and adsorbed concentration are either both determined or alternatively the equilibrium solution concentration can be measured with the adsorbed concentration derived from the difference between initial solution and equilibrium solution concentrations.

Many workers have investigated the nature, speed, and extent to which sorption equilibrium is achieved in field conditions (Karickoff, 1981; Wauchope and Myers, 1985; Pignatello and Huang, 1991; Beck *et al*, 1995). Wauchope and Myers (1985) found their adsorption-desorption data fitted a sequential-equilibria model which assumes that two reversible equilibria occur sequentially:

$$C_e \rightleftharpoons C_{s\text{-}1} \rightleftharpoons C_{s\text{-}r}$$

where C_e, $C_{s\text{-}1}$, and $C_{s\text{-}r}$ are pesticide in solution, on 'labile' soil surface sites, and 'restricted' soil sites respectively. The first equilibrium is assumed to result from rapid solution-surface interchange and the second from a much slower, reversible interchange of pesticide between labile and restricted soil sites. Through the use of fast sampling and filtration techniques to study the adsorption-desorption kinetics of linuron and atrazine, they found the rate of adsorption and desorption to be very fast, approaching 75% of the 24 hour equilibrium values within 3 to 6 minutes. This was after a pre-desorption equilibration period of two hours.

However, for atrazine and isoproturon equilibrated for longer periods of time (months), the apparent soil partition coefficient, K_{app}, was found to increase as the fraction of pesticide associated with restricted soil sites increased with time. The ratio K_{app} / K_d was found to be proportional to the age of the pesticide residue, i.e. the time between sampling and the pesticide application (Pignatello and Huang, 1991; Beck *et al*, 1995).

Sorption equilibrium has also been found to be affected by dissolved organic carbon (DOC) which has been shown to solubilise relatively insoluble pesticides and hence shift equilibrium in favour of mobile soil solution (Dousset *et al*, 1994).

When direct measurement of the soil partition coefficient is unavailable for a given soil-pesticide combination, an estimation must be made. Soil organic carbon content has been shown to be significantly related to pesticide sorption behaviour in soils and can be used to predict the soil partition coefficient (Kenega and Goring, 1978; Rao and Davidson, 1980). It is assumed that the soil partition coefficient is linearly proportional to the soil organic carbon content.

$$K_{oc} = K_d / f_{oc}$$

Where K_{oc} is the carbon partition coefficient and f_{oc} is the mass fraction of organic carbon present within the soil. Karickhoff (1981) has shown that for neutral organic compounds, K_{oc} can be determined from the octanol-water partition coefficient K_{ow}.

$$K_{oc} = 0.411\ K_{ow}$$

Further, Wauchope *et al* (1992) have shown that K_{oc} can be predicted from pesticide solubility since the tendency for a pesticide molecule to transfer from water to soil organic matter should be similar to the tendency to transfer from water to its own phase.

$$K_{oc} = 3000 / \sqrt{S} \qquad \text{where (S) is the pesticide solubility.}$$

This equation has been used to predict the majority of K_{oc} values to within a factor of three compared to directly determined data.

3.1.4 The retention of pesticides in the hard surface environment

As in the case of the soil environment, when a pesticide is applied to a hard surface it is subject to number of dissipation processes which are, in part, determined by the nature of the hard surface substrate as well as pesticide physico-chemical properties and local climatic factors. The term 'hard surface' refers to roads, railways, non-soil sports grounds, airport pavements, pedestrian pavements, paths and gravel surfaces. By their nature most hard surfaces have rapid drainage, low infiltration rates, and low water-holding capacity. Most load-bearing hard surfaces are designed for rapid drainage to preserve structural integrity and reduce the risk of flooding. The low infiltration capacity of most hard surfaces promotes the rapid movement of rainfall by routing overland surface runoff into nearby engineered drainage systems. The contrasting hydrology of hard surfaces in relation to the hydrology of soils, ensures that a pesticide applied onto a hard surface is unlikely to infiltrate downwards into the bulk of the material, where it may encounter possible sorption sites. Rather, with the onset of rainfall the pesticide, if unretained, is likely to move rapidly with the surface water into a drainage system.

With the exception of tarmacadam roads, the construction of hard surfaces is generally characterised through the use of inorganic materials including stone aggregate, sand, and concrete. Railways are usually built with a heavy ballast (granite, basalt or limestone) top layer overlaying a well drained sub-base. Tarmacadam is composed of stone chipping bound together by a heavy grade tar. Although considerable amounts of work have been carried out to assess the retention of pesticides applied to soil surfaces, very little work has been focused on the sorption mechanisms that may retain pesticides applied onto hard surfaces. As discussed in Section 3.1.3.1, for soils, it is widely assumed that pesticide retention is related to soil organic carbon content and, for soils of low organic carbon content, mineral adsorption becomes more important. Except for tarmacadam, the composition of hard surfaces suggests that intrinsic levels of organic carbon are likely to be negligible.

The surface adsorption capacity is highly dependent on the number of adsorption sites available which is in turn directly proportional to the surface area of the adsorbent. Sorption to the organic fraction of tarmacadam may be possible along with sorption to the mineral components of other hard surface materials. However, the high surface area associated with the particulate nature of soils is absent on a hard surface and therefore its adsorption capacity is likely to be significantly reduced.

In order to minimise surface runoff losses, pesticide applications are normally performed under dry conditions when the moisture content of most types of hard surface is likely to be low. In similar soil moisture conditions, a number of workers have observed increased adsorption capacity with decreasing levels of soil moisture (Gaillardon and Dur, 1995). In these conditions, adsorption sites are more likely to become available through the removal of blocking water molecules. Thus, it could be suggested that the low moisture content of most hard surfaces may enhance their surface adsorption capacity, whilst receiving pesticide application.

Driven by the occurrence of pesticides in drinking water resources, following applications to hard surfaces, this area of research is likely to expand (Court *et al*, 1995). White and Pinkstone (1993 and 1995) suggest that in order to understand the fate of pesticides applied to hard surfaces, the retention mechanisms of pesticides applied to hard surfaces should be investigated. Hard-surface partition coefficients are required for a variety of hard-surface constructions including tarmacadam roads, concrete pavements and railway tracks. Where applicable, account should be taken of specific material characterisation, such as differing concrete formulation, and the subsequent effect on pesticide partitioning between surface water and the material surface. By definition, sorption isotherms are measured at equilibrium. Through the use of slurry methods, the determination of a soil partition coefficient is relatively straightforward. However, the bulk nature of most hard-surface materials will not allow the formulations of slurries which would in reality be totally unrepresentative of actual sorption conditions. Therefore, a different means of determining the partition coefficient is required, which takes into account the bulk impermeable nature of the hard-surface material. An indirect method could involve the use of techniques commonly used in thin layer chromatography (TLC) where the chromatographic plate is replaced by, for example, a representative thin slab of concrete. Through empirical theory it may be possible to define the partition coefficient in terms of the TLC retardation factor (Rf).

Heather and Carter (1996), have recently commenced a collaborative study to investigate the mechanisms that affect the movement of pesticides from hard surfaces in surface runoff. As project collaborators, Rhone Poulenc have carried out artificial rainfall-surface runoff tests for common non-agricultural pesticides, applied to typical hard surfaces. At present the results of the work are unpublished and unavailable (Heather, 1995, pers comms).

The movement and degradation of diuron in Swedish railway embankments and agricultural soils has been investigated by Torstensson (1994). The railway embankment material was composed of a mixture of gravel and sand with an average of 0.15 % (range 0.1% to 0.2%) organic carbon content. The soils used in the work were composed of on average 10.75% (range 1.0% to 35.7%) organic carbon and 16.5% average clay content (range 4% to 39%). Data from conventional adsorption experiments were linearised using the Freundlich adsorption isotherm to produce average diuron K_d values of 0.39 (range 0.24 to 0.56) and 19.45 (range 2.4 to 49.5) for the embankment material and soils respectively. It was estimated that the vertical leaching potential of diuron was up to 40 times greater in the embankment material compared to the agricultural soils used in the study. This work demonstrates that diuron retention on railway ballast material can be approximately two orders of magnitude lower than in the soils tested. Given the flat impervious nature of hard surfaces, such as concrete, which present less surface area and lower opportunities for the accumulation of organic carbon, it is likely that retention on such surfaces is lower than that which Torstensson found on railway embankment material.

3.1.5 The chemical and biochemical degradation of pesticides in the soil environment

Excluding loss to the atmosphere or to surface and groundwater, pesticide persistence on the soil surface and within the soil matrix is governed by chemical and biochemical degradation mechanisms, which in turn are dependent upon soil characteristics, climatic factors and the physico-chemical properties of the pesticide. Pesticide persistence or disappearance rate within a soil is normally expressed as a half life value ($t_{1/2}$). A full treatment of abiotic and biotic degradation mechanisms is outside the scope of this work, however, excellent reviews are provided by Wolfe *et al* (1990) and Bollag and Liu (1990).

It is often difficult to determine whether a pesticide undergoes chemical or biochemical degradation as they play a dual role in the route to final pesticide mineralization. Chemical degradation tends to be important in areas of low organic carbon or in situations where the pesticide is likely to be exposed to sunlight, resulting in photodegradation. Thus chemical degradation may dominate on the soil surface and in the sub-soil where levels of organic carbon or biomass are low.

Biochemical degradation has been closely linked to the presence of organic carbon or biomass and is therefore likely to dominate in the top soil layer, rich in organic carbon. Kordel *et al* (1995) showed that a strong correlation exists between the half life values of chlorotoluron and simazine, and biomass for an individual soil and its different horizons.

Many pesticides contain functional groups which are susceptible to hydrolysis, however, in general the pH of soil water does not favour hydrolysis and therefore in most soils the reaction is usually slow. The surface area and charged nature of many clay minerals enable adsorption-based catalysis to occur usually in the form of hydrolysis or various types of rearrangement reactions. It is also known that many functional groups associated with organic matter are able to catalyse molecular transformations. It has been suggested that the hydrolysis of chloro-s-triazines occurs through the interaction of the pesticide with carboxyl groups of the soil organic matter (Armstrong and Konrad, 1974). Degradation pathways can be different under anaerobic and aerobic conditions, for example, under reducing conditions nitro groups are likely to be reduced to amines.

The degradation of pesticides through microbial metabolic processes is considered to be the primary mechanism of biochemical degradation. Essentially, five processes are involved in the microbial degradation of pesticides:

- *Biodegradation*, in which the pesticides can serve as a substrate for growth.
- *Co-metabolism*, in which the pesticide is transformed by metabolic reactions but does not serve as an energy source for the microorganism.
- *Polymerisation* or *Conjugation*, in which pesticide molecules are linked together with other pesticides, or naturally occurring compounds.
- *Accumulation*, in which the pesticide is incorporated into the microorganism.
- *Secondary effects of microbial activity*, in which the pesticide is transformed because of changes in pH, redox conditions, reactive products, etc., in terrestrial or aquatic environments brought about by microorganisms.

Pesticidal active ingredients are designed so that once applied to the target area they will persist long enough to achieve their aim and then degrade to inactive metabolites. However, it has been found that application of certain pesticides, conditions soil microorganisms to degrade subsequent applications more rapidly (Cain and Head, 1991; Felsot, 1991). The phenomenon is known as 'enhanced degradation' and has resulted in the use of microbiological techniques to develop 'extenders' to prevent rapid degradation negating the purpose of application. Conversely, such techniques have also been involved in the search for microorganisms which can decontaminate soils which can no longer support crops due to the presence of persistent pesticide residues.

To estimate the relative importance of chemical and biochemical mechanisms, degradation in normal soils is compared with that in the same soil which has been sterilised by heat treatment or by irradiation. Pathways and rates of disappearance can be determined in the laboratory by incubating soil samples with ^{14}C-labelled pesticides. Helweg (1993) used such a technique to study the soil degradation of mecoprop. He found that the rate of mecoprop disappearance increased with soil temperature and organic matter content. Increasing the soil moisture content, initially increased the rate of disappearance, however, once the soil was saturated the onset of degradation was delayed. Similarly, as shown in Figure 3-3, Nicholls *et al* (1993), found that the persistence of isoproturon, in a heavy clay soil, decreased with temperature and soil moisture content.

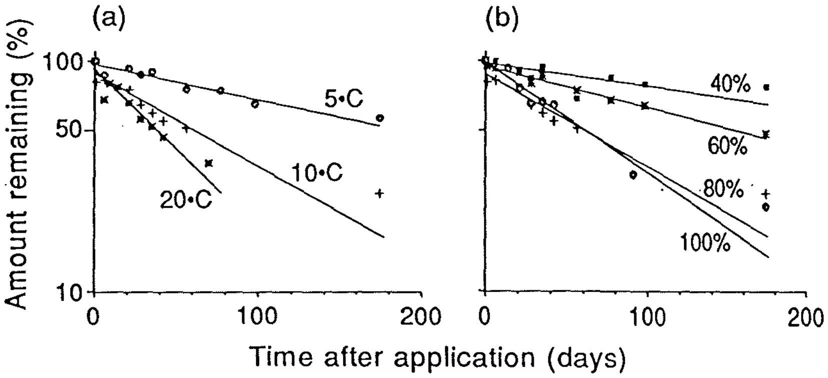

Figure 3-3 Degradation of isoproturon in Brimstone Farm soil (a) effect of temperature at 80% field capacity (b) effect of moisture content (% field capacity) at 10 °C. (From Nicholls et al, 1993)

3.1.6 The chemical and biochemical degradation of pesticides in the hard surface environment

Very little research has directly dealt with the chemical and biochemical degradation of pesticide applied to hard surfaces. However, from what is understood of the nature of hard surface environments it is possible to identify the most probable degradation mechanisms that may operate to degrade pesticides applied in such environments (Haq and Perkins, 1993). Due to the very low levels of organic carbon present within the hard surface environment it is probable that chemical rather than biochemical mechanisms dominate the degradation of applied pesticides.

The aggregate nature of railway ballast compared to the bulk impervious nature of concrete and tarmacadam pavements and roads, is more likely to allow the accumulation of organic matter. Therefore within railway ballast, biochemical degradation may be more significant than in road and pavement environments. However, in either type of hard surface environment, biochemical degradation is far less important than it is in the soil environment. Torstensson (1994) [Section 3.1.4] investigated the half life of diuron in Swedish railway embankments composed of gravel and sand with a mean organic content of 0.15 %. In such material he found the half life of diuron to be approximately two years and estimated the time for ninety-percent disappearance to be approximately seven years, this compares to a diuron soil half life of 90 days (Wauchope *et al*, 1992). Further, a simulated rainfall-runoff test carried out on a sample of limestone railway ballast, showed the presence of atrazine seven years after the last known application. This showed that when applied to limestone railway ballast, atrazine will persist far longer than its soil derived half life of 60 days would predict (Ellis *et al*, 1997).

Within the hard-surface environment, chemical hydrolysis and photolysis are probably the dominant processes which contribute to overall pesticide degradation. The relative importance of each mechanism may depend on the type of hard surface considered which will affect the chances of the pesticide being exposed to sunlight and also determine the moisture content of the immediate environment. Once applied to a relatively dry hard surface it is probable that the pesticide will remain coated on to the hard surface and that photolysis rather than hydrolysis will be the initial primary mechanism of chemical degradation. For hydrolysis to occur, the pesticide needs to be dissolved in aqueous solution usually brought about through rainfall. With the onset of rainfall combined with general low retention capacity of pesticides on hard surfaces, the majority of applied pesticide is likely to be transported in surface runoff rather than undergo in situ aqueous hydrolysis. In some cases, hydrolysis may be favoured if the rainfall accumulates or ponds on the hard surface, however, this is unlikely since most hard surfaces are engineered to enhance surface runoff .

The pore water of recently constructed concrete surfaces has an alkaline pH due to the presence of dissolved calcium hydroxide. Therefore, pesticides applied to such surfaces may be more susceptible to base catalysed hydrolysis than expected. However, the effect will become less important as the concrete ages due to carbonation brought about through the surface ingress of carbon dioxide and the subsequent conversion of calcium hydroxide to calcium carbonate and consequent reduction in pore water pH.

Photolysis of pesticides occurs by two processes: direct and indirect photolysis. Direct photolysis requires absorption of sunlight by the pesticide which is then degraded to by-products. Indirect photolysis begins by absorption of light by a substance or chromophore other than the pesticide. The absorption initiates a series of reactions that finally result in the transformation of the pesticide. A number of species have been identified as photosensitisers including humic substances, clay minerals, transition metals, and polycyclic aromatic hydrocarbons (PAHs) (Schwarzenbach *et al*, 1993). Within the urban hard surface environment, metals and PAHs are likely to be of most importance as significant levels of these substances have been found in urban and highway runoff (Eganhouse *et al*, 1981; Ellis *et al*, 1997). Oxidation is the principal photolytic process. Most organic pollutants require > 250kJ mol^{-1} to achieve their excited states necessary for reaction, however molecular oxygen only requires 94kJ mol^{-1} for promotion to its first excited state as singlet oxygen. The excitation energy is transferred to molecular oxygen from the photosensitisers, producing singlet oxygen which goes on to react chemically with the pesticide.

Direct photolysis requires absorption of sunlight; this may occur while the pesticide remains on the dry hard surface or dissolved in surface water. In either case, the photolysis rate is directly dependent on the overlap of the absorption spectrum of the pesticide with the spectral distribution of incident sunlight. Radiation at wavelengths below 290nm is efficiently absorbed by the ozone layer and therefore only pesticides absorbing radiation above 290nm will be susceptible to direct photolysis. Durand *et al* (1990) investigated the photodegradation of atrazine and diuron in sea water and distilled water. The major photodegradation products were hydroxyatrazine and the related herbicide monuron. The results of their work showed that atrazine degraded faster in sea water compared to distilled water whereas the reverse was observed for diuron where degradation appeared to be quenched by the presence of chloride ions in the sea water.

Both the rate of hydrolysis and photolysis will increase as the temperature of the hard surface environment increases. The relationship between reaction rate and temperature is normally expressed as the Arrhenius equation:

$$k = A\,e^{-Ea/RT}$$

where Ea is the activation energy of the reaction, R is the ideal gas constant, T is the absolute temperature, and A is a constant. For the majority of reactions, the rate of reaction is approximately doubled for a 10K increase in temperature. Exposed hard surfaces such as pavements and roads are relatively easily warmed by the radiant energy of the sun, compared to the bulk and depth of soil environments. Thus hard surface temperature may be a significant factor affecting the overall rate of chemical degradation, especially during Spring when many herbicide applications are made to control emerging vegetation.

3.1.7 The movement of pesticides to the atmosphere from the soil and hard-surface environments

In some cases the loss of pesticides by volatilisation to the atmosphere is the dominant process that determines the effective life time of a pesticide in its target area. The factors that influence volatilisation are therefore of major interest for understanding the contribution it makes to the fate of a pesticide applied to soil and hard surfaces. As is the case for other processes affecting the environmental fate of pesticides, the vast majority of the work investigating the importance of volatilisation has concentrated on pesticides used in the soil environment.

The volatilisation of pesticides from soils is essentially dependent on the physico-chemical properties of the pesticide, the nature and composition of the soil, and the prevailing climatic conditions. Primarily, the rate of volatilisation is determined by the vapour pressure (or vapour density) of the pesticide. Further, the rate of volatilisation is directly proportional to the pesticide concentration in soil water at the surface of the soil. Movement between the water/air boundary is defined by the partition behaviour of the pesticide between the two phases. Partition between soil surface and soil water is usually represented by the Freundlich equation (Section 3.1.3.2). The partition of a pesticide between soil water and air can be represented by Henry's law constant, H, which is defined as the ratio of a pesticide-saturated vapour pressure over its concentration in a saturated solution (equation 3.1.). Alternatively, partition can be expressed as the dimensionless equilibrium constant, K_{aw}, relating the air concentration to the concentration in water (equation 3.2.).

$$H = \text{vapour pressure / aqueous solubility} \qquad [3.1]$$

$$K_{aw} = \text{air concentration / water concentration} \qquad [3.2]$$

The value of H provides a means to describe the vapour phases equilibrium between water and air and estimate susceptibility of pesticides to atmospheric loss through volatilisation. A comprehensive review of Henry's law constants is given by Suntio *et al* (1988). It could be inferred that the rate of volatilisation would increase with temperature, however, this is not always the case. As previously mentioned, pesticide vapour pressure is dependent on solution concentration and thereby any process affecting solution concentration will ultimately affect volatilisation. It has been shown that at elevated temperatures, pesticide vapour pressures actually decrease due to lower soil moisture contents. At the lower soil moisture contents, adsorption sites are vacated by water molecules and replaced by pesticide molecules, thus solution concentration falls. As the soil moisture content falls below 3% ($^{w}/_{w}$), vapour pressure decreases rapidly towards zero. Therefore, pesticide applications made to dry soil can be completely inert until activated by rainfall (Taylor and Spencer, 1990). Conversely, at elevated temperatures, which promote evaporation of soil water from the soil surface, water and dissolved pesticide are drawn up through the soil to replace that which has evaporated, thus countering to a minor extent the immobilisation of pesticides through soil adsorption.

Soil organic-matter content can also affect pesticide volatilisation through removing pesticide solutes from solution by adsorption and hence lowering solution concentration. It has been shown that vapour pressures over wet and dry soils are inversely proportional to soil organic matter content (Taylor and Spencer, 1990). The volatilisation of pesticides can be reduced by incorporating the pesticide into the soil directly after application. In one American study, 90 % of surface applied trifluralin was lost in 7 days compared to 22 % of soil incorporated trifluralin in 120 days (Riley and Eagle, 1990).

Very little work has looked at the volatilisation of pesticides from hard surfaces. Once applied to a hard surface, a pesticide will either remain resident until it is taken up by the target, is lost to another environmental compartment, or degrades chemically and/or biochemically. Considering the low retention of pesticides by hard surfaces, as discussed in Section 3.1.4, it is reasonable to suggest that the volatilisation behaviour of a pesticide from a hard surface may be predicted from the volatilisation of the pesticide into air from the pure substance. Therefore, unlike the soil environment, volatilisation from the hard-surface environment is probably solely dependent on the pesticide vapour pressure and the prevailing temperature. Given the relatively low pesticide retention capacity of the hard-surface environment and its physically exposed nature compared to the soil environment, it is likely that pesticide loss through volatilisation from the hard-surface environment is considerably greater than that from the soil environment for the same pesticide under similar climatic conditions.

3.1.8 The movement of pesticides to surface waters from the soil environment

The transport of pesticide residues by storm runoff from agricultural land to surface waters has been a major environmental concern for the last thirty years. Concern has arisen from the contamination risk to drinking water resources and effects on aquatic ecosystems, through the normal use of pesticides principally for the production of crops (Thorma and Nicholson, 1989; Leonard, 1990; Madhum and Freed, 1990).

Although surface runoff is not the only pesticide transport mechanism, in many situations it may be the most significant route for pesticide entry into the aquatic environment (Haith 1980; Haith, 1986). In a detailed study of the Granter Catchment in the Anglian region of the UK, Clarke *et al* (1991) indicate that the numbers and concentrations of pesticides in surface water are higher at times of high river flow, and that most of the annual pesticide load to the River Granter is from surface runoff and not groundwater. This behaviour has also been observed by Squillace and Thurman (1992), during their investigation of herbicide transport mechanisms in the Cedar River, Iowa, USA. Here, a computer model was used to separate the discharge hydrograph into groundwater and surface runoff components. When groundwater was the major component, the concentration of herbicides in the river was less than 1.0μg/l and averaged 0.2μg/l. The maximum concentration of herbicide occurred when surface runoff was the major component of river discharge, with levels exceeding 50μg/l for total herbicides.

Early work focused on the runoff into surface waters of the persistent organo-chlorine insecticides such as DDT and the 'drins' (Epstein and Grant, 1968; Merkle and Bovey, 1974). Due to their damaging effects on non-target organisms caused by their persistence, bioaccumulation, and biomagnification within food chains, most organo-chlorine insecticides have since been restricted from extensive use or banned (Turnbull, 1996). However, as discussed in Section 2.2.2, the use of pesticides, especially herbicides, in modern intensive agriculture has grown significantly over the last 20 years and is paralleled by the occurrence of modern herbicides in natural surface waters and drinking water resources (Croll, 1986 and 1991; NRA, 1992 and 1995). In the UK, the extensive use of isoproturon for cereal production has been matched by its ubiquitous presence in the surface waters of crop producing areas and has led to the restriction of its use in agriculture (Court *et al*, 1995; European Chemical News, 1995).

3.1.8.1 Storm runoff hydrology

The transport of a pesticide from its site of application is ultimately dependent upon rainfall induced hydrological processes. Once rainfall has been intercepted by the soil surface, excluding other losses, it will eventually move as runoff to surface waters and/or infiltrate downwards to groundwater. There is no clear distinction between flow routes and they often occur concurrently. Whether rain water moves as runoff or infiltrates downwards depends on many factors including soil texture and structure, soil under-drainage, soil topography, soil compaction, underlying geology, soil water content, and the duration and intensity of rainfall (Ward, 1975; Leonard, 1990). While concerns for surface water quality are often separated from those of groundwater quality, the hydrological cycle provides direct connection in many geological regions. Depending on hydraulic gradients, surface water may recharge groundwater or be replenished by groundwater. Therefore, levels of pesticide in surface waters may affect groundwater or be affected by groundwater (Clarke *et al*, 1991; Gomme *et al*, 1991).

Figure 3-4 schematically represents the various components which make up the runoff from the soil environment. Direct precipitation into the streams, lakes, and reservoirs make an immediate contribution to stream flow. In relation to the other components, however, the amount is normally very small considering the small percentage of catchment usually covered with water. Overland flow comprises the rainwater which, failing to infiltrate the surface, travels over ground to the flow channel usually in the form of rivulets following natural surface irregularities or often following tracks or tram lines compressed into the ground by farm machinery.

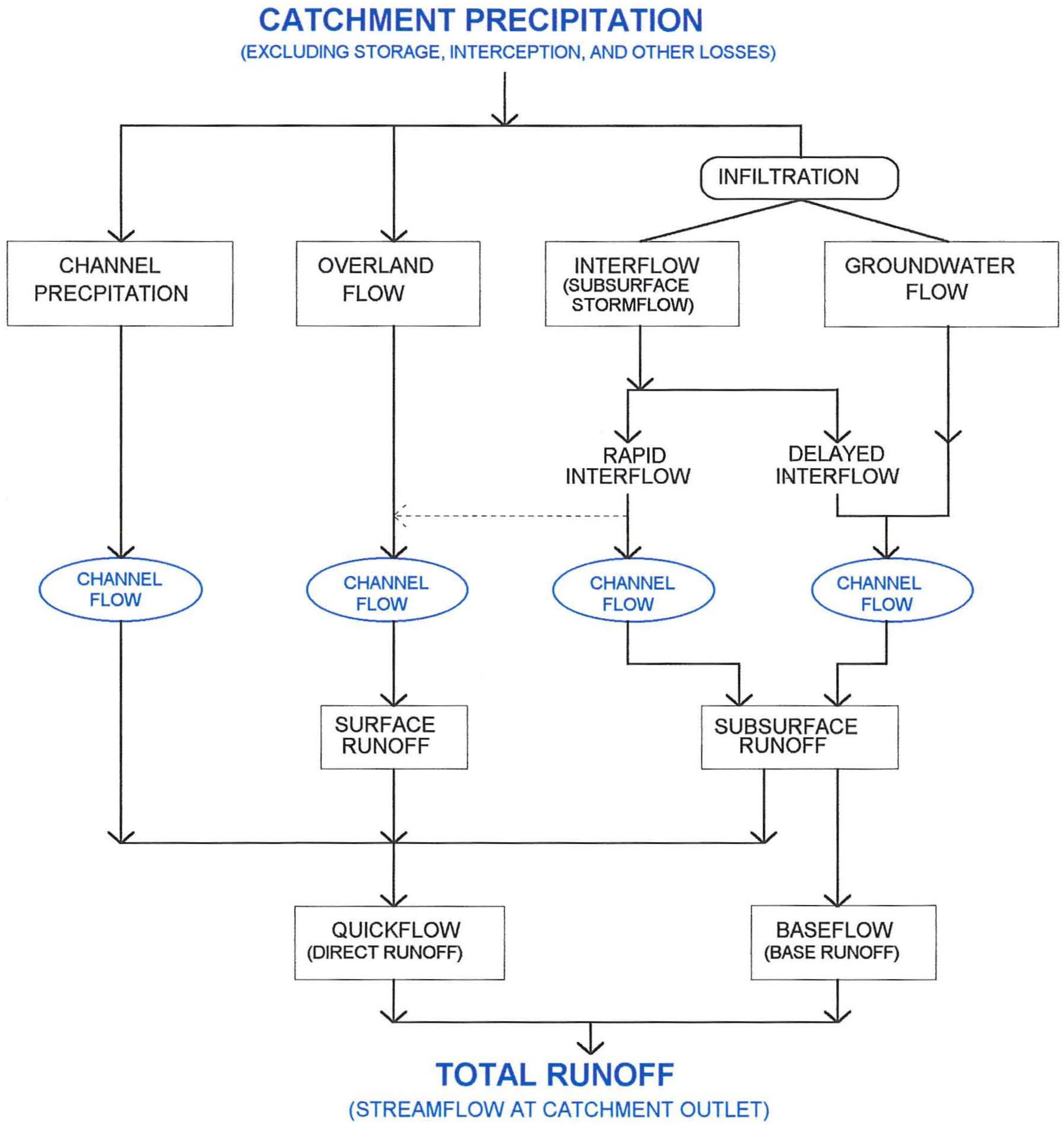

Figure 3-4 Schematic representation of the runoff process from the soil environment

Overland flow can be observed if (i) the water table has risen to the ground surface as a result of prolonged and/or intense rainfall, (ii) the rain intensity exceeds the soil infiltration capacity which can be affected by soil composition and compaction, (iii) the soil becomes hydrophobic as is the case for some dry soils, and (iv) the soil topography slopes significantly. Water which infiltrates the soil surface may then move laterally through the upper soil horizons towards the flow channel, either as unsaturated flow or, more commonly, as shallow-perched saturated flow above the main water table. This flow route is referred to as interflow. It occurs because the lateral hydraulic conductivity in the surface horizons of the soil is substantially greater than the overall vertical conductivity through the soil profile. During prolonged or intense rainfall, water will enter the upper part of the soil profile more rapidly than it can pass vertically through the lower part, thus forming a perched saturated layer from which water will 'escape' laterally towards the direction of the greater hydraulic conductivity.

Lateral hydraulic conductivity will vary according to local differences in soil structure, soil cracks - giving rise to matrix by-pass flow, and in most agricultural clay soils - soil drainage systems. Thus, in practice lateral interflow will pass at differing speeds through a variety of flow routes and consequently reach the flow channel at different times. Such flow behaviour is differentiated as rapid and delayed interflow. When conditions permit, near-surface rapid interflow will come to the surface to continue its journey to the flow channel as overland flow.

A proportion of rainfall which percolates through the soil profile to the main underlying groundwater will eventually reach the main flow channel as groundwater or base flow through the zone of saturation. Since water can only move slowly through the ground, the outflow of baseflow into the flow channel will lag behind the occurrence of rainfall for a time ranging from hours, days and weeks according to catchment soil hydrology and hydrogeology. In general, baseflow represents the main long term component of total runoff and is particularly important during dry periods.

In the context of pesticide transport to surface waters during a storm event, runoff is specifically defined as 'quickflow' or 'direct runoff' as illustrated in Figure 3-4. As previously mentioned, the components of quickflow will vary according to individual soil and rainfall characteristics. Pesticide runoff includes dissolved, suspended particulate, and sediment-adsorbed pesticide that is transported by water from the treated land surface as surface and subsurface runoff.

3.1.8.2 Factors affecting pesticide loss in runoff from the soil environment

The factors that determine whether a pesticide is susceptible to loss in runoff and the extent of the loss are to some degree an amalgamation of the various dissipation processes described previously, including biochemical and chemical degradation, soil retention, and volatilisation etc.. The greatest loss of pesticide in runoff to surface waters will occur if, soon after application, it is transported by the most direct hydrological route to the receiving surface water whilst encountering the minimum of retention in the soil or dissipation through soil-based degradation mechanisms or is sufficiently persistent to resist degradation (Wauchope, 1978). In practice this can be brought about by the transport of pesticide in overland flow occurring very soon after pesticide application. Movement in overland flow, soon after application, rather than through the soil profile as interflow some time after application, negates any significant pesticide retention through sorption with soil organic matter and/or mineral content. Further, biochemical and chemical degradation processes which in time would otherwise gradually degrade the pesticide are by-passed, minimising the impact on surface waters if transport in runoff subsequently occurred.

At the other extreme, the ideal scenario would entail the pesticide being applied to soil where it associates with the organic matter and mineral content of the upper soil profile and once there, exists in equilibrium between soil adsorption and soil solution such that sufficient pesticide is present in solution to allow for pesticide efficacy but not enough to lead to excessive leaching. The pesticide then persists long enough to achieve its task and degrades to harmless by-products. Meanwhile, soil hydrology ensures that rainfall, however prolonged or intense, infiltrates the soil surface and either moves as matrix interflow to a flow channel or percolates downwards through the soil matrix to groundwater. As rainfall infiltrates down through the pesticide bearing upper layers of the soil, it may carry with it pesticide previously in equilibrium with the soil water. However, as the rainwater and pesticide move downwards, pesticide movement is retarded by retention on the soil matrix which, in conjunction with chemical and biochemical degradation, gradually mineralises the pesticide before it is transported to a flow channel or to the groundwater.

In practice, the reality lies somewhere between the two extreme scenarios described, and is the interactive product of a number of factors associated with the weather, the soil, field management, and pesticide properties. The main factors have been reviewed by Willis and McDowell (1982) and Leonard (1990) and are shown below in Tables 3-2, 3-3, 3-4, and 3-5 along with more recent research findings.

Table 3-2 Climatic factors affecting pesticide loss in runoff

Factors	Comment	Selected references
Rainfall/runoff timing with respect to pesticide application	Highest concentrations of pesticide in runoff occur in the first significant runoff event after application. Pesticide concentration and availability at the soil and foliar surfaces dissipates with time thereafter.	Trichell *et al*, 1968; Wauchope, 1978; Leonard *et al*, 1979; Weber *et al*, 1980; Wauchope & Leonard, 1980; Glotfelty *et al*, 1984
Rainfall intensity	Surface runoff occurs when rainfall rate exceeds infiltration rate. Increasing intensity increases runoff rate and energy available for pesticide extraction and transport. May also affect depth of soil interaction. Increasing intensity reduces time to runoff within storm	Weber *et al*, 1980; Johnson, 1995
Rainfall duration /amount	Affects total runoff volumes; pesticide runoff concentration increases with increased unit area runoff; pesticide washoff from foliage related to total rainfall amount, leaching below soil surface also affected.	Squillace and Thurman, 1992; Southwick *et al*, 1988
Time to runoff after inception of rainfall	Runoff concentrations increase as time to runoff decreases. Relatively soluble pesticide concentrations and availability are greater in the first part of the event before significant reduction occurs as a result of leaching and incorporation by raindrop impact.	Baker and Laflen, 1979; Baker *et al*, 1982;

As can be seen from Tables 3.2, 3.3, 3.4, and 3.5, pesticide loss to surface waters can be affected by a multitude of factors. Generally, however, the most important factors are associated with the pesticide: persistence and soil adsorption (Baker, 1992, Nicholls, 1988), and with the climate: duration and intensity of rainfall and the time period between application and rainfall occurrence (Weber *et al*, 1980; Johnson, 1995). As described in the previous sections, once applied to the soil, pesticides are associated either with the organic matter or to a lesser extent with clay mineral surfaces of the upper soil layer (Leonard *et al*, 1979; Nicholls *et al*, 1993). The degree of adsorption is reflected by the soil or organic matter partition coefficient K_d and K_{oc} respectively (Section 3.1.3.2) and the pesticide resistance to chemical and biochemical degradation is defined in terms of the pesticide soil half life value ($t_{1/2}$) (Section 3.1.5).

Table 3-3 Soil factors affecting pesticide loss in runoff

Factor	Comment	Selected references
Soil texture and organic matter content	Affects infiltration rates; runoff is usually higher on finer-textured clay soils, however clay soils are also prone to cracking leading to rapid movement of pesticide with interflow to flow channels and also to groundwater. Time to subsurface runoff is greater on sandy soils reducing initial runoff concentration of soluble pesticides. Organic matter content affects pesticide adsorption and mobility. Soil texture also affects soil erodibility and particle transport potential	Rao & Davidson, 1980, Waite *et al*, 1992, Nicholls, 1988, Riley & Eagle, 1990; Traub-Eberhard *et al*, 1993; Demon *et al*, 1994; Haria *et al*, 1994; Brown *et al*, 1995; Williams *et al*, 1995
Surface crusting and compaction	Crusting and compaction decreases infiltration rates, reduces time to runoff, and increases initial concentration of soluble pesticides.	Baker, 1992; Rose *et al*, 1991; Kordel & Klöppel, 1993; Wauchope *et al*,1993
Soil moisture content	Initial soil moisture content at beginning of storm event may increase runoff potential, reduce time to runoff. Lower soil moisture content promotes greater pesticide adsorption .	Ng *et al*, 1995 Kosking and Harper, 1990
Slope	Increasing slope may increase runoff rate, soil detachment and transport, and increase effective surface depth for pesticide extraction	Trichell *et al*, 1968; Wauchope, 1978; Buttle, 1989

During the soil-based lifetime of a pesticide, whether the pesticide is transported in surface runoff or in subsurface runoff, the ultimate source of the pesticide is the upper soil layer where the pesticide is most abundant. A number of researchers have referred to this layer as the 'runoff mixing zone' or 'the runoff active zone' (Baker, 1992; Leonard, 1990), and it is mainly from this zone that dissolved or sorbed pesticide is 'extracted' during the course of a runoff event. Leonard *et al* (1979) and Baker and Laflen (1979) examined pesticide data from a number of catchments and found surface runoff concentrations over a wide range of storm event conditions to be strongly correlated with pesticide concentrations in the first ten millimetres of soil (see Figure 3.5.). The greater the persistence of a pesticide in the runoff mixing zone then the greater the potential for loss in runoff (Mills and Leonard, 1985). Generally, pesticides exhibiting a greater degree of adsorption or high K_{oc} or K_d are less likely to be lost in surface and subsurface runoff (Nicholls, 1988). The degree of adsorption also determines whether the pesticide moves predominantly in the solution phase or the sorbed phase. Once a pesticide is placed in the soil water system in the field, it will attempt to set up an equilibrium between dissolution in the soil water and sorption on the soil matrix. The higher the proportion of total applied pesticide equilibrated into soil water, the higher the potential loss in runoff.

Table 3-4 Pesticide properties affecting loss in runoff

Factor	Comment	Selected references
Solubility	Soluble pesticide may be more readily removed from the soil surface during the initial rainfall or be leached into the soil. When time to runoff is short, runoff concentration may be enhanced by increasing solubility	Trichell *et al*, 1968; Wauchope, 1978; Nicholls, 1988
Sorption properties	Pesticide strongly adsorbed to soil will be retained near the application site, i.e. at the soil surface and will be more susceptible to loss in surface runoff but less susceptible to leaching in subsurface runoff.	Leonard *et al*, 1979; Leonard, 1990
Polarity / ionic nature	Adsorption of nonpolar pesticide determined by soil organic matter; ionised compounds and weak acids and bases more affected by mineral surfaces and soil pH. Lipophilic compounds are retained on foliage by leaf surfaces and waxes, whereas polar compounds are more easily removed from foliage by rainfall	Rao & Davidson, 1980; Wauchope and Leonard, 1980; Nicholls, 1988
Persistence	The greater the pesticide resistance to volatilisation, photochemical, chemical, and biochemical degradation, whilst present in the runoff mixing zone, then the greater the potential for loss in surface or subsurface runoff.	Wauchope, 1978; Mills and Leonard, 1985
Formulation	Wettable powders are particularly susceptible to entrainment and transport. Liquid forms may be more readily transported than granular.	Wauchope, 1978; Wauchope and Leonard, 1980
Application rate	Runoff concentrations are proportional to amounts of pesticide present in the upper layer of the soil or surface runoff zone. At usual rates of application for pest control, pathways (e.g. sorption and degradation rates) are not affected by initial amounts present, therefore runoff potential is proportional to amounts applied.	Leonard *et al*, 1979; Glotfelty *et al*, 1984; Jones *et al*, 1995
Placement	Pesticide incorporation or any placement below the soil surface reduces concentrations exposed to surface runoff process.	Leonard *et al*, 1979; Wauchope, 1978, Wauchope and Leonard 1980

With the onset of rainfall, pesticide present in the soil solution will be extracted and transported in surface runoff or will infiltrate the soil surface, depending upon rainfall duration and intensity in combination with the soil infiltration capacity. As soon as pesticide is applied to the soil it will begin to degrade reducing the amount available for potential loss in runoff. Therefore, the greatest losses occur as a result of a minimal time period between application and runoff inducing rainfall (Glotfelty *et al*, 1984).

For strongly adsorbed pesticides such as permethrin (K_{OC}: 100,000 from Wauchope *et al*, 1992), soil-water equilibrium strongly favours sorption giving very low soil water pesticide concentrations in the runoff mixing zone during a storm event. The low pesticide concentration in runoff water is fairly constant with time. Major losses that do occur are predominantly associated with suspended sediment, from eroded soil, transported in surface runoff resulting from intense rainfall (Caro and Taylor, 1971).

Table 3-5 Soil / Field management factors affecting pesticide loss in runoff

Factor	Comment	Selected references
Season of application	Autumn applications more likely to produce runoff than Spring applications. Spring water table is likely to be lower than autumn due to greater crop evapotranspiration, and higher temperature, promoting evaporation and pesticide degradation.	Nicholls, 1988; Traub-Eberhard *et al*, 1993
Conservation tillage and erosion control practices	Reduces transport of pesticides adsorbed on suspended sediment. Also reduces transport of soluble compounds if surface runoff volumes are reduced at critical times after pesticide application.	Baker *et al*, 1978; Buttle, 1989; Baker, 1992
Conservation tillage - Residue management	Reduces pesticide runoff by maintaining natural soil drainage structure thereby increasing infiltration, decreasing runoff volumes, increasing time to runoff, and decreasing erosion and sediment transport. However, pesticide runoff may be increased under conditions where pesticides are washed from the crop residue directly into runoff water. Higher soil organic matter and microbial content enhances degradation.	Baker *et al*, 1978; Baker, 1992; Beck *et al*, 1995; Hall *et al*, 1989; Levanon *et al*, 1993
Subsurface mole drainage	Reduces chance of surface runoff by lowering water table. However, in clay soils, may lead to enhanced subsurface runoff by promoting rapid movement of interflow and pesticide residues through soil cracks and macropores into field drains .	Mackney *et al*, 1975; Rose *et al*, 1991; Harris *et al*, 1993; Kladivko *et al*, 1991; Johnson *et al*, 1994; Brown *et al*, 1995
Vegatative buffer strips	Buffer strips around treated fields may reduce the transport of some pesticides by secondary infiltration, sediment deposition and sorption on plant surfaces and debris.	Muscutt *et al*, 1993; Real *et al*, 1993; Patty *et al*, 1997

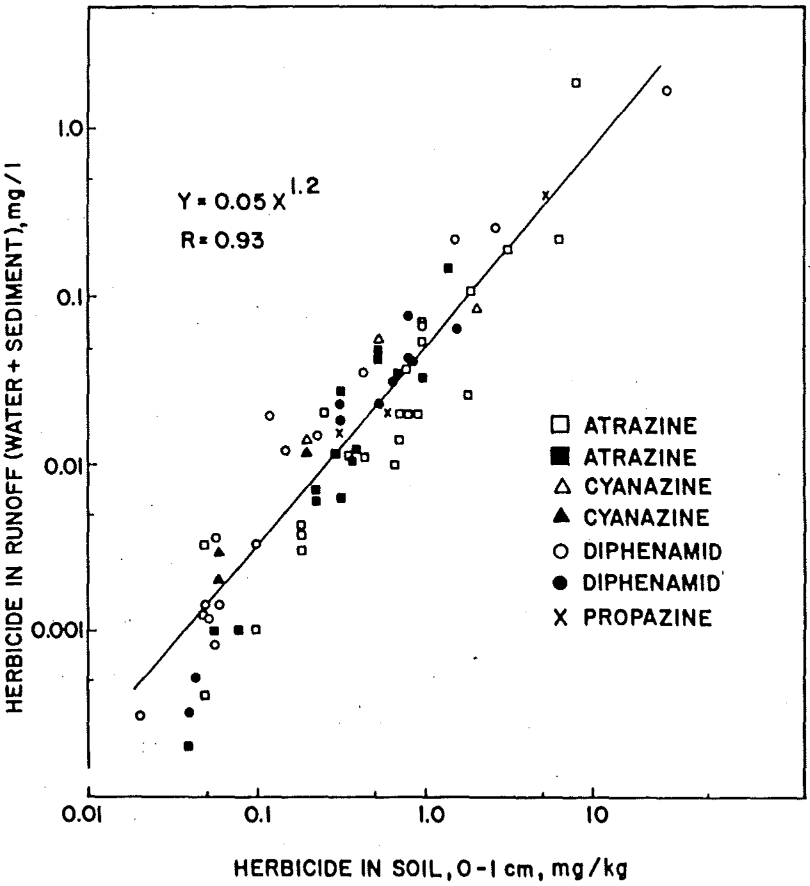

Figure 3-5 Relationship between pesticide concentrations in 0 to 10mm surface soil and concentrations in surface runoff (Leonard *et al*, 1979)

For weakly adsorbed pesticides such as dimethoate (K_{oc}: 20 from Wauchope *et al*, 1992), the pesticide is readily released to soil water in the runoff mixing zone and losses with sediment are very small. The pesticide concentration in runoff can be initially high but decreases quickly with time during an event as water moving through or over the runoff mixing zone depletes the pesticide present. The amount of infiltration that occurs before surface runoff begins will be a large factor in determining surface runoff losses (White *et al*, 1976).

For moderately adsorbed pesticides such as atrazine (K_{oc}: 100 from Wauchope *et al*, 1992), the pesticide is in greater equilibrium with the soil water of the runoff mixing zone and therefore runoff losses occur mainly in the solution phase rather than the sorbed phase (Wauchope, 1978; Wills and McDowell, 1983). Concentrations of moderately adsorbed pesticides in runoff water usually peak just before or with the runoff hydrograph peak and then concentration declines rapidly through the recession of the hydrograph. Williams *et al*, (1995) suggest that in the initial stages of a runoff event, the rainfall displaces pesticide-bearing soil water and forces it to infiltrate the soil profile and may subsequently move it to a flow channel as subsurface runoff. Equally, the pesticide could move in surface runoff if the soil has become water-logged or if the rainfall has exceeded the soil infiltration rate. During the remaining course of the event there is insufficient time for full equilibrium to be established between the new soil water and the pesticide adsorbed to the soil matrix. Therefore, the remaining water moving to the flow channel is of lower concentration. Between rainfall events, equilibrium is re-established and the next event begins with a pesticide peak although it may be lower in magnitude compared to the previous peak due the previous runoff losses and intervening loss of pesticide through degradation. Researchers monitoring the concentrations of moderately adsorbed pesticides in subsurface field drains draining agricultural land, have found an inverse correlation between soil adsorption behaviour, K_{oc}, and pesticide concentration in subsurface drainage water (Monke *et al*, 1988; Kladivko *et al*, 1991).

For a moderately adsorbed pesticide applied at the same rate to the same soil, the concentration in overland or surface runoff is likely to be higher than in subsurface runoff (Johnson *et al*, 1994; Harris *et al*, 1994). A pesticide extracted and transported in surface runoff is effectively removed from the soil matrix and the associated retention and degradation mechanisms. Conversely, a pesticide extracted in rainfall which goes on to infiltrate the soil surface and move to a flow channel with subsurface runoff, will be constantly exposed to the soil matrix where its movement will be attenuated by soil adsorption. This will provide opportunities for chemical and biochemical degradation to reduce the mass of pesticide eventually occurring in the subsurface field drainage and flow channel. As well as rainfall factors, the rate at which soil water and solute pesticide leach downward is in part related to the matrix flow characteristics of a given soil which is dependent on soil structure and texture (Nicholls, 1988). In general, sandy soils have a much higher hydraulic conductivity than heavy clay soils due to the coarser texture and relatively larger flow channels associated with sandy soils (Mackney *et al*, 1975). Also, the organic matter content of soils tends to increase with increasing clay content (Riley and Eagle, 1990). Therefore, clay soils generally inhibit pesticide leaching due to their low hydraulic conductivity and their significant soil partition coefficients resulting from relatively high levels of organic matter.

However, workers in a number of countries including America, Germany and the UK have shown how this relationship can break down (Levanon *et al*, 1993; Traub-Eberhard *et al*, 1993; Haria *et al*, 1994). They have reported the appearance of significant pesticide concentrations in subsurface runoff, from clay soils, prior to the soil reaching field capacity* at times much earlier than estimations from soil matrix conductivity and pesticide soil retention behaviour would have otherwise predicted. Harris *et al* (1994) describe how soils characterised by high clay contents are susceptible to cracking that is induced by the normal shrink-swell processes which occur because of normal fluctuation in soil moisture content. During the drier summer months, the soil moisture content falls and soil cracks develop; further Harris *et al* (1993) suggest that the installation of mole drainage can accentuate soil cracking. With the onset of autumn rainfall there is insufficient time for the soil to swell and rainwater therefore by-passes the soil matrix and rapidly moves through the soil profile following the soil cracks. The by-pass or preferential flow will then either be intercepted by a field drain or move as sub-surface interflow eventually

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* Field capacity is the water content of the soil (volume fraction) after the saturated soil has drained under gravity to equilibrium, at this stage rainfall cannot be received into the soil without drainage loss

reaching a drainage ditch. Thus pesticide rapidly transported in preferential flow will by-pass contact with the soil matrix and its associated concentration attenuation through retention and degradation .

Johnson *et al* (1994) suggest that drained heavy clay soils which exhibit preferential flow characteristics represent a particular contamination threat. A moderately persistent herbicide such as isoproturon with a half life of approximately 30 days (Nicholls *et al*, 1993), applied to winter cereals sown on heavy clay soil may represent a potentially serious contamination threat to surrounding watercourses. According to Cannel *et al*, (1984), clay soils which may exhibit preferential flow, represent up to 33% of the land area of England and Wales, and a large proportion of the area is used for the production of cereal crops.

At present the factors which lead to the rapid transport of pesticides in runoff from under-drained heavy clay soils are poorly understood. Consequently, in the UK, a number of collaborative research programmes have been set up to investigate the factors affecting pesticide movement in storm runoff with particular attention being paid to understanding the factors and conditions that promote pesticide loss in preferential flow (Table 3-6).

Table 3-6 UK research programmes investigating the movement to surface waters of pesticide applied to cracking clay soils

Experiment Location	Type of Experiment	Collaborators	Selected Publications
Brimstone Farm, Oxfordshire	Lysimeter 0.2 ha field plots	Inst. Env. Bio. Sci., Lancs. Uni; ADAS Land Centre, Cambridge; Rothamsted ES, Harpenden	Beck *et al*, 1995; Harris *et al*, 1994; Nicholls *et al*, 1993; Harris *et al*, 1993; Beck *et al*, 1995 Armstrong *et al*, 1995; Jones *et al*, 1995
Cockle Park Farm Northumberland	0.25 ha field plots	Dept. Ag. Env. Sci., Uni of Newcastle upon Tyne; ADAS Land Centre, Cambridge	Brown *et al*, 1995; Brown *et al*, 1995; Harris *et al*, 1993
Wytham Farm Oxfordshire	0.125 ha field plot	Inst. of Hydrology; Wallingford; Horti. Res. Int., Wellsbourne	Johnson *et al*, 1995; Johnson, 1995; Johnson *et al*, 1994; Haria *et al*, 1994
Rosemaund Farm, Herefordshire	180 ha catchment	ADAS Rosemaund; Inst. of Hydrology; Wallingford; ADAS Land Centre, Cambridge BRE, Watford; MAFF Burnham on Crouch, Environment Agency, Cardiff; Soil Survey & Land Research Centre, Cranfield	Williams *et al*, 1991; Williams *et al*, 1995; Matthiessen *et al*, 1992; Turnbull *et al*, 1995;

The experiments range from a catchment study to the use of hydrologically isolated field plots which allow the effects of different drainage and tillage systems to be simultaneously evaluated under field conditions. In general, the individual findings of the programmes reflect the extent to which their respective soils are susceptible to cracking. Harris *et al* (1993) reported subsurface drainflow concentrations of isoproturon one order of magnitude higher at Brimstone farm when compared to a storm event of similar magnitude and timing at Cockle Park for similar application rates of isoproturon. The difference was attributed to the more extensive cracking of the Brimstone soil which was reflected in its higher clay content (60%) compared to that of the Cockle Park soil (35%). Brown *et al* (1995) have reported that for a given soil clay content, the development of soil cracks was strongly related to the soil moisture regime. Further, it was reported that the highest concentrations of isoproturon were associated with surface runoff from undrained field plots. It was found that, although the installation of subsurface drainage systems facilitates the rapid movement of isoproturon to subsurface drains in by-pass flow, such losses when combined with the consequently lower surface runoff losses, were overall lower than the losses in surface runoff from the undrained plot. Harris *et al* (1994) also have reported higher isoproturon concentrations in surface runoff than subsurface drainflow and proposed that a soil drainage system that minimises both surface runoff and rapid by-pass flow to the drainage system would be the best compromise.

Jones *et al* (1995) report on an experiment using sixteen hydrologically isolated field plots at Brimstone farm to investigate the affect of field management practices for reducing movement of pesticides to surface waters from cracking clay soils. Studies conducted during the first two years of the experiment (93/94 and 94/95) have examined the effect of drainage restriction, application rates, soil tillage, soil sealants, and pesticide sorption properties. Pesticides of wide-ranging sorption properties were used from triasulfuron (K_{oc}=9 and isoproturon K_{oc}=125) to pendimethalin (K_{oc}=5000). The results show that individual losses were inversely related to pesticide sorption behaviour which agrees with similar work reported by Monke *et al,* (1989) and Kladivko *et al,* (1991).

Losses between full and half-rate isoproturon applications, expressed as a percent of the amount applied, were found to be not significantly different when drainflow variability was taken into account. However, the use of drainflow restrictors, which were expected to encourage the closure of cracks and enhance water storage, were found to reduce the losses of less mobile pesticides by approximately 25%. No definite conclusions were drawn regarding the effects of soil sealants and soil tillage though it is reported that the results are encouraging enough to warrant further investigation.

3.1.9 The movement of pesticides to surface waters from the hard surface environment

A review of the literature detailing reports of the occurrence of pesticides in surface waters reveals that the vast majority of research has focused on the movement of pesticides from the soil environment to surface waters in surface runoff. Although some work has been done in America and Japan in the urban environment, it has mainly dealt with the aquatic fate of pesticides applied to urban turf and golf courses. Very little work has been carried out on the transport of pesticides from urban or hard-surface environments to surface waters (Sudo and Kunimatsu, 1992; Morioka and Cho, 1992; Racke and Leslie, 1993).

As previously discussed in Section 2.5.3, it was essentially the passing of the EC Drinking Water Directive, and associated pesticide standards, in 1980 that first initiated detailed surveys in the UK of surface and groundwater quality with respect to pesticides. In a survey of surface waters and groundwaters in East Anglia, Croll (1986) suggested that the widespread occurrence of atrazine in surface waters was unlikely to be caused by agricultural sources since only minor quantities were used on sweet corn and maize, both of which were minor crops in the UK. It was suggested that it was more likely that the presence of atrazine at most sampling points arose from its use for the total control of weeds on railway embankments, roadsides, and industrial areas.

These findings have since been duplicated by a number of workers (Clarke *et al*, 1991; Croll, 1991; Gomme *et al*, 1991). Overall, in the UK on a national basis, it can be concluded that even though the non-agricultural use of pesticide represents only 2-5% of the agricultural use of pesticide (Carter, 1992; Garnett, 1995), their occurrence often equals or exceeds that of the most widely used agricultural pesticides (NRA, 1995). Due to the widespread occurrence of atrazine and simazine in surface and groundwaters, their approval for non-agricultural use was revoked by the Advisory Committee on Pesticides in 1992. Since the ban, their occurrence in surface waters has steadily declined (Carter and Heather, 1996); however, in many cases users have replaced the use of simazine and atrazine with the contact herbicide, glyphosate, and the residual-acting herbicide, diuron. As a result one problem has been replaced with another as the reduction in the occurrence of the triazines has to some extent been replaced by that of diuron (NRA, 1995).

The pattern of occurrence of non-agricultural pesticides in surface and groundwaters has led to concern amongst water utilities, the Environment Agency, and the agrochemical companies manufacturing pesticides. The water utilities are required by the 1989 Water Supply (Water Quality) Regulations to supply drinking water with no more than 0.1µg/l of an individual pesticide, and have been forced to install further water purifying equipment based on granular activated carbon and ozonation to clean up contaminated source water (Court *et al*, 1995). It is considered by the water utilities and the Environment Agency that the problem is best solved by prevention rather than cure. Therefore, it has been suggested that the use of pesticides in the hard surface environment principally to control vegetation, needs to be re-appraised with measures introduced to minimise risk to water resources (White and Pinkstone, 1995; National Rivers Authority, 1993 and 1995). This has involved the water utilities and manufacturers embarking on catchment protection campaigns aimed at the users of non-agricultural pesticide to encourage their adoption of best working practice to minimise contamination risk to surface waters (White and Pinkstone, 1995; Court *et al*, 1995; Davies *et al,* 1995). This has been backed up by the distribution of advice on the adoption of best working practice by the Department of the Environment (Department of the Environment, 1994).

White and Pinkstone (1993) have called for fundamental research into the factors that affect the transport of pesticides following their application to hard surfaces. Presently however, in the UK, apart from this study at Middlesex University, very little research is being carried out in this area. A collaborative study has recently been established between a number of water utilities, the regulators, and a number of agrochemical manufacturers which is being co-ordinated by the Soil Survey and Land Research Centre, Cranfield University (Heather and Carter, 1996). Due to the commercial aspects of the programme there is some doubt whether the findings of the research will be widely available in the public domain (Heather pers comms, 1996).

3.1.9.1 Factors affecting pesticide loss in runoff from the hard surface-environment

The literature search summarised in Table 3.7 shows that very little work has been carried out on the aquatic fate of pesticides applied to hard surfaces and even less work on the factors that affect their transport to surface waters. The majority of these studies report on the occurrence of pesticides in surface waters that are likely to have been transported in surface runoff. However, Torstensson (1994) and Ellis *et al* (1997) report that pesticides are relatively more mobile when applied to hard-surface materials such as railway ballast, compared to soil, due to much lower sorption and retention. Further, because of the relative absence of organic matter, pesticides persist far longer when applied to hard surface materials provided they are not exposed to sunlight. Similar results have been reported by Roy and Krapac (1994) who found the mobility of atrazine to be significantly higher in sand compared to soil.

Although very little work has actually been carried out to investigate the factors that affect the transport of pesticides from hard surfaces to surface waters in surface runoff, it is possible to estimate the main factors through consideration of those features which differentiate between the hard surface and the soil environment. The first major difference between hard surfaces and soil environments is their respective hydrology. As described in Section 3.1.4, hard surfaces are usually constructed of materials such as macadam and concrete which allow minimal infiltration.

Further, they are engineered to promote the rapid movement of rainwater to surface drainage systems which channel the storm water to the nearest open water course via a storm sewer or to the nearest sewage works in a combined storm-foul water sewer (Connolly and Blaine, 1991). The practical differences are illustrated in Figures 3-6 and 3-7 which show the rainfall-runoff relationship for a hard surface urban catchment and a soil based catchment of similar area, respectively.

Table 3-7 Literature survey detailing research findings on the aquatic fate of pesticides applied to hard surfaces

Title	Author	Year	Comment
Herbicide losses from hard surfaces and their effect on ground and surface water quality	Heather and Carter	1996	Considers the risks of using pesticides on hard surfaces in relation to the construction and hydrology of hard surfaces. Discusses possible influences on pesticide loss to surface water.
Mobility and Transformation of Diuron in Railway Embankments	Torstensson	1994	Reports the killing of pine trees lining the route of a railway resulting from the intensive use of diuron for the total control of vegetation on railway tracks. Tests showed that diuron was up to 40 times more mobile and persisted 8 times longer in embankment material compared to soil.
Pesticide application and deposition - their importance to pesticide leaching to surface waters	Harris *et al*	1992	In part, reports of the contamination of rural watercourses from roadside ditches and from disused railway ballast used as hard-core on field tracks.
The transport of pesticide residues to surface waters in small clay-based catchments	Harris *et al*	1993	In part, reports that the detection of atrazine and simazine was likely to result from non-agricultural use on hard surfaces.
Pesticide in Streams Draining Agricultural and Urban Areas in Colorado	Kimbrough and Litke	1996	Monitoring showed that commonly used non-agricultural pesticide were routinely detected in surface waters; detection correlated with seasonal application periods and concentrations were greatest in storm runoff.
A stewardship programme on diuron aimed at protecting UK water quality	Davies *et al*	1995	Reports that diuron sprayed over open drains or in the gullies/channel around non-porous surfaces posed the greatest risk to water quality.
Distribution and seasonal variation of pesticide residues in Yodo river basin, Japan	Yamaguchi *et al*	1992	Reports that over 50% of pesticides detected down-stream of an urban area were correlated with pesticide use patterns in the urban area.
Transport and the Environment: Effects on Water Quality	Ellis *et al*	1997	Reports that up to 34% of diuron was lost in surface runoff during a storm event occurring 27 days after application to roadsides. Further, it reports that when applied to railway ballast, the triazines persist far longer than their respective soil derived half-lives would predict and are consequently likely to leach to surface or groundwaters long after application

The total runoff from a hard surface urban catchment is essentially made up of quickflow or direct runoff with very little contribution from baseflow (Figure 3-6) and this situation is relatively constant throughout the year. Conversely, the total runoff from a soil-based catchment is made up of varying contributions of surface runoff and subsurface runoff depending upon the soil moisture deficit at the time of the storm event. If the soil moisture deficit is very low at the beginning of the storm event, then a higher proportion of total runoff is likely to be surface runoff.

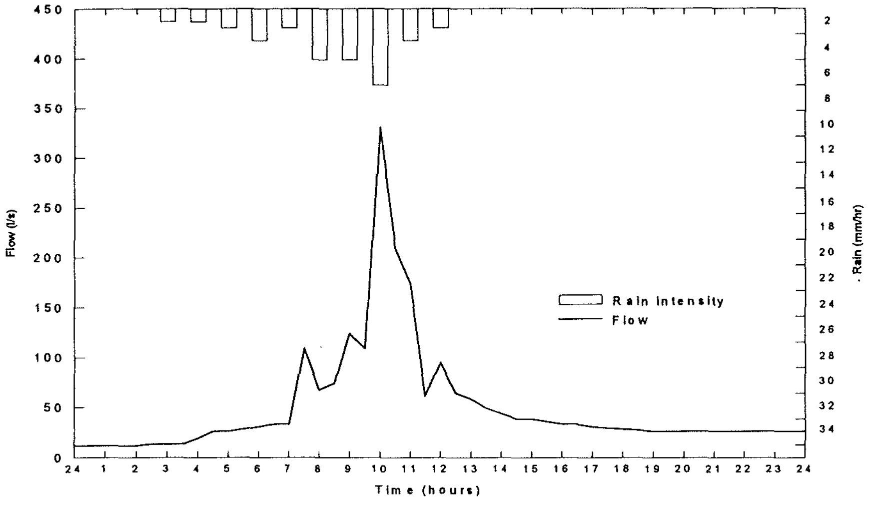

Figure 3-6 Rainfall and hydrograph of a storm event occurring within an urban catchment characterised by hard surfaces.

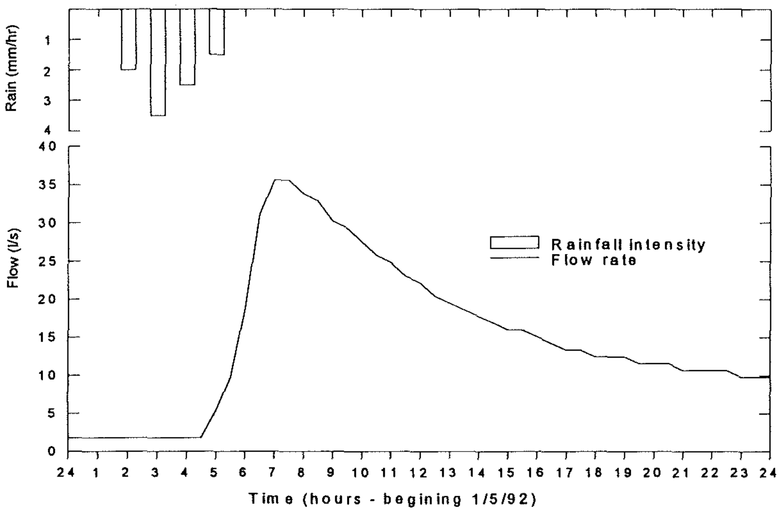

Figure 3-7 Rainfall and hydrograph of a storm event occurring within an agricultural catchment

Generally, on the commencement of rainfall upon a soil-based catchment, runoff will not begin until any soil moisture deficit has been satisfied. Therefore, there is usually a lag time between the maximum rainfall intensity and the maximum flow rate which is in part a measure of the soil moisture deficit. Due to the demand of the soil moisture deficit, the rainfall-runoff volume ratio or water balance is normally relatively low for a soil-based catchment in comparison to that of a hard-surface urban catchment characterised by little capacity for rainwater storage. Also, the water balance will vary in accordance with the soil moisture deficit which in turn will depend on seasonal water demands. In the summer months the water balance is likely to be low due to evaporation and evapotranspiration of plants and crops. Conversely, during the winter period the water balance will increase as the water demands of plants decrease along with evaporation due to lower average temperatures. Comparison of Figures 3-6 with 3-7 shows that the flow rate from the urban runoff returns to the pre-event rate much sooner than the flow rate of the runoff from the soil based catchment. This behaviour is indicative of the rainwater storage capacity of the soil profile which gradually releases the rainwater to the flow channel for a period of time long after the cessation of rainfall, as subsurface runoff, until the soil reaches field capacity.

It is probable that the key factors that affect the movement of pesticide applied to hard surfaces, in storm runoff are similar to those that affect the transport of pesticide applied to the soil environment, namely persistence, adsorption, rainfall intensity, and the time period between application and rainfall. However, in relation to the pesticide-related factors, persistence and adsorption, it is likely that the underlying mechanisms differ from those that are important in the soil environment.

For pesticides applied to the soil environment, persistence is mainly related to the biochemical stability of the pesticide in conjunction with the level of organic matter present in the soil (Section 3.1.5). However, the hard-surface environment is characterised by negligible amounts of organic matter and is almost entirely composed of inorganic material (Section 3.1.6). Therefore, biochemical stability is likely to be of minor importance in determining the persistence of a pesticide applied to hard surface.

When applied to hard surface such as concrete or tarmacadam a pesticide has very little opportunity to infiltrate the impervious surface and will therefore be constantly exposed to climatic extremes. It is probable that the main mechanisms determining pesticide persistence will be the pesticide vapour pressure and photolytic stability. Hydrolytic stability may be important if there is sufficient moisture available to facilitate hydrolysis but not enough to induce surface runoff. Because the mechanisms suggested are strongly dependent on climatic conditions it is probable that pesticide persistence will be more variable than that of a pesticide applied to the soil environment. If a pesticide is applied to railway ballast material or something similar, it is likely that the nature of the surface will afford more protection than a flat concrete or tarmacadam surface and therefore the contribution of each mechanism to pesticide persistence may change accordingly with possible contribution from biochemical degradation (Torstensson, 1994).

Because of the impervious nature of hard surfaces and the relative absence of organic matter and clay particles, the retention of pesticides on hard surfaces is likely to be significantly less than the retention in the soil (Section 3.1.4) and therefore greatly increases the potential loss of pesticides in surface runoff. As for the soil environment, as soon as a pesticide is applied, degradation processes will begin reducing the amount that was originally present at the site of application. Therefore, maximum loss will occur if the time period between application and rainfall is a minimum.

3.1.10 The movement of pesticides to groundwater from the soil and hard-surface environment

In recent years the contamination of groundwaters with pesticide residues has caused widespread concern throughout the world. Concern has particularly focused on the contamination of groundwaters which are used as a drinking water resource, because of the implications for human health (Funari *et al*, 1988; Headworth, 1989; Pionke and Glotfelty, 1989; Walls *et al*, 1996). In the broadest context, within the soil environment, the soil profile acts a buffer attenuating the movement of pesticides downwards into vulnerable aquifers. A number of factors affect to a greater or lesser degree the downward leaching of pesticide. These include the physico-chemical properties of the pesticide, the prevailing climate and rainfall patterns, and the nature and composition of the soil. The leaching of pesticides is greatly affected by soil adsorption since only the fraction which is unadsorbed is free to move with the soil water. Pesticide solubility on its own does not limit the aqueous transport of the pesticide, however, a pesticide having lower solubility and higher lipophilicity also tends to exhibit greater adsorption to soil organic matter and clay minerals and is therefore less susceptible to leaching (Nicholls, 1988). Thus pesticides with high soil partition coefficients (K_d) applied to clay soils rich with organic carbon are less likely to leach than those with lower K_d values. Further, pesticide persistence or half-life in conjunction with leaching susceptibility will determine whether or not the pesticide will persist long enough to constitute a significant presence which is likely to pose a contamination risk to groundwater. As the pesticide is leached further down into the soil profile, organic matter and biomass will decline and reduce the rate of pesticide degradation and increase the rate of leaching due to the presence of fewer adsorption sites (Roy and Krapac, 1994).

Pesticide soil half-life ($t_{1/2(\text{soil})}$)[1] and the soil organic matter partition coefficient (K_{oc}) have been used by Gustafson (1989) to derive pesticide leaching indices or groundwater ubiquity scores from the following equation:

$$\text{Groundwater Ubiquity Score (GUS)} \quad = \quad \log_{10}(t_{1/2(\text{soil})}) \,.\, (4 - \log_{10}(K_{oc}))$$

Pesticides scoring above 2.8 are termed 'leachers', those between 2.8 and 1.8 'transition', and those below 1.8 'non-leachers'. Pesticide GUS values can provide a useful first-stage attempt at determining the probability that a pesticide may leach into groundwaters. The rate at which soil water and solute pesticide leach downward is in part related to the matrix flow characteristics of a given soil which is dependent on soil structure and texture (Nicholls, 1988). In general, sandy soils have a much higher hydraulic conductivity than heavy clay soils due to the coarser texture and relatively larger flow channels associated with the former (Mackney *et al*, 1975).

The sophistication of hard-surface drainage systems varies, and is often dependent on when the structure was built, the proximity of the structure to an urban population, and the consequent need to alleviate the risk of flooding. Often the drainage system employed routes surface runoff to soakaways or to locations below the soil profile so that the main attenuating or buffering layer has been by-passed. Where runoff is channelled to surface water bodies, pesticide-bearing water

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[1] The average time it takes, in the field, for soil residues of the parent molecule to decline by 50%

may travel into an aquifer through the normal process of groundwater recharge (Gomme *et al*, 1992; Kimbrough and Litke, 1996). Pesticides applied to roads and railways which are routed through earth-work cuttings made into aquifer outcrops can be transported directly to groundwater, with shallow groundwaters underlying application areas being particularly vulnerable (Aldous and Turrell, 1994; Heather and Carter, 1996)

3.2 Pesticide runoff modelling

The requirement to predict the behaviour of pesticides in the environment, whether for pesticide design or for regulatory purposes, is essentially driven by the prohibitive cost of running extensive field trial monitoring programmes. Computer models attempt to simulate the real world and therein the behaviour of a pesticide. Simulations are based on intrinsic pesticide properties such as solubility and extrinsic properties borne from the manner in which a pesticide interacts with the real world, such as biochemical degradation ($t_{1/2}$) and soil particle adsorption behaviour.

As the undesirable environmental effects of extensive pesticide use, particularly contamination of drinking water supplies, became apparent during the 1960s and 1970s, concerns for the environmental impact of pesticides began to become as important as pesticide effectiveness. However, the monitoring programmes established to determine the environmental fate of pesticides were found to be limited by operational expense; further, since the outcome of the monitoring experiments were determined to a great extent by prevailing weather patterns, a number of environmental scenarios remained uncertain, such as what if rainfall occurred one hour after application or one day after application?

The development of computer simulation programmes was seen as a relatively inexpensive alternative that could use and extrapolate existing field scale monitoring data to predict seasonal, spatial, and temporal variations. Today's models are used to predict the likely behaviour of new pesticides as well as existing pesticides; they are also used to predict environments that may be particularly vulnerable to contamination such as shallow groundwater overlain by sandy soils.

Computer models for describing pesticide fate and transport with regard to drinking water resources may be broadly classified as either screening or simulation models (Gustafson, 1995). Screening models typically require the minimum of input variables and the computations can usually be carried out using a hand-held calculator. They are often empirical or based on a number of simplifying assumptions in order to reduce the amount of computation required. In contrast, simulation models can require considerable resources and generally attempt to describe the behaviour of the pesticide as a full function of time and at least one dimension, usually the soil vertical profile (Cohen *et al*, 1995).

Due to their complexity and the expert knowledge required in their use, simulation models are usually used for research and aim to predict the fate of a pesticide in carefully defined soils and under identified weather patterns. Screening models with their ease of use and minimum input parameters are normally used for management purposes where an attempt is made to quantify the potential risk of a pesticide being transported in surface runoff or leaching to groundwater.

The United States has to some extent led the field in the development of simulation models, with the development PRZM (Pesticide Root Zone Model) by the US Environmental Protection Agency (Carsel *et al*, 1984). Gustafson (1995) reports that PRZM is the most widely-used model when a fully-fledged simulation of pesticide behaviour is required. Recent versions of PRZM include an improved volatilisation model and the possibility of modelling up to two degradation products during a single simulation. The US Department of Agriculture has developed GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) and its predecessor CREAMS (Chemical, Runoff, and Erosion from Agricultural Management Systems) (Leonard *et al*, 1987). These models do not have all the flexibility of PRZM but are considered to be more user friendly. A variant of the PRZM model called PELMO has been developed for regulatory use in Germany (Klein, 1991). It uses the Freundlich equation for describing pesticide sorption to the soil, optional non-linear dissipation kinetics, and an explicit treatment of temperature-driven depth-dependence pesticide degradation rate. CALF (Calculation Flow) was developed in the UK primarily by Peter Nicholls and Allan Walker; it is the only widely-used simulation model to directly account for the slow increase in soil sorption with time (Walker and Barnes, 1981).

The most widely-used screening model, GUS (Groundwater Ubiquity Score) uses a single numerical index for predicting the water-contamination potential of a pesticide based on its organic carbon-water partition coefficient (K_{oc}) and its soil half life ($t_{1/2}$) (Gustafson, 1989). This model is described more fully in Section 3.1.10.. Other screening models include the Cohen Criteria (Cohen *et al*, 1984); Jury screening model (Jury *et al*, 1987); and the Hornsby screening model (Nofzinger and Hornsby, 1988).

Other modelling approaches have attempted to predict the amount of pesticide lost in surface runoff induced by storm events. Wauchope and Leonard (1980) describe a semi-empirical method for the prediction of maximum pesticide concentrations in agricultural runoff. Haith (1987 and 1990) describe the use of a Monte Carlo simulation for the stochastic modelling of pesticide concentrations in storm event runoff.

A more recent approach to pesticide modelling has employed the fugacity principle to predict the distribution of pesticides within environmental compartments (Mackay and Paterson, 1991).The approach has been further developed by Di Guardo *et al* (1994) to predict the average pesticide concentration in surface runoff. Fugacity has also been used on a global scale to predict the environmental distribution of persistent organic pollutants (Wania and Mackay, 1993 and 1996). A fuller description of the principles and use of fugacity modelling is given in Section 8.2.1..

CHAPTER FOUR

4. Site description, Sampling, and Analytical methodology

4.1 Introduction

The experimental catchment at North Weald was originally established by Middlesex University and the Epping Forest District Council in 1985 to study the surface water hydrology of the area because the village was particularly susceptible to flooding. In 1988, MAFF commissioned the ADAS Soil and Water Research Centre (SWRC) to examine the problem of nitrate and pesticide residues leaching from agricultural land into surface water. In order to investigate the influence of varying climate, soil type and field management, the SWRC established a number of experimental sites throughout the UK including North Weald, where the research programme was run on a collaborative basis with Middlesex University (Rose *et al*, 1991; Harris *et al*, 1993).

4.2 North Weald site description

The studied catchment is located around the village of North Weald in Essex, approximately four miles north-east of Epping town, at grid reference TL 495 045. The catchment can be divided into two hydrologically distinct areas characterised by the differing land use traversed by the main watercourse which originates in the predominantly arable agricultural area and then flows through an urban area to the main catchment outfall. After leaving the catchment, it flows into the Cripsey Brook which eventually flows into the River Roding. The agricultural area will be referred to as the *agricultural sub-catchment* and the urban area as the *urbanised catchment*. The watercourse was monitored at site A as it flowed from the agricultural sub-catchment into the urbanised catchment and also at site D near the overall catchment outfall (Figure 4-1). The agricultural sub-catchment covered an area of 160 ha of which approximately 33.1% was arable land, 22.5% was grassland and 44.4% mixed woodland, and which was bordered on its southern boundary by the M11 motorway (Figure 4-1).

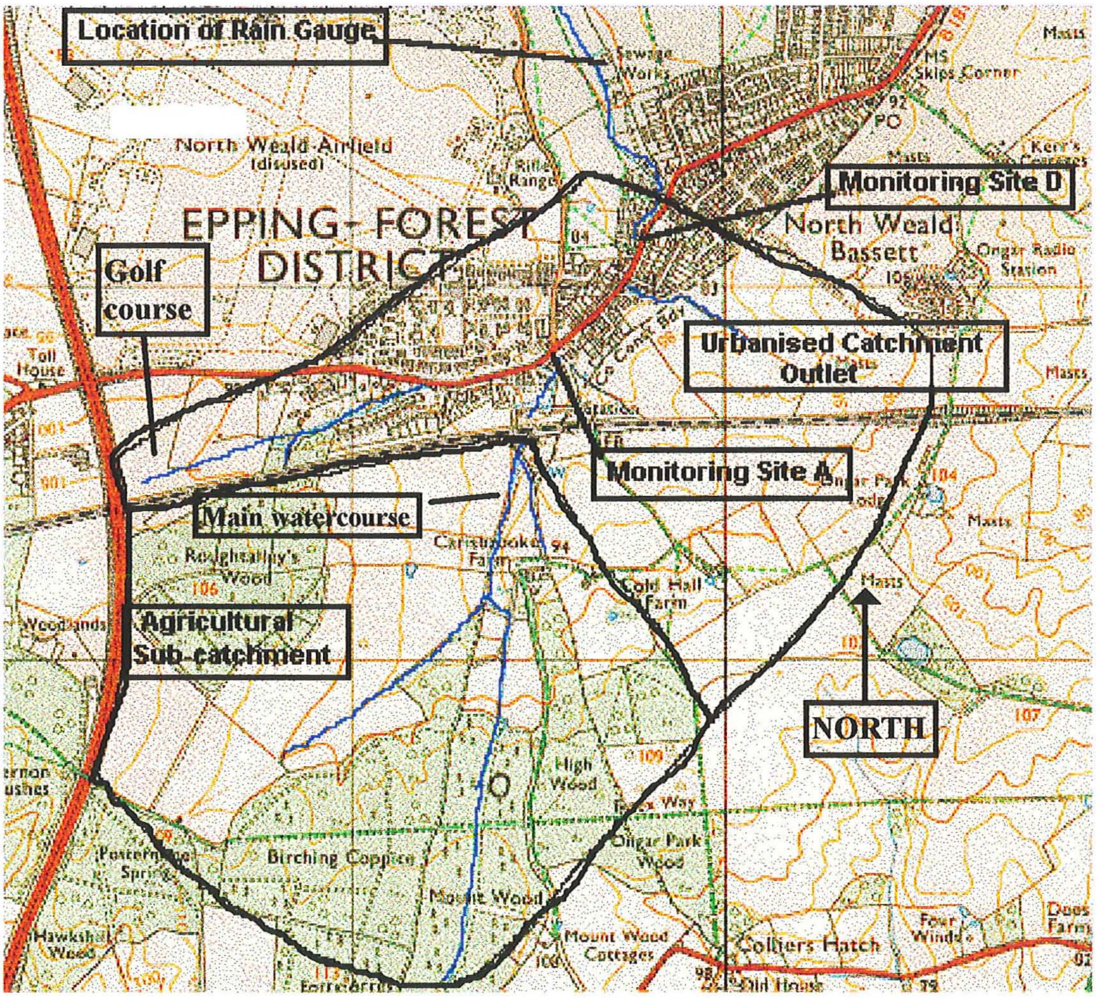


Figure 4-1 The North Weald catchment

Plate 4-1 shows a view looking southwards from near the outlet of the agricultural sub-catchment. The path of the main watercourse can be clearly seen between borders of two neighbouring fields whose slopes converge towards the watercourse.

The urbanised catchment outlet area was 150ha of which 66% was predominantly residential, though it included a small industrial estate and a nine-hole public golf course; the remaining area was made up of grassed and minor arable areas (Figure 4-1). Plate 4-2 shows a typical view of the residential aspect of the urbanised catchment outlet. The overall catchment was bisected by the London Underground Central Line which was the approximate boundary between the agricultural and urban land areas; surface runoff from the railway track was considered to drain into the urban land area.

and urban land areas; surface runoff from the railway track was considered to drain into the urban land area.

Plate 4-1 A view of the agricultural sub-catchment showing wooded and arable areas

Plate 4-2 A view of the urbanised catchment outlet showing a typical residential area

The highest point in the entire catchment was at Forty Acres wood, in the south of the agricultural sub-catchment, and was 113 metres above sea level (Grid reference TL 489021). The slope of the land converged and gradually fell in a northerly direction to a height of 83 metres near the urban catchment outlet (Grid reference TL 498042).

In 1988, due to the periodic flooding of the village, Epping Forest District Council constructed a flood alleviation scheme to route flood water away from the centre of the village during periods of intense and/or prolonged rainfall and therefore to minimise the risk of flood damage. The scheme involved installation of a sub-terraneous pipe (1m i.d.) leading from the main watercourse in the centre of the village to the sewage treatment works, approximately one mile north east of the village centre. During periods of high flow, storm water passed over a side-of-channel weir (Plate 4-3), and overflowed into the by-pass channel being led towards the sewage works, where it re-entered the main watercourse through two pipes (0.6m i.d.) (Figure 4-1).

Plate 4-3 Storm water entry through side-weir into flood by-pass channel

The scheme was designed so that, during storm events with return periods of one in twenty years or greater, flood water passing though the by-pass would overflow into a detention basin, near the sewage works, before re-entering the main watercourse.

4.2.1 Site survey

At the beginning of the research programme the entire catchment was comprehensively surveyed on foot. The purpose of the survey was two-fold; firstly to become fully familiar with the surface hydrology and to identify minor watercourses; and secondly to identify minor pesticide use within the agricultural sub-catchment. Major usage of agricultural and non-agricultural pesticide is discussed in Chapters 6 and 7.

Surface hydrology investigations within the agricultural sub-catchment showed that the watercourse draining the wooded area had been diverted into a large pond near High Wood (Figure 4-1). It was considered that this pond may act as a detention basin reducing the flow, at the sub-catchment outlet, from the wooded area. With respect to minor pesticide use, a number of private addresses were visited and the property owners were informally interviewed to determine the level of pesticide use. The only identified pesticide use was within a plant nursery where very small quantities of insect fumigant were occasionally used.

Within the urbanised area, the survey revealed two minor watercourses in addition to the main watercourse. The first was an ephemeral stream originating near the Central Line within the wood to the east of the golf course and meeting the main watercourse in the centre of the village before the by-pass channel (Figure 4-1). This watercourse was considered to be important because during storm conditions surface runoff possibly containing pesticide residues from the railway line, would drain into it. The second minor watercourse originates in the east of the urbanised catchment outlet in the vicinity of Ongar Radio Station and drains the north-west sloping land between the Radio Station and the village. The stream meets the main stream in the centre of the village after the by-pass channel.

4.2.2 Soil survey of the agricultural sub-catchment

At the commencement of the research programme, ADAS commissioned the Soil Survey Land Resource Centre (SSLRC) to carry out a detailed soil survey of the soils in the agricultural sub-catchment. The main soils found in the agricultural sub-catchment are a product of superficial glacial drift which overlays the original solid geology. The tertiary London clay produced from the original geology is the parent material of a number of soil series identified in the area. The mixture of glacial drift and original geology has produced a relatively complex soil system with twelve soil series identified by the SSLRC investigation. A slowly-permeable frequently waterlogged clayey soil (Hadleigh and Wickham series) forms the low ground just south of the railway line with areas of flinty loam over clayey drift (Oak series) covering the high ground to the south near the M11 motorway.

The organic matter (OM) content of the soil was not measured during the SSLRC survey. However, from the literature relating to similar pesticide runoff studies, it is possible to define a range within which the soil OM content of the agricultural sub-catchment was probably located. Similar studies include the work carried out at the Rosemaund catchment (see Williams *et al* 1995) where the soil OM content was 1.36%; the work at Cockle Park (see Brown *et al*, 1995) where the soil OM content was 1.88% and the work carried out at Brimstone Farm (see Jones *et al*, 1995) where the soil OM content was 4.5%. The comparison of the dominant soil series at North Weald with the other sites suggested that the closest match would have been the heavy clay soil at Brimstone Farm. Therefore, given that both sites had soil made up of similar soil series and that the field management was also similar, it was likely that the OM content of the North Weald agricultural sub-catchment would probably have been closer to the value of 4.5% for Brimstone Farm than the value of 1.36% of the Rosemaund catchment.

The soil series identified belong to the stagnogley soil group and have relatively impermeable horizons which impede the natural drainage of rainwater and therefore in the wetter seasons are often waterlogged and prone to relatively high levels of surface runoff (Plate 4-4). In order to improve productivity, the soil has been underdrained with a network of tile and mole drains to increase the infiltration capacity of the soil during periods of rainfall.

However, on investigation by ADAS in 1988, it appeared that the field underdrainage systems were coming to the end of their useful lifetime and needed to be upgraded with at least the installation of new mole drains. It was the opinion of ADAS (Jennings pers comms, 1988) that the area was in need of a modern field drainage system and compared to surrounding arable land the area was 'backward' with respect to field drainage. ADAS records showed that very little underdrainage of the land has attracted grant aid unlike similar adjacent land that has been extensively drained; since 1988 the land underdrainage has not been improved.

Plate 4-4 Seasonally waterlogged soil of the agricultural sub-catchment during the 1992/93 winter

Like similar UK clay soils (Brown *et al*, 1995) it is considered that the soils of the agricultural sub-catchment are particularly prone to extensive cracking during dry summer weather, leading to rapid 'by-pass flow' of water to drainage system depths. The infiltrating waters may potentially contain high concentrations of autumn-applied pesticides.

4.3 Field methodology

In order to assess the temporal surface hydrology of the catchment and to determine the effect of rainfall on surface runoff, the flow rate (l/s) of the main watercourse was continuously recorded at the outlet of the agricultural sub-catchment and at the urbanised catchment outlet and related to rainfall data recorded at a location just outside the overall catchment. (Figure 4-1)

To determine the movement of pesticides during storm events, surface runoff was sampled using programmable automatic samplers located at the flow gauging sites; on some occasions to supplement the automatic samples, manual samples were also taken at the flow gauging sites and at various locations around the catchment. During storm events the activation or triggering time of the automatic samplers was recorded on the flow-rate data logger at each gauging site. This allowed sample pesticide concentrations (μg/l) to be converted into pesticide loading rates (μg/s) and the total mass of pesticide (mg) transported during the storm to be calculated.

4.3.1 Streamflow gauging at the outlet of the agricultural sub-catchment

The flow of the main watercourse leaving the agricultural sub-catchment was continuously recorded at monitoring site A (Figure 4-1 and Plate 4-5). Here, the hydraulic head over a rectangular notch thin plate weir (designed to BS 3680 [1981]) was measured by means of an autographic Munro (vertical float) water level chart recorder. The Munro had been modified to record the stage both graphically and by means of a data logger. The hydraulic head was also measured by a second autographic water level meter which served as a back-up in the event of the Munro failing. The raw stage data was processed by ADAS and converted using a standard formula into a flow record (Equation 4.1).

$$Q = 2.8\, b\, H^{2/3} \qquad \text{Equation 4-1}$$

where: Q = flow (m^3s^{-1}); b = weir width (0.686m); and H = water head over weir (from Munro stage record)

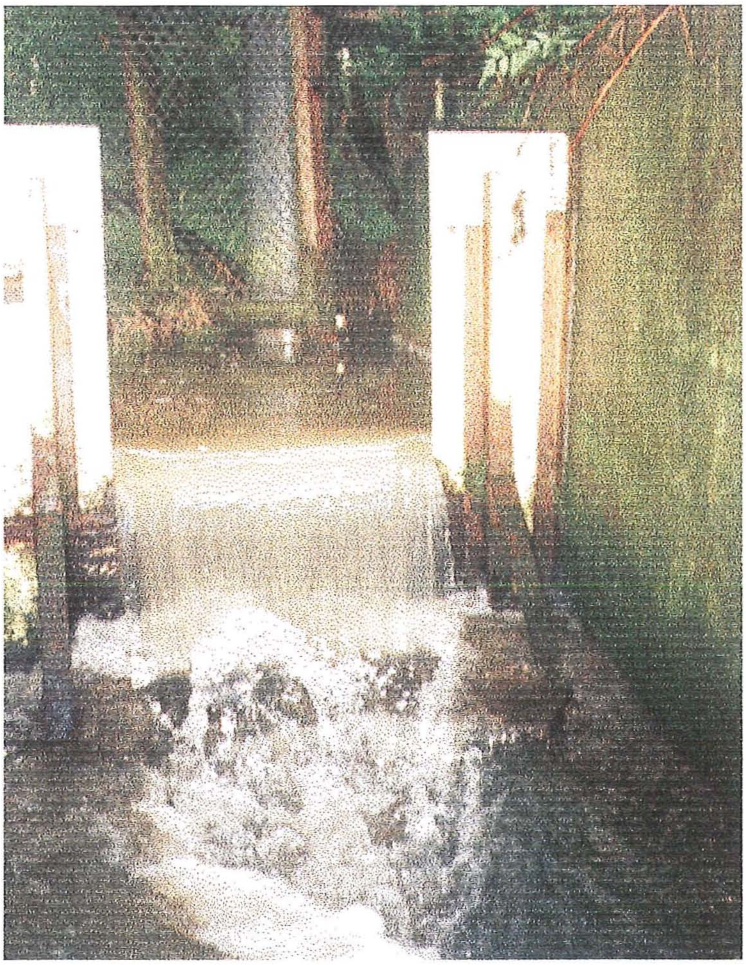


Plate 4-5 Flow measurement equipment at the outlet of the agricultural sub-catchment

4.3.2 Streamflow gauging at the urbanised catchment outlet

At the urbanised catchment outlet the flow of the main watercourse was measured at monitoring site D (Figure 4-1). Here, the main watercourse flowed underneath a main road through a culvert constructed of red bricks (Grid reference TL 498042). The culvert was originally constructed with an ovoid bottom section which, through such geometry, did not lend itself to measuring flow by means of a simple, formula-derived, rating curve. Therefore, once permission was granted by Epping Forest District Council, a concrete step-weir was constructed in the base of the culvert. This involved diverting the normal flow for approximately sixteen hours and moulding the weir from approximately one tonne of rapid-hardening concrete. The layout and aspect of the brick culvert is shown in Plate 4-6.

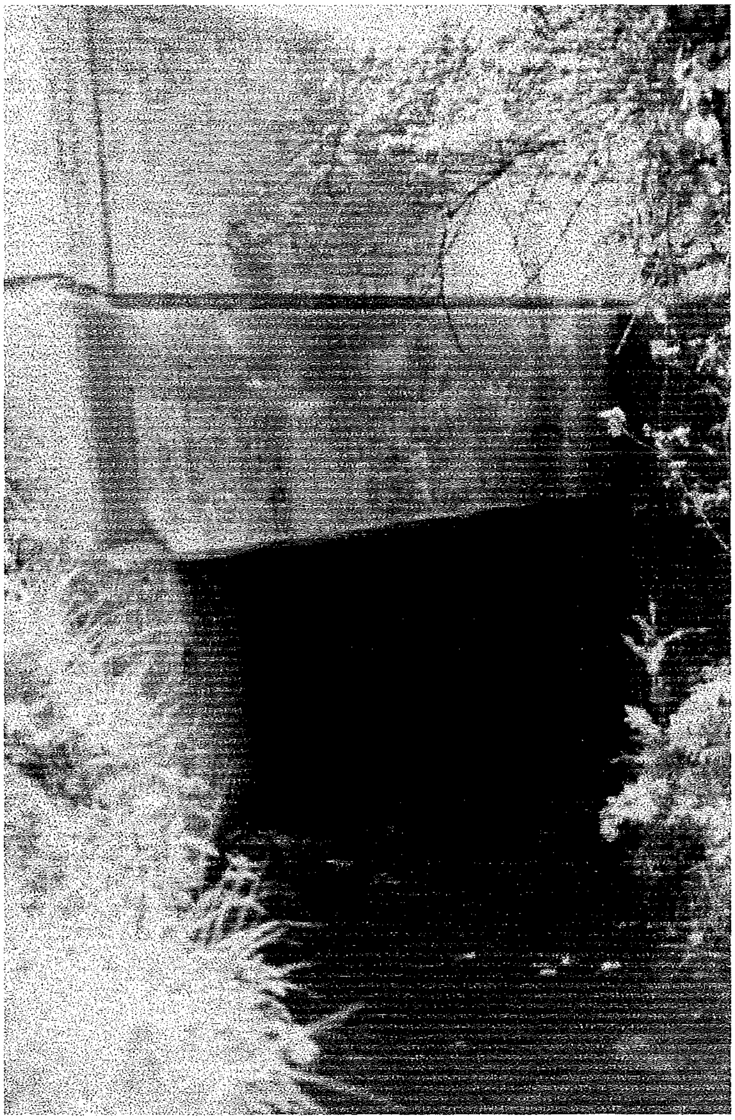


Plate 4-6 The layout and aspect of monitoring site (D) at the outlet of the urbanised catchment

The head over the step-weir was gauged by two hydraulic head recorders; a Druk electronic pressure transducer with an electronically-logged output signal and an Arkon autographic pneumatic pressure transducer which proved to be very unreliable. The raw stage data was processed by ADAS using an empirically-derived rating curve based on the Manning formula which was constructed using flow and stage data obtained using dilution and simple float gauging techniques (Equation 4-2).

$$Q = \frac{AR^{2/3}\sqrt{S}}{n}$$ Equation 4-2

Where:

Q = Flow rate of stream (m^3s^{-1})
A = Cross-sectional area of wetted flow channel(m^2) (W.H)
R = Hydraulic mean depth of wetted flow channel (m)(A / P)
S = Slope of flow channel bed (0.002)
n = Manning's roughness coefficient of channel bed (0.013)
P = Hydraulic perimeter of wetted flow channel (W + 2.H)
W = Width of flow channel (1.68 metres)
H = Hydraulic depth (m)

The Manning's roughness coefficient value of 0.013 was chosen from the literature (Shaw, 1991) to represent the channel roughness of the brick lined culvert and the concrete step-weir.

4.3.3 Flow gauging of the flood by-pass channel

As described in Section 4.1 (North Weald site description), after being routed through the by-pass channel, the storm water was returned to the watercourse via two pipes (0.60m i.d.). The flow rate of the storm water in the by-pass channel was continuously recorded by means of an electronic water head pressure transducer and the electronic data logger was periodically downloaded by Epping Forest District Council; unfortunately due to reliability problems the data logger occasionally failed resulting in periods of no by-pass flow record for January, February, March and April 1992.

4.3.4 Rainfall measurement

Throughout the experiment rainfall was measured using a Rimco 0.5 mm tipping bucket rainfall gauge situated in the grounds of the Thames Water sewage treatment works (Figure 4-1). The rainfall data was recorded using a Campbell 21X data logger, to the nearest second of each bucket tip and every hour the logger also recorded the cumulative rainfall totals. The data shown below in Table 4-1 covers a period of 14 years and was supplied from the SSLRC's climatic database and is intended to give a general picture of the rainfall in the North Weald area. According to Meteorological Office records the annual rainfall depth for the North Weald area is 650 mm.

Table 4-1 Mean monthly averages of rainfall (mm) for the North Weald area from a 14 year SSLRC database

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
53	38	44	50	48	49	49	59	60	44	67	52	613

4.3.5 Automatic stream water sampling

At monitoring sites A and D (Figure 4-1), runoff water samples were automatically taken during storm events using Epic programmable water samplers. The water was drawn through a single tube extending from the stream through a peristaltic pump to a bottle unit. The bottle unit normally consisted of 24 x 2.5 litre brown glass bottles into which the sample water was directed by a distribution arm. The 24th sample channel was used as a wash channel which allowed the sample tube to be flushed out prior to the taking of a sample, and thus minimised the risk of cross-contamination with the residue of the previous sample. To further reduce the risk of contamination, the sample tubes were made from PTFE, and the internal parts of the sampler were either constructed from stainless steel or coated with PTFE.

At both sites, the inlet tube was firmly anchored to the stream bed immediately upstream of the weir. The sampling frequency was programmed to be approximately flow proportional with the greatest frequency of sample collections set to coincide with the rapidly rising limb of the storm hydrograph. The sampling programme was activated by means of a float switch triggered at a predetermined stage height. Sampling times were electronically logged enabling precise estimation of in-stream pesticide loads with respect to stream discharge. Samples collected from both stations were transferred to the laboratory and stored at 4°C prior to extraction within fourteen days of collection. For the pesticides included in the analysis suite (see Section 4.4.1), Harris *et al* (1991) have shown that under the described storage conditions the pesticides are stable and incur minimal losses due to biochemical degradation.

4.3.6 Manual stream water sampling

Manual samples were routinely taken by immersing a 2.5 litre darkened glass bottle into the watercourse. All bottles were rinsed in-situ before the final water sample was taken. Bottles were then sealed with a plastic cap lined with a PTFE insert. Manual samples were taken during storm events in order to supplement automatic samples and also to locate suspected pesticide sources possibly present in minor stream flow inputs into the main watercourse, particularly in the urbanised catchment outlet. Manual samples were also taken during non-storm conditions to determine baseflow pesticide concentrations.

4.3.7 Railway line ballast sampling

Harris *et al* (1992) have described the leaching of atrazine from a farm track constructed from disused railway line ballast, into a nearby watercourse. At North Weald it was known that annual herbicide applications to control weeds were made to the railway line by London Underground using specially adapted rolling-stock. Therefore, in view of the findings of Harris *et al* (1992), the railway line ballast at North Weald was sampled and analysed to assess the behaviour of any pesticides associated with it. For safety reasons the sampling was carried out by London Underground staff; approximately 5 kg of railway line ballast was removed from the surface of the track bed and placed in a heavy duty plastic bag. Within twenty four hours the sample was placed in a freezer at -18°C prior to analysis.

4.4 Laboratory methodology

Generally the methods were divided into techniques for sample preparation and sample determination. The majority of samples analysed were storm runoff water samples although some work was done on the analysis of samples of railway line ballast.

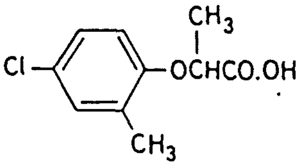
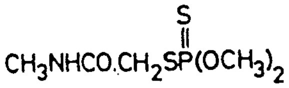
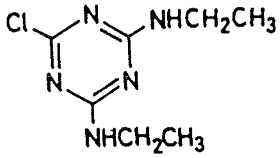
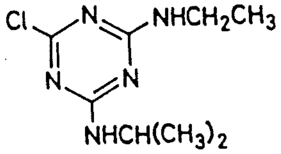
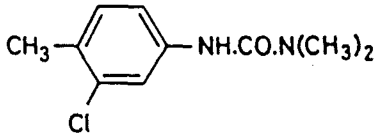
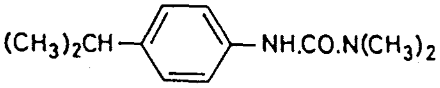
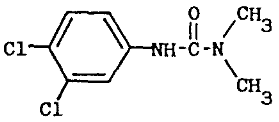
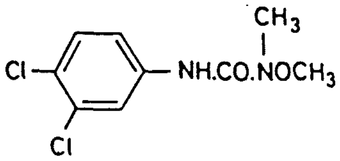
4.4.1 Pesticides selected for analysis

The pesticides chosen for analysis are shown in Table 4-2 together with relevant physical and chemical properties. The majority of the pesticides are pre-emergent herbicides which act by disrupting plant photosynthesis and hence inhibiting plant development. Mecoprop is a post-emergent herbicide which upon application is translocated throughout the plant and causes death. Dimethoate is an insecticide which on contact, usually with nematodes, will move throughout the host's body and inhibit the transmission of nerve impulses thus affecting the development and reproduction of the target pest.

The pesticides chosen for analysis were selected for a number of reasons. Firstly, the pesticides listed in Tables 4-2 and 4-3 have been reported to occur widely within surface and underground drinking water resources (Croll, 1991; Gomme *et al*, 1991). Not surprisingly, as discussed in Section 2.4, the pesticides selected were those in highest usage in the agricultural and non-agricultural sectors. The runoff experiment at North Weald was operated on a collaborative basis with ADAS and therefore, it was important that the results of the North Weald project harmonised with other ADAS runoff experiments in order to allow comparative analysis (Harris *et al*, 1993). Lastly and most importantly, except for a few exceptions, it was known from the initial survey that the pesticides chosen for analysis were applied by various industrial and agricultural users within the catchment.

Initially, diuron was not included within the analysis suite. However, with the restriction on the use of atrazine and simazine in 1992 it was considered likely that non-agricultural users would switch from atrazine and simazine to using diuron for vegetation control. Therefore, the analytical methodology for the determination of the phenylureas (chlorotoluron, isoproturon, and linuron) was extended to include diuron.

Table 4-3 The chemical and structural formula of pesticides selected for analysis

Mecoprop Formula: $C_{10}H_{11}ClO_3$ Mr: 214.6	
Dimethoate Formula: $C_5H_{12}NO_3PS_2$	 $CH_3NHCO.CH_2S\overset{S}{\overset{\|}{P}}(OCH_3)_2$
Simazine Formula: $C_7H_{12}ClN_5$ Mr: 201.7	
Atrazine Formula: $C_8H_{14}ClN_5$ Mr: 215.7	
Chlorotoluron Formula: $C_{10}H_{13}ClN_2O$ Mr: 212.7	
Isoproturon (Formula: $C_{12}H_{18}N_2O$) Mr: 206.3	
Diuron Formula: Mr 265.1	
Linuron Formula: $C_9H_{10}Cl_2N_2O_2$ Mr: 249.1	

4.4.2 Initial method development of multi-residue analytical method

At the onset of the research programme the Pesticide Analysis Group of the MAFF Central Science Laboratory (CSL), Cambridge was consulted on the multi-residue analytical method used for their pesticide determination. This methodology was evaluated and where necessary modified to improve performance and efficiency.

4.4.2.1 Review of Central Science Laboratory pesticide determination methodology

The pesticide active ingredients were extracted from water samples using liquid-liquid extraction into dichloromethane. Collected water samples (1 litre) were shaken with two consecutive volumes of dichloromethane (100ml). Following separation, the combined dichloromethane extracts were reduced in volume to approximately 5ml using a rotary evaporator. Subsequently the sample was split into two equal sub-samples; one was cleaned up using column liquid chromatography for determination of the neutral pesticides dimethoate, simazine, atrazine, chlorotoluron, isoproturon, and linuron; the other was pre-treated for the determination of the polar pesticide mecoprop.

The first fraction was loaded and eluted through a glass clean-up column, packed with anhydrous sodium sulphate and 15%(w/w) water deactivated alumina. Once eluted with a small volume of dichloromethane, the sample was collected in a glass vial, evaporated to dryness under a stream of nitrogen gas and then redissolved in methanol (1ml).

The other fraction was analysed for mecoprop which in its pure state is an acidic non-volatile polar compound and therefore does not lend itself to analysis by gas chromatography since it binds irreversibly to the analytical column. Mecoprop was therefore converted to its volatile methyl ester using diazomethane and analysed and confirmed using gas chromatography-mass spectrometry (GC-MS).

The neutral analytical sample was primarily determined using reverse phase high performance liquid chromatography (RPHPLC) utilising a C_{18} column and confirmed by normal phase high performance liquid chromatography (NPHPLC). Dimethoate was determined using gas chromatography using a nitrogen/phosphorus detector (GC/NPD).

4.4.2.2 Modification of Central Science Laboratory pesticide determination methodology

The initial development work concentrated on investigating techniques for analytical sample determination using prepared analytical standards. The analytical techniques were limited to the instrumental resources of the laboratory. Initially GC-MS was evaluated as the primary method of analysis for all components of the pesticide suite (Table 4-2). However, work using a Hewlett Packard 5995 GC-MS operated in single ion monitoring mode (SIM) indicated that due to the rather dated design of the transfer line, the limit of detection of the technique was limited to approximately 30μg/l of pesticide active ingredient once sample pre-concentration had been taken into account. Therefore, further work concentrated on developing a RPHPLC technique as this has shown to be sensitive to sub-μg/l levels for all components of the suite (Llewellyn *et al*, 1992).

The RPHPLC method used by CSL was modified by changing the composition of the mobile phase from 60:40 % v/v methanol:water to 50:50 % v/v water:methanol. This produced enhanced resolution of the chromatographic peaks of the pesticide standards which aided peak integration and subsequent quantification. Also the injection loop volume was reduced from 50μl to 20μl to prevent occasional column overloading and consequent peak broadening.

It was observed that when using approximately the same instrumental and analytical conditions, the pesticide standard elution order was not consistent between the two laboratories. The elution order determined by the CSL method was mecoprop, dimethoate, simazine, chlorotoluron, atrazine, isoproturon, and linuron (MDSCAIL) compared to mecoprop, dimethoate, simazine, atrazine, chlorotoluron, isoproturon, and linuron (MDSACIL) for the revised method. This difference was fully discussed and was attributed to the use of the different types of C_{18} analytical columns by the two groups. CSL used an ODS1 column and Middlesex University an ODS2 column; the difference between the columns being the percentage loading of octadecylsilane grafted onto the inert silica support of the column stationary phase. The higher loading corresponds to increased non-polar characteristics of the column.

4.4.2.3 Evaluation of pesticide recovery levels

The sample clean-up procedure for the CSL method used a glass column (150mm x 5mm) packed with 0.5g anhydrous sodium sulphate followed by 0.2g activated alumina (15% w/w water deactivated). The column, after conditioning with dichloromethane, was loaded with the sample dissolved in dichloromethane and eluted with a further volume of dichloromethane. It was suggested by CSL that when incorporated into the full extraction/determination procedure, recoveries of 60-70% for dimethoate, simazine, atrazine, chlorotoluron, isoproturon, and linuron were achievable when spiked into double-distilled water.

Due to the inherent variability problems associated with alumina deactivation, the initial development work of the clean-up method was carried out using 100% activated alumina. However, when incorporated into the full extraction/determination procedure low recoveries were generally obtained. Typical recovery values are shown in Table 4-4.

Table 4-4 Recoveries of pesticide standards extracted from spiked pure water and cleaned up using 100% deactivated alumina

Pesticide	Recovery(%)	Pesticide	Recovery(%)
mecoprop	1	chlorotoluron	22
dimethoate	1	isoproturon	21
simazine	36	linuron	92
atrazine	78		

In order to increase recovery levels, rather than investigate alumina deactivation, the effect of eluting the clean-up column with a solvent of higher elutropic strength was investigated. Excluding mecoprop, it was found that column elution with acetone produced overall recoveries of approximately 90% (see Section 4.4.5). Acetone also had the advantage of being sufficiently volatile at room temperature to allow evaporation to dryness of the sample within a short time limit. Full details of the experimental procedure are described in Section 4.4.3.2.

In order to achieve a realistic recovery level for mecoprop, the activated alumina, after being eluted with acetone and then dried in a stream of nitrogen gas, was eluted with an alkaline solution to liberate the bound undissociated mecoprop as a soluble salt. The aqueous alkaline eluate containing the mecoprop salt was then acidified and extracted into dichloromethane, isolating the undissociated mecoprop. The dichloromethane extract was dried with anhydrous sodium sulphate and then evaporated to dryness. The dry residue was dissolved in 200 µl of mobile phase prior to RPHPLC analysis. Using this procedure recoveries of 95% were obtained. (see Section 4.4.3.3).

4.4.3 The determination of mecoprop, dimethoate, simazine, chlorotoluron, atrazine, isoproturon, diuron, and linuron from surface water

The following sections describe the full methodology used for the determination of pesticides in samples of surface water taken at North Weald. Essentially, pesticides were liquid-liquid extracted from sample water; the extracts cleaned up using column chromatography; and their concentrations determined by reverse phase high performance liquid chromatography.

4.4.3.1 Materials

Analar grade dichloromethane, acetone, sodium chloride, anhydrous sodium sulphate, sodium hydroxide, hydrochloric acid (1.18 g/ml) and alumina (Active neutral Brockman Grade 1), and HiPerSolve grade methanol were obtained from BDH. All aqueous reagents were prepared in double distilled, double deionised water. Analytical pesticide standards for mecoprop, dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron, and linuron were obtained from Promochem, Herts, U.K. All glassware was cleaned, dried, and rinsed with an appropriate solvent prior to use.

4.4.3.2 Sample extraction and analysis pre-treatment for dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron, and linuron.

Isolation of the pesticide analytes was achieved by means of liquid-liquid extraction of the water sample with dichloromethane. A 1 litre volume of sample water was placed into a 2 litre glass separating funnel fitted with a PTFE tap, to which was added 30g of sodium chloride. The mixture was shaken until the contents were fully dissolved. The presence of sodium chloride increased the ionic strength of the aqueous phase and enhanced the partitioning of the organic components into the organic phase.

25ml of 2 M hydrochloric acid and 100ml of dichloromethane were added to the contents of the separating funnel. The acidification of the sample ensures that acidic compounds are present in their undissociated form and therefore likely to partition efficiently into the organic phase. The separating funnel was vigorously shaken by hand for 2 minutes and the organic and aqueous phases allowed to separate.

Due to the presence of suspended particulates the organic phase often separated out as a fine emulsion which was successfully broken down by using sonification. The separating funnel was carefully orientated to a horizontal position and semi-submerged in an ultrasonic bath for approximately 2 minutes. The funnel was then carefully returned to its former vertical position, and the separated dichloromethane run off into a 500ml conical flask containing 25g of anhydrous sodium sulphate, which removed any traces of water from the solvent extract.

To increase the extraction efficiency the water sample was extracted with a second 100ml volume of dichloromethane following the same procedure as described above. The combined, dried dichloromethane extracts were filtered through a Whatman N°1 filter paper into a 500ml round-bottomed flask. The internal surface of the 500ml conical flask and residual sodium sulphate were washed with two 30ml volumes of dichloromethane which were also passed through the filter into the round-bottomed flask.

The round-bottomed flask was attached to a rotary evaporator and the solvent volume reduced to approximately 5ml. The water-bath temperature was set initially at 45°C and the vacuum maintained at 35 mmHg.

The contents of the round-bottomed flask were quantitatively transferred onto a clean-up column which had been previously conditioned with 10ml of dichloromethane. The clean-up column consisted of a glass tube (150mm x 5mm) packed with 0.5g of anhydrous sodium sulphate followed with 0.6g of activated alumina separated by a glass wool plug. The column had been thermally conditioned at 260°C overnight, followed by cooling and storage in a desiccator prior to use.

Once sample transfer was complete, the clean-up column was eluted with approximately 5ml of acetone. The column eluate was collected in a 12ml glass vial, and then evaporated to dryness and dissolved in 200 μl of methanol; to assist dissolution the glass vial was carefully semi-immersed in an ultra-sonic bath. The sample was then stored at -18°C prior to analysis. The extraction of 1 litre of water to eventually give an analytical sample of 200 μl gave a sample preconcentration factor of 5000.

4.4.3.3 Sample extraction and analysis pre-treatment for mecoprop

The extraction conditions described in Section 4.4.3.2 were also applicable to the efficient extraction of mecoprop from water samples; therefore it was co-extracted with the main suite of pesticides and the same procedure was followed as far as the solvent extract clean-up step.

The clean-up method described in Section 4.4.3.2 above was efficient for dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron, and linuron, but not for mecoprop because of its polar characteristics. When present in an undissociated acidic form, mecoprop is tenaciously bound to the polar surface of the activated alumina to which it remains partitioned when the clean-up column is eluted with acetone. However, mecoprop was efficiently recovered from the column by eluting the alumina with an alkaline solution, which converted it into a water-soluble mecoprop salt. The undissociated acid form was then regenerated and isolated by acidifying the alkaline solution and extraction with dichloromethane. The experimental procedure is described below.

Following the initial elution of the main pesticide suite with acetone, the clean-up column was dried for five minutes with nitrogen gas. The sodium sulphate layer (0.5g) was carefully removed and the remaining alumina eluted with 5ml of 2 M sodium hydroxide which was collected in a 20ml separating funnel containing 5ml of 5 M hydrochloric acid. The contents of the separating funnel were hand shaken for 1 minute and then cooled for 10 minutes. Mecoprop was extracted from the acidified solution with two sequential 5ml volumes of dichloromethane. The contents of the separating funnel were hand shaken for 2 minutes and the organic and aqueous phases allowed to separate before the organic phase was run off. The dichloromethane extract was loaded onto a drying column (a glass column 150mm x 5mm, packed with 0.5g of anhydrous sodium sulphate) pre-conditioned with dichloromethane, and eluted with 5ml dichloromethane. The eluate from the drying column was collected in a 12ml glass vial, evaporated to dryness and dissolved in 200 µl of HPLC mobile phase (60/39.9/0.1 % v/v methanol : water : trifluoroacetic acid); to assist dissolution the glass vial was gently sonificated. The analytical sample was refrigerated at 5°C prior to analysis. The extraction of 1 litre of water to eventually give an analytical sample of 200 µl gave a sample preconcentration factor of 5000.

4.4.3.4 Determination of dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron and linuron by high performance liquid chromatography

Determination of prepared analytical samples for the main pesticide suite was achieved by means of Reverse Phase High Performance Liquid Chromatography (RPHPLC) using the system described in Table 4-5. Chromatograms illustrating the determination and resolution of suite components in pure and storm runoff water are shown in Figures 4-2 and 4-3.

The mobile phase and post-run column conditioner were both pre-filtered and degassed using sonification for approximately five minutes. The injector was loaded using a 100µl luer-end Hamilton syringe which ensured that the 20µl sample loop was flushed out a least four times. After the injection of a sample or standard, the instrument was run for 45 minutes to ensure the elution of linuron, the pesticide with the longest retention time (42 minutes). At 45 minutes, the flow rate of the main pump was gradually reduced to zero and the secondary pump brought on-line.

Table 4-5 Reverse Phase High Performance Liquid Chromatograph system and conditions used for pesticide determination

Primary pump:	Constametric III metering pump, LDC Analytical.
Secondary pump	Altex single reciprocating pump.
Online pump selector:	Rheodyne/Altex 905-23.
Injector	Rheodyne/Altex 905-23.
Injection loop:	20 microlitre sample loop.
Guard column:	2cm x 4.6mm, Spherisorb ODS1, 5 micron, LDC Analytical.
Analytical column:	25cm x 4.6mm, Spherisorb ODS1, 5 micron, LDC Analytical.
Detector:	SpectroMonitor 5000, Photo Diode Array Detector, LDC Analytical.
Detection:	0-10 min 228nm, 10-35 min 233nm, 35-48 min 248nm.
Integration:	Trivector LA 500.
Isocratic mobile phase:	50:50%(v/v) Methanol:Water(Filtered - Nucleopore 5 µ).
Post-run column conditioner	Methanol (Filtered - Nucleopore 0.45 µm pore size).
Main pump flow rate:	1 ml/min.
Secondary pump flow rate	3 ml/min.
Column pressure:	3100 psi.
Column temperature:	Approximately 21°C.

The system was flushed with methanol for 15 minutes after which time the main pump was brought back on-line and the column equilibrated for 20 minutes with the mobile phase. Typical sample turn around time was approximately 80 minutes. The flushing of the system with methanol was carried out to maintain the chromatographic performance of the column and to ensure that sample artefacts eluting after 45 minutes were flushed out of the column to prevent possible interference with the following sample determination.

The RPHPLC system was calibrated using external standards and peak area integration; retention times for dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron, and linuron were approximately 9.5, 13.8, 21.75, 22.95, 25.9, 30.0, and 42.0 minutes respectively. During routine analysis slight variations in standard retention time were attributed to: (a) manual injection technique, (b) temperature variation, and (c) slight variation in the composition of the mobile phase.

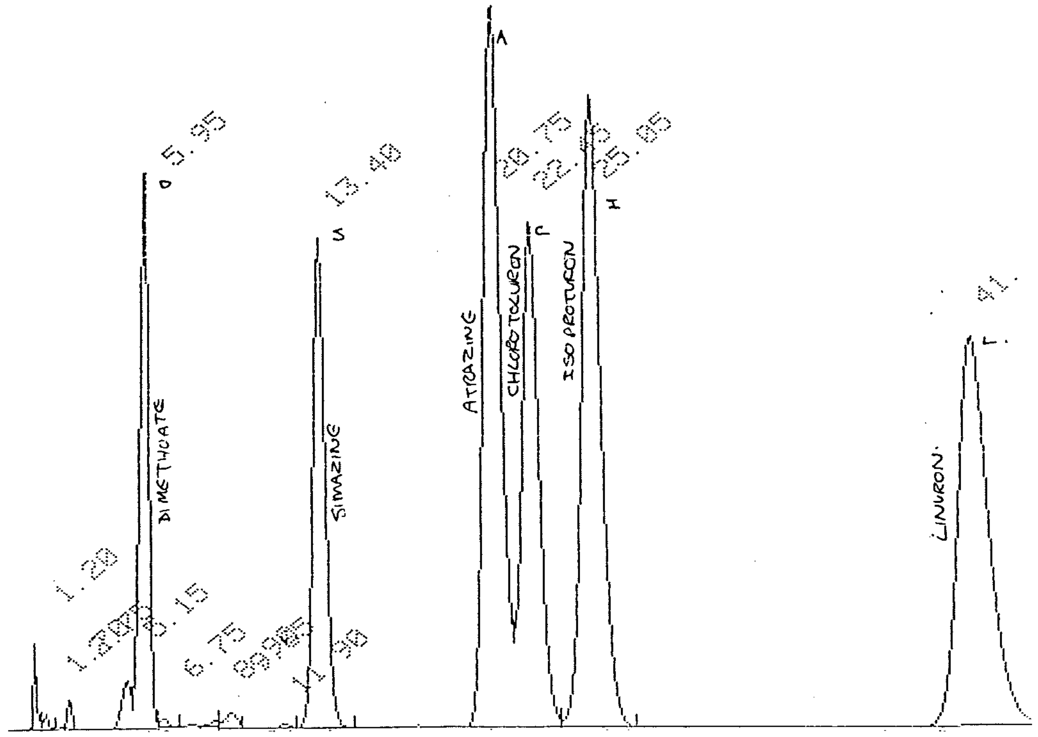


Figure 4-2 Chromatogram of pure water spiked to 10µg/l showing the detection of dimethoate, simazine, atrazine, chlorotoluron, isoproturon and linuron

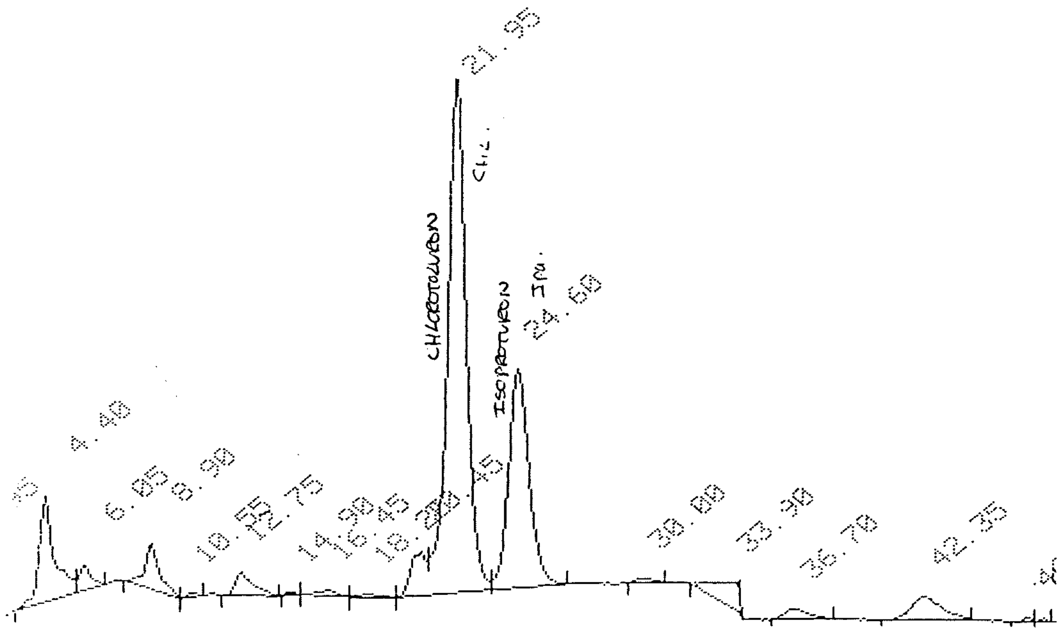


Figure 4-3 Chromatogram of a water sample collected during a storm event, showing the detection of chlorotoluron and isoproturon

The detection wavelength was changed during the course of each standard or sample run to approximately coincide with the ultra-violet absorption maxima (λ_1 max) of the pesticides passing through the detection cell to optimise the detection sensitivity with respect to individual or groups of pesticides.

For sample runs, peak identity was established by comparing retention times and confirmed by comparing photo diode array ultra-violet spectrum scans with those of the standard compounds.

4.4.3.5 Determination of mecoprop by high performance liquid chromatography

The same RPHPLC system and procedure was used as described in Section 4.4.3.4 with the following modifications:

Detection:	228nm.
Isocratic mobile phase:	60/39.9/0.1 % v/v methanol : water : trifluoroacetic acid, filtered - Nucleopore 5µm pore size

Using these conditions the retention time of mecoprop was 14.5 minutes. The method is similar to that used by Di Corcia *et al* (1989). The system was calibrated using an external standard and peak area integration.

4.4.3.6 Instrumental calibration

Standard solutions of mecoprop, dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron, and linuron were prepared at concentrations of approximately 0.5, 1.0, 5.0, 10.0 and 20.0 mg/l in methanol and were each run five times. The mean and coefficient of variation of peak areas were calculated for each pesticide at each concentration level. For each pesticide, at standard concentrations of 0.5 mg/l, the coefficient of variation (CV) was less than 8% except for dimethoate where the value was 28%. In comparison with the other components of the suite, dimethoate is approximately one order of magnitude less sensitive to UV detection due to its lack of aromaticity.

Using linear regression with the intercept set to pass through zero, external calibration graphs were constructed for each pesticide and in every case regression correlation coefficients of 0.999 were obtained. An example of a calibration graph is shown below for chlorotoluron (Figure 4-2).

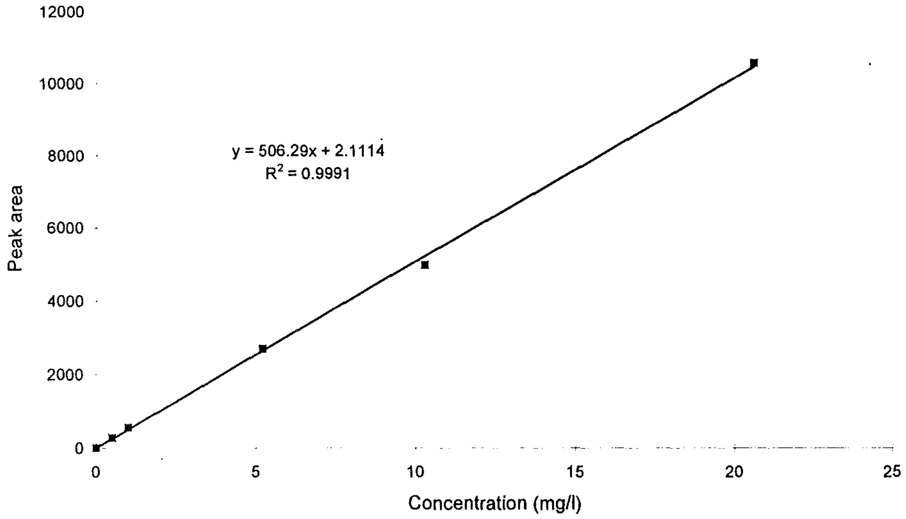


Figure 4-4 Calibration graph for chlorotoluron showing linear regression equation and correlation coefficient

Taking the extraction pre-concentration factor of 5000 into account, in real terms the actual water sample concentration was 5000 times lower than that determined using the RPHPLC. For example, an analytical sample determined at a concentration of 15 mg/l, would equate to an original water sample concentration of 3 μg/l .

The limit of detection is conventionally taken as three times the standard deviation of the baseline noise which essentially depended on whether pesticides were extracted from DDW or environmental water. Since the baseline noise from environmental water was quite variable it was decided to use the baseline noise of DDW, which in practice was negligible. Therefore, the limit of detection for each pesticide in the suite was taken as the concentration of the lowest calibration standard having a CV of less than 10%, which in every case except for dimethoate equated to 0.1μg/l; dimethoate had a limit of detection of 1.0μg/l. In practice, detections down to

0.05μg/l were obtained through peak confirmation by photodiode array scans on pesticide peaks of samples extracted from environmental water (see Section 4.4.4).

4.4.4 Confirmation of pesticide identity

The photo diode array detector used in the analytical procedure had the facility for recording the characteristic ultra-violet spectra between 190nm and 360nm of each eluting compound. Therefore, by comparing the spectra of pesticide standards to those obtained during the determination of unknown samples, the presence of pesticides could be confirmed with much higher confidence than if retention times alone had been used. The absorption maxima values for the pesticide suite are given in Table 4-6 together with secondary maxima values.

Table 4-6 UV absorption maxima for the pesticide suite

Pesticide	λ_1Max (nm)	λ_2 (nm)	Pesticide	λ_1Max (nm)	λ_2 (nm)
mecoprop	229	281	chlorotoluron	209	242
dimethoate	196		isoproturon	202	240
simazine	221	262	diuron	207	249
atrazine	222	262	linuron	210	248

λ_1Max First UV absorption maxima

λ_2 Secondary UV absorption maxima

4.4.5 Pesticide recovery studies for water samples

A 1l sample of DDW was placed in a 2.5 l separating funnel and carefully spiked using a Hamilton syringe with mecoprop, dimethoate, simazine, atrazine, chlorotoluron, isoproturon, diuron, and linuron. The pesticide spike was made up in methanol and the final aqueous pesticide concentration was approximately 10 μg/l for each pesticide in the suite. The water was extracted and analysed using the techniques described in Sections 4.4.3.2 to 4.4.3.5. The recovery results and number of replicates are given below in Table 4-7. The results show excellent recovery efficiency and repeatability with all pesticides exceeding 90% recovery except for simazine at 89.8%.

Table 4-7 Pesticide recovery efficiency from double distilled deionised water

Pesticide	Recovery (%)	CV (%)	n	Pesticide	Recovery (%)	CV(%)	n
mecoprop	98	4.5	4	chlorotoluron	98.4	8	5
dimethoate	96.7	5.4	4	isoproturon	95.5	5.7	5
simazine	89.8	7.5	5	diuron	97	6	3
atrazine	92.5	5.5	5	linuron	93	6	5

CV coefficient of variation

n number of replications

4.4.6 Method performance: Precision

The HPLC determination precision was obtained by injecting all component standards ten times. For all of the suite components except dimethoate, CV values of less than 8% were obtained at the 0.5mg/l level (0.1μg/l taking preconcentration into account) which is within the acceptable precision limit (<11%) as suggested by the Association of Official Analytical Chemists (AOAC, 1993). As discussed in Section 4.4.5 the overall method precision for spiked water samples was within same AOAC limit. However, for determination of suite components from environmental water it was considered that method precision would worsen due to the variable affects of sample matrix interference. Therefore, to determine that routine method precision remained below 10%, sample extracts were periodically determined up to three to four times depending on sample the volume available. Also, to ensure that the overall analytical methodology was free of contamination, procedural blanks were periodically run during each sample set.

The precision of the automatic sampling carried out at the two field stations was not assessed. It was considered that a significant factor that may have affected sampling precision would have been the reproducible collection of suspended sediment (present in the stream water) from the water column at the time of sampling. However, since the suspended-sediment association of the suite components was considered to be negligible, it was assumed that any variation in the suspended sediment content of replicate samples would have had no significant affect on the pesticide concentration of the samples. In conclusion, due to the turbulent nature of the streamflow during the occurrence of a storm event, it is assumed that pesticide present in the aqueous fraction of the water column would have been well mixed. Therefore the precision associated with the sampling of stream water from a sample inlet tube located approximately at the centre of the stream flow, would have been negligible.

When interpreting the pesticide concentration data presented in chapters six and seven, it should be noted that the precision associated with the data is in the order of 4 to 8%. Therefore at the extremes of precision limits, two slightly differing concentration values could in theory be considered identical.

4.4.7 Method performance: Accuracy

Apart from in-house checks using prepared solutions of know concentration, method accuracy was also assessed through an inter-laboratory exercise with a government laboratory. This aspects of the method validation is fully described below.

Since the pesticide data generated by Middlesex University (MU) was to be used as part of the wider ADAS national experiment on pesticide movement in storm runoff, it was considered necessary to check the analytical accuracy of the MU methodology against that of CSL who carried out the majority of the SWRC pesticide analysis. It was also a useful exercise for MU since it allowed the methodology to be appraised against that of a professional government laboratory and gave credibility to the data produced using the MU methodology.

This exercise involved the analysis of samples taken from a storm event occurring during the period 1-2 May, 1992. Fifteen samples were analysed from the agricultural sub-catchment (site A) and fourteen from the urbanised catchment outlet (site D). Each 2.5 litre sample was split into two 1 litre samples which were analysed within fourteen days of receipt by MU and CSL.

The results are shown below in Tables 4-7, and 4-8 and in Figures 4-2 and 4-3 along with the respective pesticide recovery data in Table 4-9.

Table 4-8 Analysis results of inter-laboratory comparison - Agricultural sub-catchment (Site A)

Sample	Pesticide concentration (µg/l)							
	Simazine		Atrazine		Chlorotoluron		Isoproturon	
	MU	CSL	MU	CSL	MU	CSL	MU	CSL
1	0.11	nf	0.21	nf	0.06	1.5	0.07	nf
2	0.11	0.2	0.11	0.6	0.79	nf	1.00	nf
3	0.12	0.2	0.14	nf	0.56	0.8	0.46	2.2
4	0.29	0.3	0.14	0.4	0.41	nf	0.56	1.1
5	0.27	nf	0.13	nf	0.28	nf	0.39	0.9
6	0.26	*	0.11	*	0.27	*	0.27	*
7	0.16	nf	0.10	nf	0.22	nf	0.32	0.2
8	0.22	*	0.11	*	0.20	*	0.28	*
9	0.27	0.1	0.10	0.2	0.19	0.3	0.26	1.1
10	0.21	*	0.09	*	0.15	*	0.21	*
11	0.24	*	0.09	8	0.13	*	0.20	*
12	0.19	nf	0.08	nf	0.11	nf	0.20	nf
13	0.14	*	0.07	*	0.07	*	0.13	*
14	0.16	nf	0.07	nf	0.08	nf	0.14	nf
15	0.28	nf	0.06	nf	0.10	nf	0.20	nf

nf = not found

* = not analysed

The majority of results are below 1.0 µg/l and close to the limit of detection. Therefore results from either laboratory in this region cannot be judged to be significantly different with respect to the error associated with determinations at this level.

Table 4-9 Analysis results of inter-laboratory comparison - Urbanised catchment (Site D)

Sample	Pesticide concentration (µg/l)							
	Simazine		Atrazine		Chlorotoluron		Isoproturon	
	MU	CSL	MU	CSL	MU	CSL	MU	CSL
1	0.10	nf	0.21	nf	0.28	nf	0.09	nf
2	0.06	0.1	0.10	0.5	0.43	nf	0.25	nf
3	0.12	0.3	0.11	0.5	0.32	0.4	0.34	0.4
4	0.20	0.3	0.16	nf	0.21	nf	0.28	nf
5	0.10	0.2	0.10	nf	0.16	nf	0.18	nf
6	0.10	0.2	0.09	0.3	0.11	nf	0.14	nf
7	0.14	*	0.18	*	0.08	*	0.13	*
8	*	*	*	*	*	*	*	*
9	0.17	nf	0.15	0.4	0.08	nf	0.09	nf
10	0.16	*	0.11	*	0.1	*	0.19	*
11	0.14	*	0.10	8	0.06	*	0.08	*
12	0.19	1.1	0.23	0.5	0.46	nf	0.08	nf
13	0.18	*	0.13	*	nf	*	0.08	nf
14	0.14	*	0.13	nf	0.07	nf	0.06	nf

nf = not found

* = not analysed

Instances where MU reported substantial positive values and CSL reported 'not found' were explained by CSL as lack of confirmation even when a substantial peak was present on their chromatogram. The MU data set was produced in order of sample occurrence whereas the CSL data set was produced randomly. The MU method had the advantage of higher confirmation confidence since results generated formed part of a logical trend. For CSL this lack of confirmation confidence through not analysing samples sequentially was clearly illustrated by the results for chlorotoluron at Site A (see Table 4-8 and Figure 4-5), where CSL reported that samples 1, 2, 3, and 4 had concentrations of 1.5 µg/l, 'nf', 0.8 µg/l and 'nf'; this compares with 0.06, 0.79, 0.56, and 0.41 µg/l respectively for the MU results.

Occasions where CSL reported larger concentrations than MU were explained by CSL as instances of using external calibration graphs produced using aged calibration standards with actual concentrations significantly lower than the original design values as a result of degradation. This behaviour is clearly shown for the results for atrazine at Site D (Table 4-7 and Figure 4-6), where the concentrations reported by CSL were at least double those reported by MU.

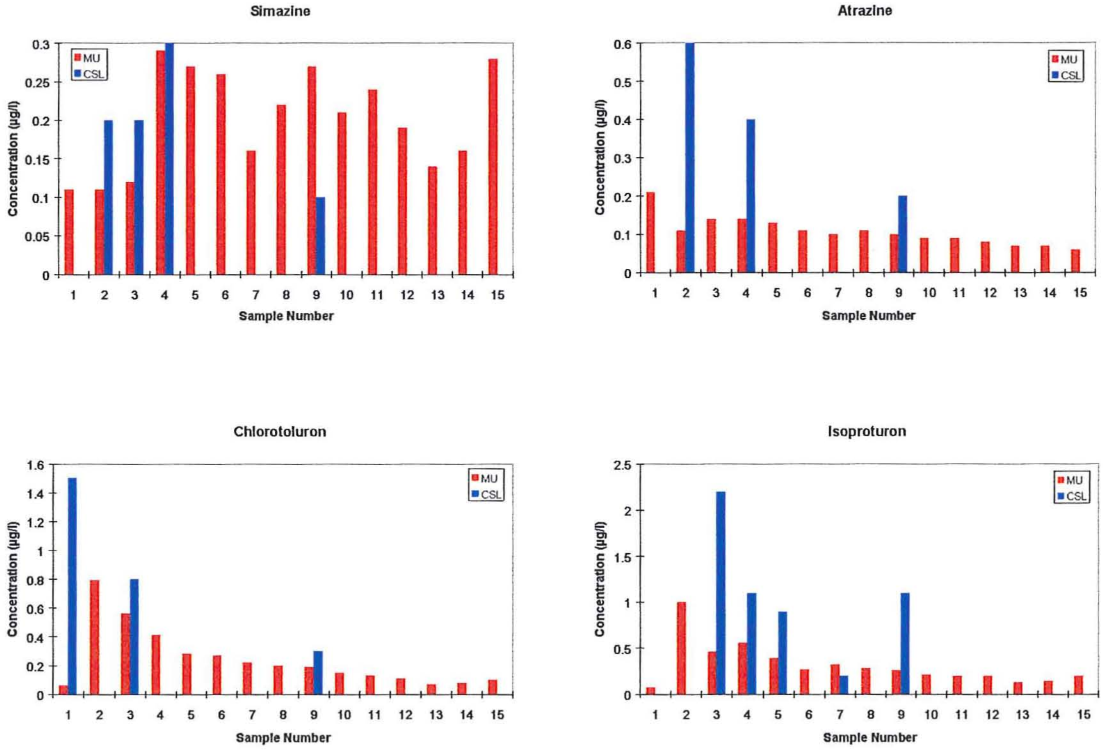


Figure 4-5 Analysis results for inter-laboratory comparison - Agricultural catchment

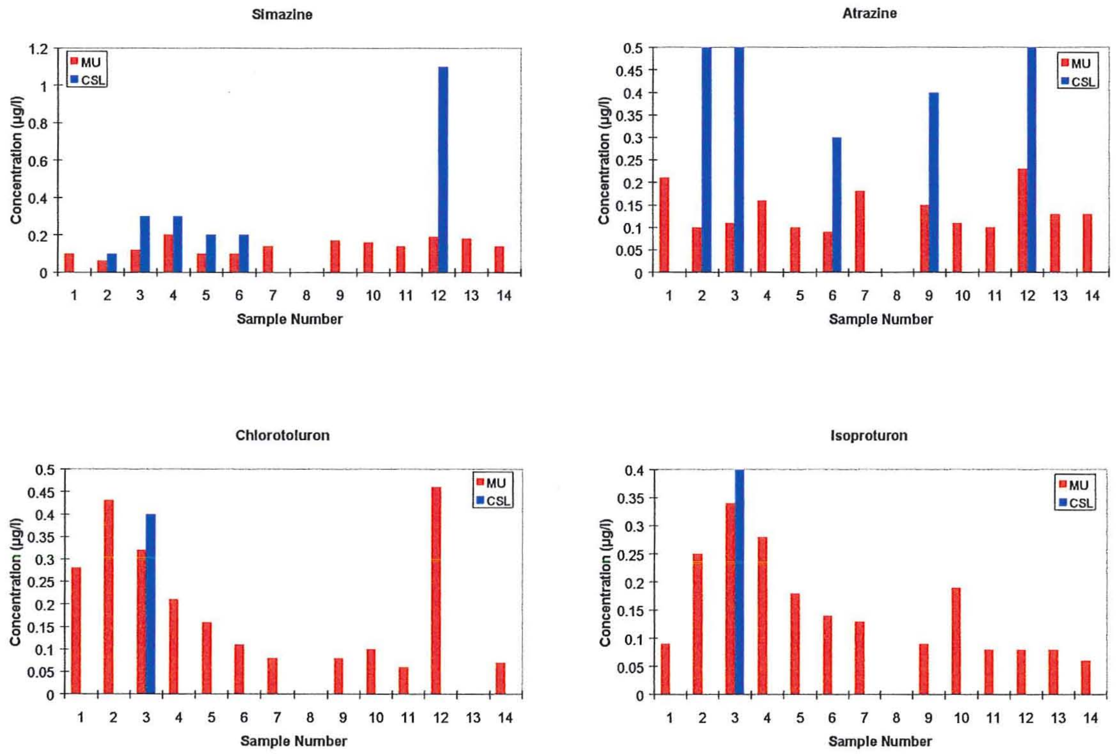


Figure 4-6 Analysis results for inter-laboratory comparison - Urbanised catchment

On discussion of the results of the inter-laboratory exercise, CSL agreed that the results generated by MU were more accurate and consistent with pesticide data from similar runoff events, unlike their own data; they also agreed that the extraction performance of the MU methodology was superior. Overall, the exercise illustrated the validity and accuracy of the MU pesticide determination methodology and showed that the data generated was at least as acceptable as that produced from a government laboratory.

Table 4-10 Analysis results of inter-laboratory comparison - Method efficiency

	Pesticide							
	Simazine		**Atrazine**		**Chlorotoluron**		**Isoproturon**	
	MU	**CSL**	**MU**	**CSL**	**MU**	**CSL**	**MU**	**CSL**
Recovery(%)	90	58	92.5	69	98	85	95.5	87
CV (%)	7.5	11	5.5	35	8	13	5.7	32
n	5	5	5	5	5	5	5	5

cv = Coefficient of variation
n = number of replications

4.4.8 Investigation of pesticide levels associated with railway line ballast

As described in Section 3.1.2., the London Underground Central Line bisects the overall catchment, dividing it approximately into the agricultural sub-catchment and the urbanised catchment. In order to minimise the risk of fire from dried vegetation and also to ensure that signalling equipment was not hidden from view by dense vegetation, the railway track received periodic herbicide applications to control the proliferation of weeds and scrub. The design and construction of railway tracks ensures the rapid drainage of surface water and therefore it was considered likely that available herbicide applications would easily move laterally in storm runoff or move downwards possibly by-passing the soil layer, into groundwater. At North Weald, the railway line passed very close to the path of an ephemeral stream (in the west of the urbanised catchment outlet near the golf course) which was considered to be at high risk from receiving contaminated runoff from the railway line (Figure 4-1).

Ballast from disused railway lines is often used for secondary purposes such as permeable fill in the construction of minor non-tarmacked roads and car parks. In this situation, the ballast may act as an important source of contaminated runoff, having previously been considered as an inert material with respect to such phenomena. An occurrence of this type was identified by ADAS within one of its agricultural catchments located to the north of Cambridge at Swavesey. For a number of years atrazine, which was not used in the area, was frequently detected in a stream draining agricultural land. From the results of a comprehensive sampling programme the source was located as a drain from an agricultural track constructed from ballast originally taken from a disused railway line (Harris *et al*, 1992).

Experiments were carried out on samples of ballast from the railway line at North Weald to determine the levels of pesticide residues and to ascertain whether it was present in a bound state or free to leach into rain water. The work was also carried out to provide an indication of pesticide persistence within the ballast. This would provide a general indication of the behaviour of pesticide applied to the material and the period for which the material may act as a contamination source particularly when used for a secondary purpose. The results of this work are shown and described in Section 7-3.

4.4.8.1 Description of railway line ballast

Three samples of track ballast taken from the Central Line were supplied by courtesy of London Underground Limited (LUL). The samples were taken during the week ending 12th March 1993 from the railway line at North Weald. A description of the ballast samples is given in Table 4-11.

Of the ballast samples obtained, it was contemplated that the limestone fraction of the sample taken from the centre of the track would be the most susceptible to pesticide leaching. From a geological perspective, limestone is a semi-porous and permeable rock that is often the dominant constituent of underground aquifers. Thus, it was considered that the limestone property of absorbing and transmitting water may also lead to it absorbing and ultimately leaching water-borne pesticide residues.

Table 4-11 Description of railway track ballast samples

Track sampling location	Ballast description	Average diameter (mm)
Left hand side of track	A mixture of ash and gravel	< 5
Centre of track	A mixture of large pieces of limestone and granite; the sample was made up of approximately 75% limestone and 25% granite	> 40 < 80
Right hand side of track	A mixture of ash and gravel	< 5

4.4.8.2 Simulated rainfall-runoff experiment on railway line limestone ballast followed by dichloromethane extraction

A simulated rainfall-runoff test was carried out on the sample of limestone ballast using a simple apparatus constructed on a laboratory bench (Plate 4-7). For a period of approximately two hours simulated rainfall was directed on to the surface of the ballast sample which was contained within a large glass funnel. This arrangement allowed the collection of approximately 10 litres of simulated runoff which was gradually collected in a succession of 1 litre brown glass bottles. Using the analytical methodology described in Section 4.4.3, the simulated runoff was analysed for pesticide residues.

Plate 4-7 Simulated rainfall-runoff test

After drying for 24 hours at 30°C, the ballast sample was extracted two times by immersing the ballast sample in a beaker of dichloromethane placed in an ultra-sonic bath. The two dichloromethane extracts were then filtered and analysed using the methodology described in Section 4.4.3.. Limestone ballast (1722g) was carefully placed into a glass funnel (170mm wide, 150mm deep) which was held in position by a retort stand (Plate 4-7). Immediately above this a second glass funnel was held in an inverted position with the conical inlet of the funnel covered with *Parafilm* which had been randomly punctured to create a sprinkler nozzle. The inverted outlet of the second funnel was connected to the outlet tube of a 2.5 l glass separating funnel which acted as the simulated rainfall reservoir; the outlet tap of the separating funnel was adjusted to control the rate of simulated rainfall.

Using this apparatus double-distilled double-deionised water was evenly sprinkled on to the sample surface at an approximate rate of 100 cm^3/min. The simulated runoff was collected in 1 litre volumes in a succession of 1 litre brown glass bottles; at the end of the test 10 litres of simulated runoff had been collected. The ten 1 litre runoff samples were extracted using dichloromethane and the sequential extracts combined in pairs to eventually give five analytical samples representing the duration of the simulated runoff test. This procedure was followed in order to increase the overall detection limit for the analytical determination. Extracting 2 litres of water to give a final analytical sample volume of 200μl gave an overall pre-concentration factor of 10,000 instead of 5000 thereby the limit of detection from 0.1μg/l to 0.05μg/l. The five analytical samples were analysed following the procedures described in Section 4.4.3.

For the dichloromethane extraction, approximately 961g of the dry limestone ballast was placed into 1 litre glass beaker and covered with 500 ml of dichloromethane. The beaker was covered with a large glass petri dish and placed in an ultra-sonic bath for one hour. The procedure was repeated with a further 500 ml of dichloromethane for ten minutes. The two volumes of dichloromethane were then combined, filtered and reduced in volume. The combined extract was then analysed using the analytical procedure described in Section 4.4.3.

4.4.8.3 Constant aqueous immersion experiment on railway line ballast

This involved immersing samples in 500 ml of deionised water for a period of twenty four-hours and then repeating. The two volumes were then combined and analysed as described in Section 4.4.3.

Approximately 807g of limestone ballast was immersed in 500 ml of double distilled double deionised water contained in a 1 litre glass beaker for 24 hours; during the test the beaker was covered with a large watch glass to prevent evaporation. After 24 hours the ballast was carefully removed and the water passed through a Whatman No1 filter into a 1 litre brown glass bottle. This procedure was repeated for a further 24 hours and the second volume of water added to the first to give a final sample volume of 1 litre which was analysed using the analytical procedures described in Section 4.4.3.

CHAPTER FIVE

5. The hydrology of the North Weald catchment

5.1 Introduction

The North Weald catchment can be divided into two hydrologically distinct sub-catchments, the agricultural sub-catchment and the urbanised catchment (see Section 4-2). Over a period of sixteen months from 1st January 1992 to 30th April 1993, the runoff from each sub-catchment was recorded half hourly and the local rainfall recorded in increments of 0.5mm to the nearest second. The techniques employed for the measurement of runoff and rainfall are fully described in Section 4.3. During the course of this chapter the assessments of the hydrological characteristics of each sub-catchment are examined and discussed. It is not the intention to provide an in-depth hydrological analysis of the North Weald catchment but rather to describe the hydrological regime of the catchment and to examine the factors that determine the extent to which surface runoff contributes to total catchment outflow.

For the agricultural sub-catchment, the complete record of sixteen months of rainfall and runoff data are shown. To put this record into general perspective the monthly rainfall for 1992/93 (measured at North Weald) and the long-term average rainfall totals are also shown and discussed. Monthly water balances were calculated using total monthly rainfall and total monthly runoff. The aim of this exercise was to show how the response of the sub-catchment varied according to the time of year. Therefore to simplify the calculation, the volume of total rainfall was considered to 100% effective, i.e. 100% of the rainfall left the sub-catchment as runoff. Effective rainfall refers to the fraction of rainfall remaining after losses from evaporation, detention on the soil surface - such as interception by vegetation, and retention in the soil have been taken into account. Hydrological data were analysed with particular attention being given to storm hydrograph analysis with selected storm event hydrographs being broken down into hydrological components and factors. Examination of the hydrological factors allowed the underlying processes that affect the relationship between rainfall and runoff to be better understood and also highlighted the manner in which relationships changed with time due to the seasonally varying response characteristics of the sub-catchment.

The plan shows the location, area, and names of the arable fields which were mainly used for the production of winter cereals. The plan also shows the position of the two main drainage channels, one which originated in the south of the arable land and the other in the south of the mixed woodland. The soil series of the agricultural sub-catchment was dominated by a relatively impermeable high clay-content stagnogley soil, which overlaid the solid geology of impermeable London Clay (see section 4.2.2). Clay catchments of this type are often associated with relatively high levels of surface runoff (Boorman et al, 1995), and therefore to increase the movement of rainwater away from the soil surface, the arable fields of the agricultural sub-catchment were under-drained (Mackney *et al*, 1975; Harris et al, 1993).

5.2.1 Overview of the hydrological regime of the agricultural sub-catchment

The rainfall and runoff records for the agricultural sub-catchment for the whole of the monitoring period (1st January 1992 to 30th April 1993) are shown in Figure 5-2.

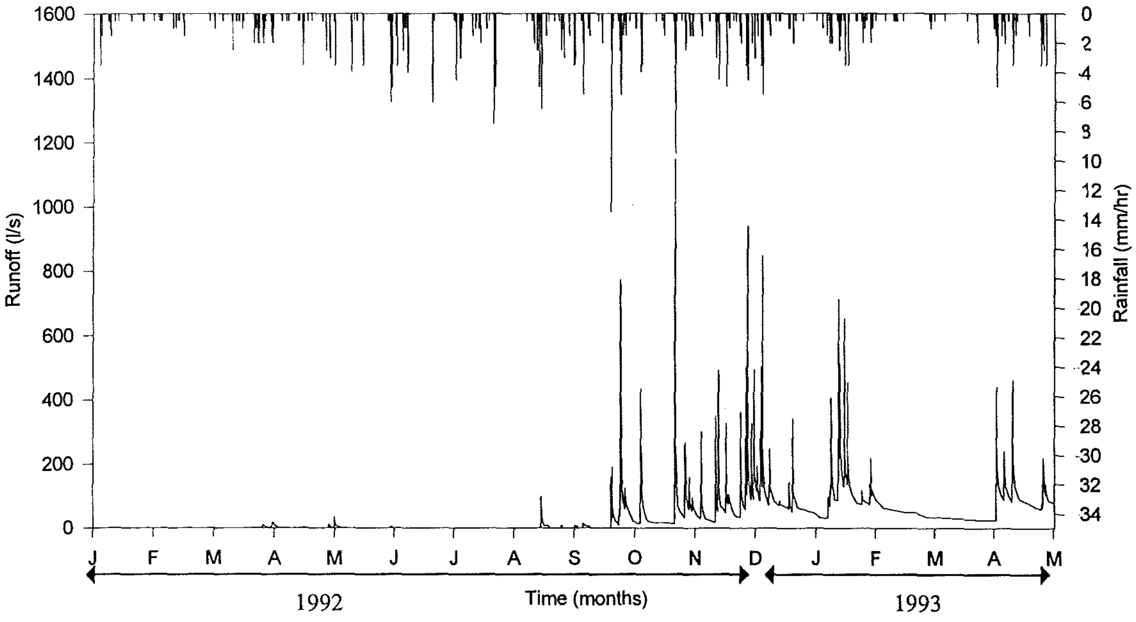


Figure 5-2 Rainfall and runoff for the agricultural sub-catchment between January 1992 and April 1993

The descending axis shows the temporal variation of rainfall rate (mm hr^{-1}) falling on the agricultural sub-catchment. The ascending axis shows the temporal variation of runoff (l s^{-1}) at the outlet of the agricultural sub-catchment at Site A. During the winter period of 1992/93 the agricultural sub-catchment was seen to rapidly respond to rainfall. The sharp, distinct hydrographs that were produced were characteristic of small clay catchments that generally respond quickly to rainfall due to relatively impermeable soil and a geology that favours surface runoff over infiltration to support baseflow. Turnbull *et al* (1995) observed a similar response to rainfall at the clay based Lugg catchment at ADAS Rosemaund over the 1992/93 winter.

Figure 5-2 shows that the runoff from the agricultural sub-catchment during the early winter months of 1992 was negligible compared to that of winter 1992/93. This behaviour may be explained by the catchment generally receiving lower-than-average rainfall during the early part of 1992 and above-average rainfall during the 1993/92 winter. Table 5-1 and Figure 5-3 show the monthly rainfall totals from July 1991 to April 1993 measured at North Weald and compared with the average monthly rainfall totals taken from the Soil Survey Land Resource Centre (SSLRC) climatic database covering 14 years of rainfall in the North Weald area.

Table 5-1 North Weald monthly rainfall between July 1991 and April 1993 compared with the Soil Survey Land Resource Centre 14 year average monthly rainfall

Month	SSLRC average monthly rainfall (mm)	North Weald Rainfall (mm/month)		
		1991	1992	1993
January	53	na	18.5 *(35%)*	70.5 *(133%)*
February	38	na	16.5 *(43%)*	9.5 *(25%)*
March	44	na	58 *(132%)*	16 *(36%)*
April	50	na	52 *(104%)*	79.5 *(160%)*
May	48	na	66.5 *(139%)*	na
June	49	na	37.5 *(77%)*	na
July	49	35 *(71%)*	68 *(139%)*	na
August	59	22 *(37%)*	85.5 *(145%)*	na
September	60	0 *(0%)*	105.5 *(176%)*	na
October	44	12.5 *(28%)*	104.5 *(238%)*	na
November	67	56 *(84%)*	106.5 *(160%)*	na
December	52	15.5 *(30%)*	44 *(85%)*	na
Year total	613	na	763	na

na - not available

(bracketed values represent percentage of mean monthly value)

It can clearly be seen that the 1992/93 winter experienced well-above-average rainfall and was considerably wetter than the preceding winter which received average to below-average rainfall. Figure 5-2 also shows that for much of the 1992/93 winter period the agricultural sub-catchment supported a significant baseflow during and between storm events, and therefore it seems probable that the soil moisture was at or near field capacity[1] for many of the winter months particularly during November and December 1992 and January 1993. In this state the soil moisture deficit[2] would have been minimal and storm rainfall would have generated surface runoff with a relatively high event-based water balance. This aspect is further examined later in the chapter. The event-based water balance, expressed as a percentage, refers to the volume of surface runoff (mm) leaving the agricultural sub-catchment with respect to the initial volume of storm event rainfall (mm).

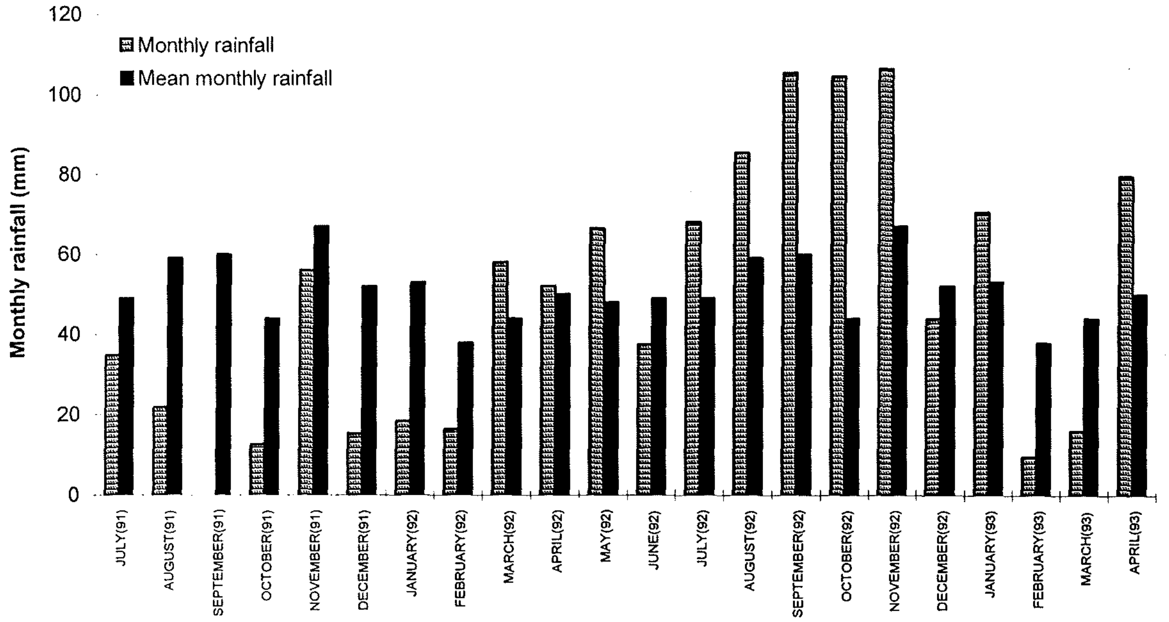


Figure 5-3 Monthly rainfall patterns at North Weald covering the period July 1991 to April 1993 compared with SSLRC's mean monthly rainfall record covering 14 years.

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[1] Field capacity is the water content of the soil (volume fraction) after the saturated soil has drained under gravity to equilibrium.

[2] Soil moisture deficit is the amount of water required to restore the soil to field capacity.

The expression of rainfall and runoff as depth in millimetres is a slightly confusing convention adopted by most hydrology literature. For rainfall, 1mm depth equates to a volume of 1mm^3 of rain falling on every 1mm^2 square area of the catchment. Often, for ease of comparison, the consequent runoff is also expressed as depth in millimetres. The runoff depth is derived by first expressing the volume of runoff as mm^3 and then dividing by the catchment area expressed in millimetres.

5.2.2 Storm event hydrology

As discussed in Chapter 1, the aim of this work was to further the understanding of the transport of pesticides in storm-event surface runoff. Therefore, an examination of the North Weald catchment storm-event hydrology was carried out to gain an understanding of the seasonal and climatic factors that lead to elevated levels of direct surface runoff. The work focused on the analysis of storm events that occurred throughout the course of the monitoring program including those that were sampled for pesticides. The selected storm events were broken down into rainfall and runoff components and catchment response factors, and common relationships identified using linear regression analysis.

5.2.2.1 Analysis of selected hydrographs

During the sixteen months of monitoring, twenty-seven storm events were analysed in terms of the following rainfall and runoff components and catchment response factors:

- Rainfall intensity, RI (mm hr^{-1}) - the cumulative volume of rainfall during each hour of the storm event.
- Mean rainfall intensity, $\text{RI}_{(m)}$ (mm hr^{-1}) - the mean rainfall intensity during the storm event time of concentration.
- Rainfall volume, RV (mm) - the volume of rainfall during the storm event.
- Peak flow, PF (l s^{-1}) - the maximum flow rate observed during the total storm runoff hydrograph.
- Total storm runoff, TRV (mm) - the total volume of runoff gauged leaving the catchment during the duration of the storm event.

- Total baseflow runoff, BFV (mm) - the volume of the baseflow component of the total runoff volume; this component of runoff has been fully discussed in Section 3.1.8.1. and the method used for its determination is discussed below in Section 5.2.2.1.1.
- Total direct runoff, DRV (mm) - the volume of the direct runoff component of the total runoff volume; this component of runoff has been fully discussed in Section 3.1.8.1. and the method used for its determination is discussed below in Section 5.2.2.1.1.
- Rainfall-runoff lag time, LAG (minutes) - the time between the rainfall centroid[1] and the occurrence of the peak flow of the hydrograph (Figure 5-4).
- Water balance, WB (%) - the percentage ratio of total direct runoff with respect to rainfall volume.
- Storm event duration, ED (hours) - the period from the beginning to the end of direct runoff (see Figure 5-4).
- Runoff coefficient, C - the coefficient of the rational formula (Equation 5-1) which represents the rapidity of response of a catchment to rainfall when generating runoff; the use of the formula is described below.
- Antecedent dry period, ADP (hours) - the time between the start of the event rainfall and the end of the previous rainfall event.

The runoff coefficient C, can be calculated using the Rational Formula as shown in Equation 5-1:

$$Q_p = 0.278\, C\, i\, A \qquad \text{Equation 5-1}$$

Where Q_p (m^3s^{-1}) is the peak catchment discharge, C is the runoff coefficient (dependent on catchment response characteristics), i (mm hr^{-1}) is the intensity of the rainfall in time T_c and A is the area (km^2) of the catchment. T_c is the time of concentration which represents the time required for rain falling on the farthest point in the catchment to flow to the gauging point of the catchment. When the time T_c following the commencement of rain has expired, the whole of the catchment is taken to be contributing to the flow. The value of i is the mean rainfall intensity during the time T_c , and assumes that all the measured rainfall over the area contributes to the

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[1] Time after which 50% of event rainfall volume has occurred

flow. The peak flow Q_p occurs after the period T_c. The Rational Formula was originally used by drainage engineers to estimate the scale of flow structures, where the runoff coefficient was dependent on catchment characteristics and had to be subjectively estimated using a catchment survey (Shaw, 1988). Values of C vary from 0.05 for flat sandy areas to 0.95 for impervious urban areas (Kiely 1997).

For each of the selected storm events, the value of the runoff coefficient was calculated using the mean storm-event rainfall intensity and the maximum event flow rate. The runoff coefficient gives an indication of how runoff volume-based response to rainfall of the agricultural sub-catchment changed during the course of the monitoring period.

Storm events were selected for analysis on the basis of ease of analysis and storm hydrographs showing a single flow peak in response to a single rainfall event were targeted. A key procedure in the storm-event analysis was the breaking down of the storm hydrograph into component parts. In particular the baseflow was separated from direct storm runoff using the procedure described in Section 5.2.2.1.1.

5.2.2.1.1 Separation of baseflow and direct runoff from the storm hydrograph

There are a number of methods used for the separation of baseflow and direct surface runoff. One method which has generally been accepted to be reliable is that used in the Flood Studies Report [FSR](Natural Environment Research Council, 1975). Figure 5-4 illustrates how the FSR flow separation was performed. In this procedure the lag time between the centroid (the time when 50% of event rainfall had fallen) of the total rainfall and hydrograph flow peak was determined The end time at which direct surface runoff ceased, was taken as four times this lag time following the end of the rainfall event. The flow rate of the baseflow prior to the storm event was interpolated through the storm event to the time at which the peak flow rate occurred. A curved line was then drawn from this point to the point already identified as marking the end of the direct surface runoff. The direct surface runoff was the portion of the flow above this separation.

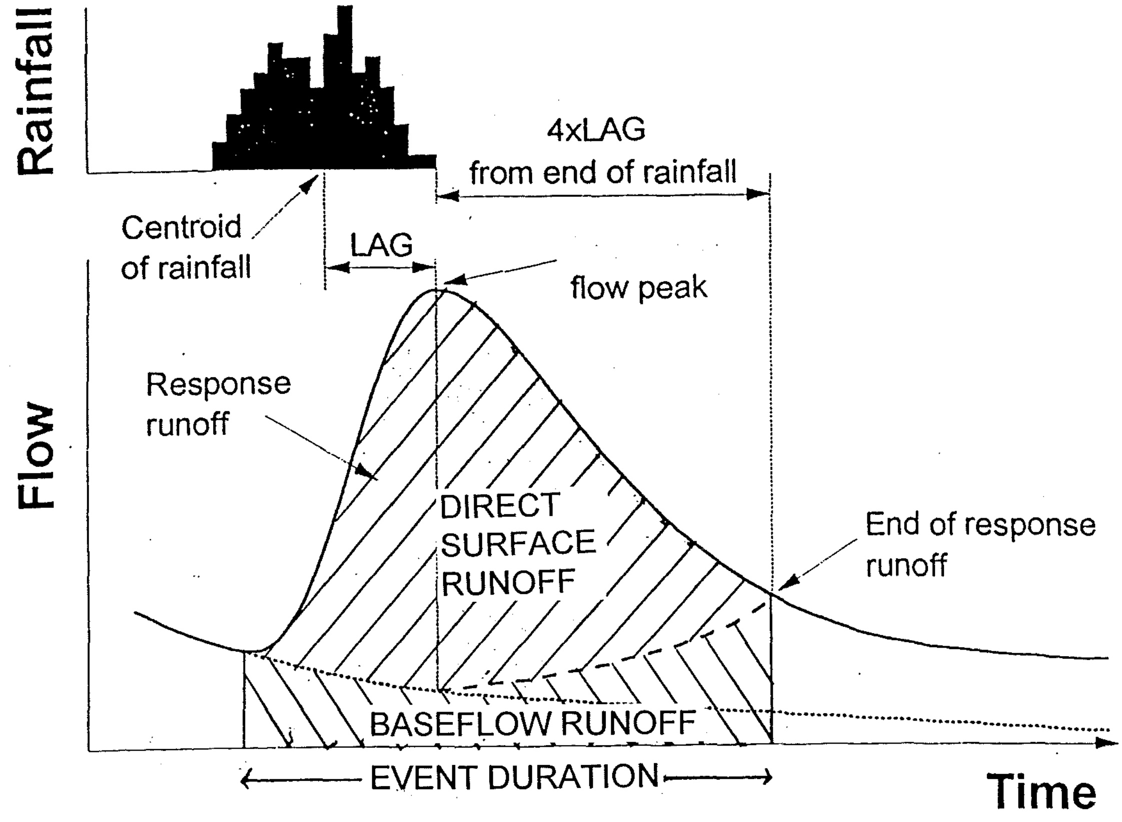


Figure 5-4 Flood Studies Report method of separating baseflow from direct runoff (Natural Environment Research Council, 1975).

5.2.2.2 Results of hydrograph analysis

The analysed hydrographs are identified in Figures 5-5, 5-6, 5-7 and 5-8 according to the Julian day on which they occurred; the water balance for the storms analysed is also shown on the figures. The data extracted from the selected hydrographs are shown in Table 5-2, along with the dates corresponding to the storm event and the corresponding Julian day values. The data shown in Table 5-2 was tested for normality and values linearly regressed against each other to generate a correlation matrix of squared Pearson product moment correlation coefficients. The resulting correlation matrix is shown in Table 5-3 and those correlation coefficients significant at the 95% confidence level are shown in bold and underlined.

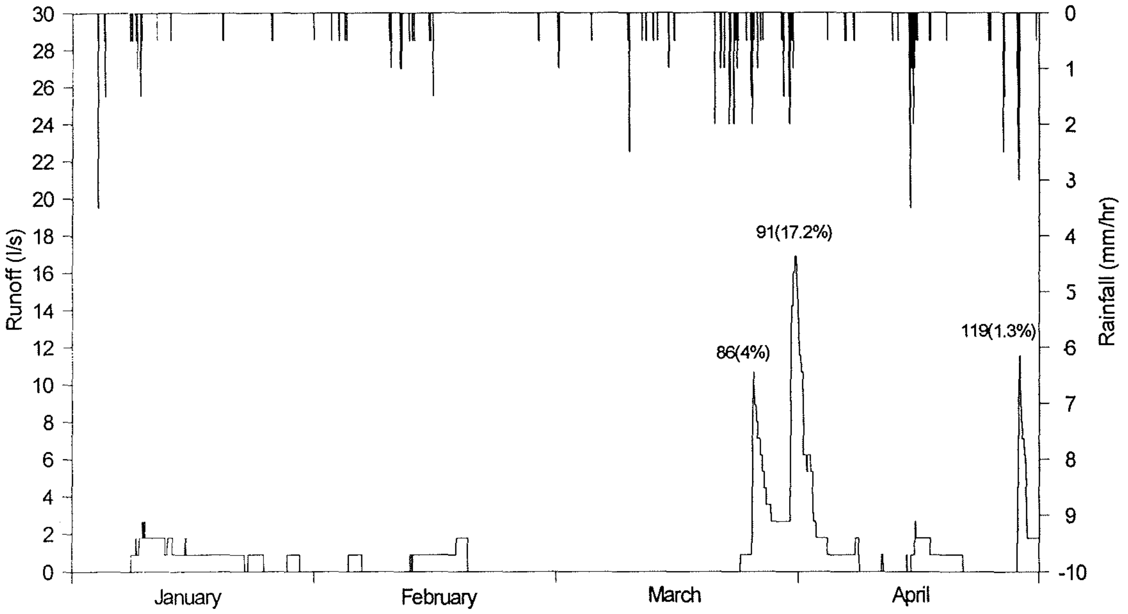


Figure 5-5 Rainfall and runoff for the agricultural sub-catchment between January and April 1992

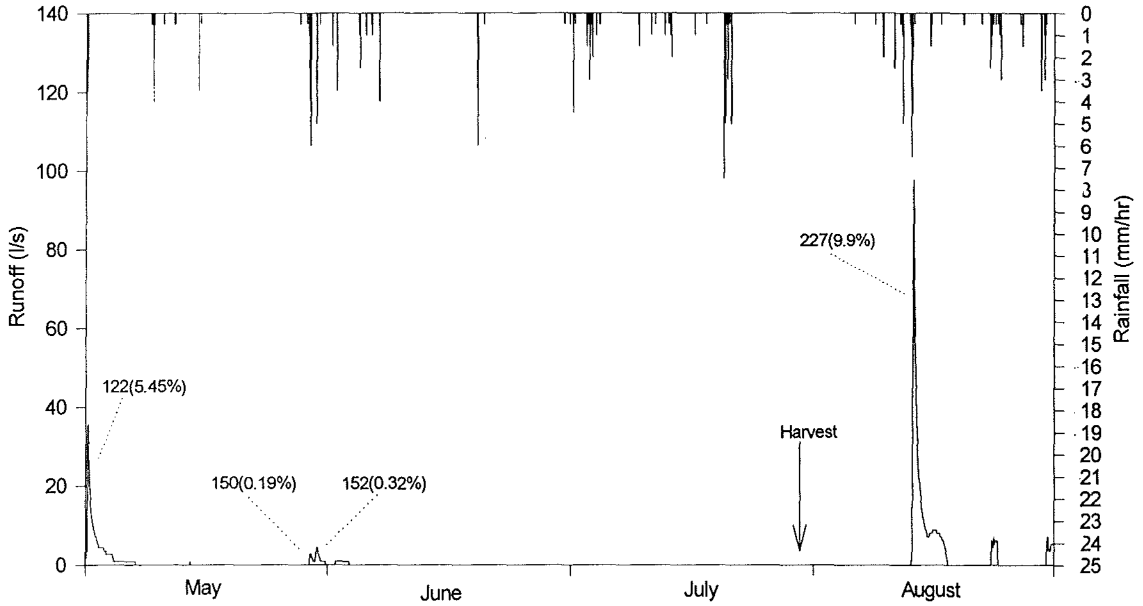


Figure 5-6 Rainfall and runoff for the agricultural sub-catchment between May and August 1992

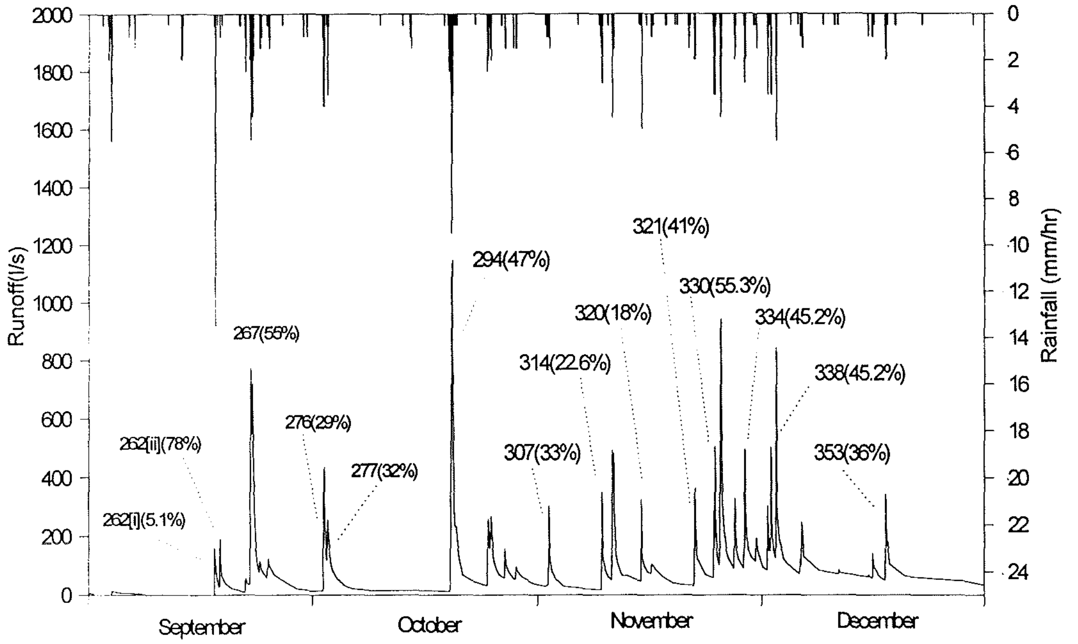


Figure 5-7 Rainfall and runoff for the agricultural catchment between September and December 1992

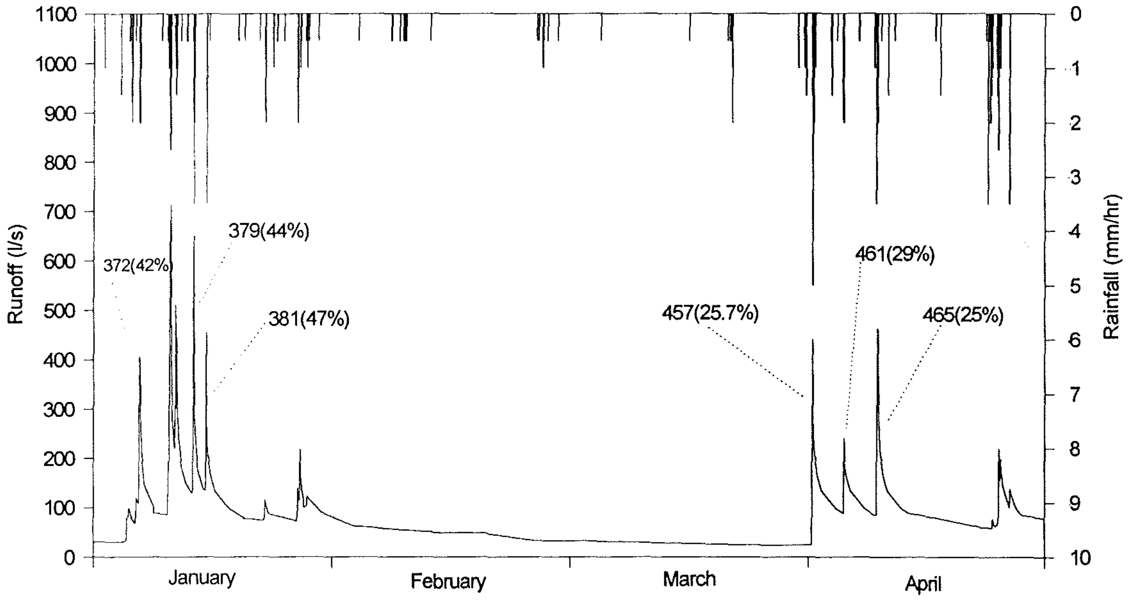


Figure 5-8 Rainfall and runoff for the agricultural sub-catchment between January and April 1993

Table 5-2 Results of selected hydrograph analysis

JD	Date	RI	$RI_{(m)}$	RV	ADP	LAG	PF	TR	BFV	DRV	PBFV	PR	WB	C	ED
86	26/03/92	2	1.1176	9.5	36.3	345	10.6	0.619	0.2398	0.3792	38.7	61.3	4	0.0213	40
91	31/03/92	2	0.5121	7.5	15	300	16.89	1.75	0.4611	1.2889	26.4	73.6	17.2	0.0741	32
119	28/04/92	3	2.3125	18.5	36.4	265	11.55	0.4205	0.1714	0.249	40.7	59.2	1.34	0.0112	24.5
122	01/05/92	3.5	2.375	9.5	60.5	260	35.55	0.762	0.2517	0.5103	33	67	5.45	0.0337	18
150	29/05/92	6	2.6842	25.5	643	337	2.66	0.0655	0.018	0.0475	27.5	72.5	0.19	0.0022	18
226	14/08/92	6.5	1.88	23.5	19.7	480	97.77	2.8195	0.4948	2.3246	17.5	82.5	9.9	0.1169	33
262	18/09/92	13.5	2.7142	22.5	104.25	81	160	1.7899	0.6446	1.1453	36	64	5.1	0.1325	7.5
267	23/09/92	5.5	2.125	31.5	11.9	206	773	21.371	4.3965	16.974	20.6	79.4	55	0.8178	23.5
276	02/10/92	4	2.3333	17.5	50.2	200	434	6.8725	1.862	5.0105	27	73	29	0.4182	14
277	03/10/97	3.5	0.7777	7	5.3	90	256	5.4384	3.3074	2.1311	60.8	39.2	32	0.7401	13.5
294	20/10/92	9.5	3.6153	49.5	214.4	171	1148	27.739	4.6344	23.105	17	83	47	0.7139	38.5
307	02/11/92	1.5	0.875	7.5	96	198	303	4.5465	2.061	2.4855	45	55	33	0.7785	16.5
314	09/11/92	3	2.2	12	164.2	145	350	4.4375	1.7199	2.7176	38.8	61.2	22.6	0.3577	14
320	15/11/92	5	1.71	7.5	80.8	77	326	2.6635	1.3151	1.3484	49.4	50.6	18	0.4286	7
327	22/11/92	2	2.6	6.5	12.3	126	363	4.867	2.2049	2.6621	45.3	54.7	41	0.3139	10.5
330	25/11/92	4.5	4.16	18	13.5	120	942	15.363	5.4158	9.9473	35.3	64.7	55.3	0.5091	14.5
334	29/11/92	3	2.7142	9.5	27.3	150	494	8.4305	4.074	4.3565	48.3	51.7	45.8	0.4092	14.5
338	03/12/92	5.5	5	8.5	15.6	75	848	6.867	3.0238	3.8432	44	56	45.2	0.3813	7
353	18/12/92	2	2.25	7	39.6	80	342	5.1446	2.6186	2.526	50.9	49.1	36	0.3417	12.5
6	06/01/93	2	2	7.5	18.5	142	407	6.7939	3.6264	3.1674	53	46	42	0.4575	13
13	13/01/93	3.5	2.1666	9	47.8	85	651	7.2506	3.303	3.9476	45	55	44	0.6755	10.5
15	15/01/93	3.5	1.5	5	51.1	49	456	5.9755	3.645	2.3305	61	39	47	0.6835	17
91	01/04/93	5	4	17.5	15.8	103	440	7.85	3.348	4.502	43	57	25.7	0.2473	17
95	05/04/93	2	1.777	8	31.5	260	240	4.8415	2.5594	2.2821	53	47	29	0.3036	18.5
99	10/04/93	3.5	2	30.5	90.2	354	459	14.284	6.636	7.6481	46	54	25	0.516	28

where:

RI	Rainfall intensity(mm hr^{-1})	$RI_{(m)}$	Mean rainfall intensity (mm hr^{-1})	PBFV	Percentage baseflow volume
RV	Rainfall volume(mm)	LAG	Rainfall - runoff lag time(min)	PR	Percentage direct runoff volume
PF	Peak flow rate (l s^{-1})	BFV	Baseflow volume (mm)		
DRV	Direct runoff volume(mm)	TR	Total runoff (mm)		
WB	Water balance (%)	ED	Event duration (hrs)		
C	Runoff coefficient derived from Rational Formula	ADP	Antecedent dry period (hours)		

Table 5-3 shows a number of significant correlations indicating relationships between rainfall and runoff components (RI, $RI_{(m)}$, RV, PF, BFV, DRV, and TR) and also relationships with catchment response factors (ADP, LAG, C, WB, and ED); though some of the coefficients may appear rather low, they are statistically significant at the 95% confidence level. In the following sub-sections the most significant relationships involving catchment response factors are discussed, followed by discussion of the most significant factors that are associated with direct surface runoff and peak hydrograph flow.

Table 5-3 Correlation matrix for the results of selected hydrograph analysis

	RI	RI(m)	RV	ADP	LAG	PF	BFV	DRV	TR	C	WB	ED
RI	1.0000	0.1774	**0.3847**	0.0872	0.0120	0.0531	0.0004	0.1180	0.0713	0.0021	0.0534	0.0000
RI(m)		1.0000	**0.4026**	0.0829	0.0940	**0.3600**	0.0969	0.1337	0.1430	0.0017	0.0878	0.0672
RV			1.0000	0.1584	0.1554	0.1646	0.0873	**0.5624**	**0.4609**	0.0129	0.0104	-0.3270
ADP				1.0000	0.0658	0.0110	0.0372	0.0006	0.0001	0.0433	0.0970	0.0063
LAG					1.0000	0.2114	0.1011	0.0016	0.0148	**0.2330**	**0.2227**	**0.5521**
PF						1.0000	**0.6349**	**0.6702**	**0.7601**	**0.4910**	**0.4706**	0.0035
BFV							1.0000	**0.4338**	**0.6406**	**0.5379**	**0.4188**	0.0002
DRV								1.0000	**0.9570**	**0.3318**	0.2300	0.1277
TR									1.0000	**0.4378**	**0.3142**	0.0783
C										1.0000	**0.6432**	0.0348
WB											1.0000	0.0451
ED												1.0000

where:

RI	Rainfall intensity(mm hr^{-1})	RV	Rainfall volume(mm)	LAG	Rainfall - runoff lag time(min)
PF	Peak flow rate (l s^{-1})	BFV	Baseflow volume (mm)	DRV	Direct runoff volume(mm)
TR	Total runoff(mm)	WB	Water balance (%)	ED	Event duration (hrs)
C	Runoff coefficient derived from Rational formula			ADP	Antecedent dry period

Values in bold and underlined are significant at the 95% confidence level

5.2.2.2.1 Relationships between catchment response factors

The correlation matrix indicates a significant relationship between the rainfall-runoff lag time (LAG) and the event duration time (ED). The correlation between these two parameters has an r^2 value of 0.5521 and is shown graphically in Figure 5-9. The relationship demonstrates that longer rainfall-runoff lag times produced longer event duration time. This may be explained by considering the cause of extended lag times.

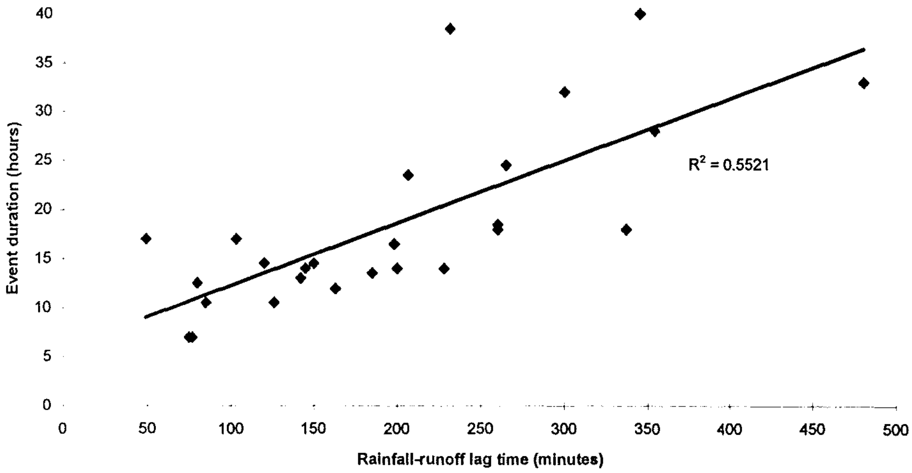


Figure 5-9 Relationship between event duration and rainfall-runoff lag

high water table and the volume of unsaturated soil below field capacity was probably very low. With the absence of interception by senescent vegetation and minimal soil moisture deficit, the lag time would have been minimal. Further, the reduced volume of pre-storm unsaturated soil would have minimised the temporary storage capacity of the soil and subsequently reduced the duration of direct surface runoff.

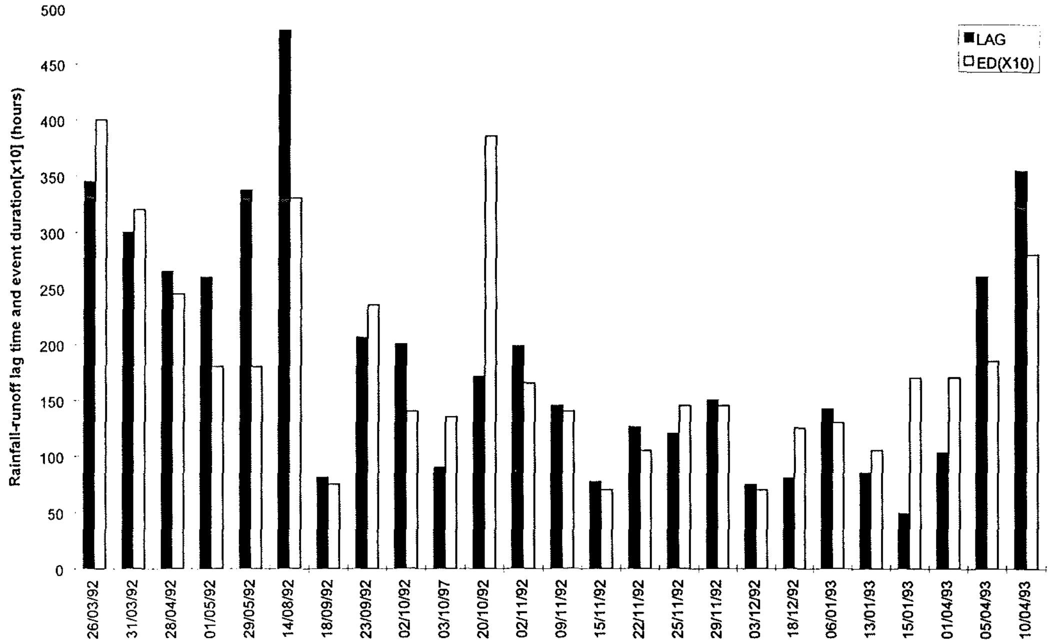


Figure 5-10 Variation of rainfall-runoff lag and event duration during the course of the monitoring programme

The correlation matrix in Table 5-3 indicates a significant relationship between the water balance (WB) and the runoff coefficient (C). The correlation is plotted in Figure 5-11 and has an r^2 value of 0.6432. The relationship suggests that higher water balance values were associated with increased peak catchment discharge for a given mean intensity of rainfall, due to increased catchment response characteristics represented by higher runoff coefficient values. Table 5-3 shows that there was no significant correlation between the event duration time (ED) and either the water balance (WB) or the runoff coefficient (C) (r^2 values; 0.0451 and 0.0348, respectively). However, there was a higher correlation between both the water balance (WB) and the runoff coefficient (C) with the rainfall-runoff lag time (LAG) (r^2 values; 0.2227 and 0.2330, respectively).

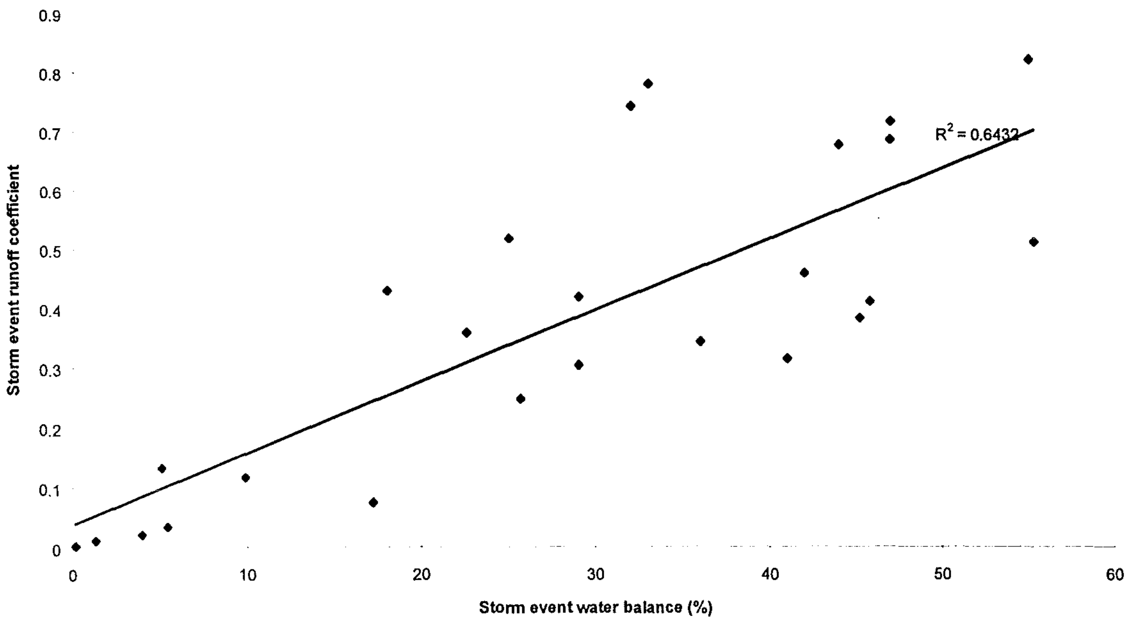


Figure 5-11 Relationship between storm runoff water balance and runoff coefficient

These relationships suggest that the increase in the runoff coefficient value can be considered the result of an increase in effective rainfall due to a reduction in evaporation, vegetation interception and rainfall losses to make up soil moisture deficits. The absence of significant correlation with event duration may suggest that the connection between the runoff coefficient and the soil moisture deficit did not involve a storage factor as was the case for the correlation between lag and event duration discussed above. This implies that vegetation interception and evaporation may have been as equally, if not more, important as soil moisture deficit in influencing the runoff coefficient. This argument is consistent with the increase in water balance and runoff coefficient as the monitoring period approached the 1992/93 winter where rainfall losses to evaporation and interception by senescent vegetation would have declined (Figure 5-12). The instances in Figure 5-12 where the runoff coefficient is significantly higher than the water balance for a given storm event may represent occasions where a proportion of the rainfall travelled as overland flow due either to soil saturation or to the rainfall intensity exceeding the infiltration capacity of the soil.

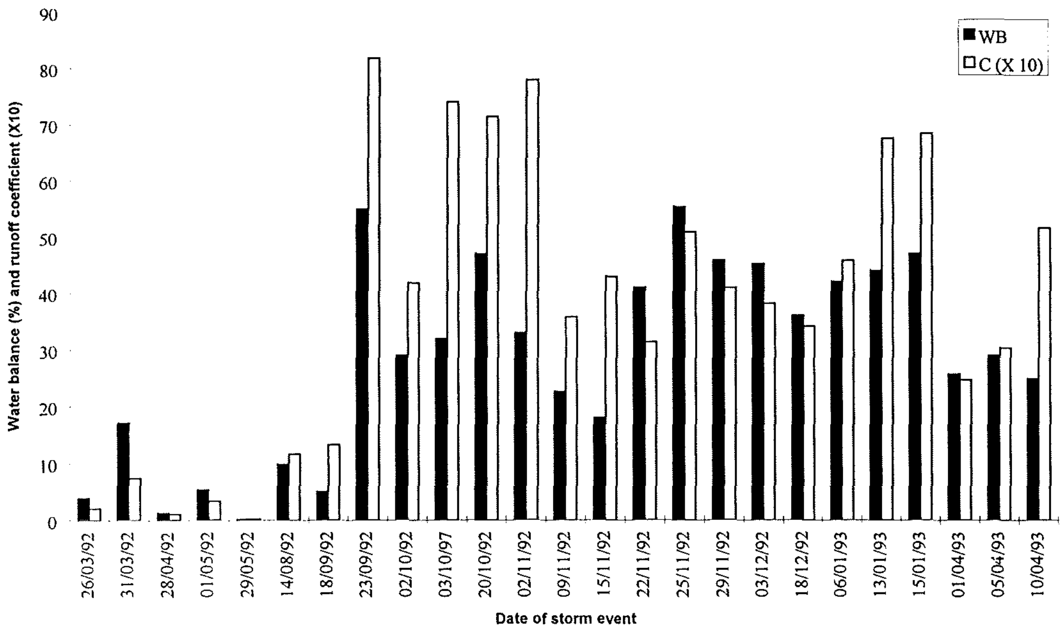


Figure 5-12 Variation of water balance and runoff coefficient during the course of the monitoring programme

5.2.2.2.2 Relationships between rainfall and runoff components

The correlation matrix in Table 5-3 shows a significant correlation between direct runoff volume (DRV) and the storm rainfall runoff volume (RV) and to a lesser extent with the runoff coefficient (C) and water balance (WB) with r^2 values of 0.5624, 0.3318, and 0.2300 respectively (Figures 5-13 and 5-14). The correlation between the rainfall volume and the direct runoff volume showed that higher volumes of direct runoff were associated with higher volumes of storm event rainfall. Also, the correlation of direct runoff volume with the event water balance and runoff coefficient showed that higher volumes of direct runoff were associated with higher water balance and runoff coefficients. This suggests that the response characteristics of the agricultural sub-catchment, represented by the water balance and the runoff coefficient were, to some degree, dependent on the volume of direct runoff. This relationship was most probably the result of various soil hydrology mechanisms or soil profile drainage routes, coming into operation depending on the amount of direct runoff. Further, it was probable that the soil hydrology of the agricultural sub-catchment would have changed according to the state of wetness of the catchment.

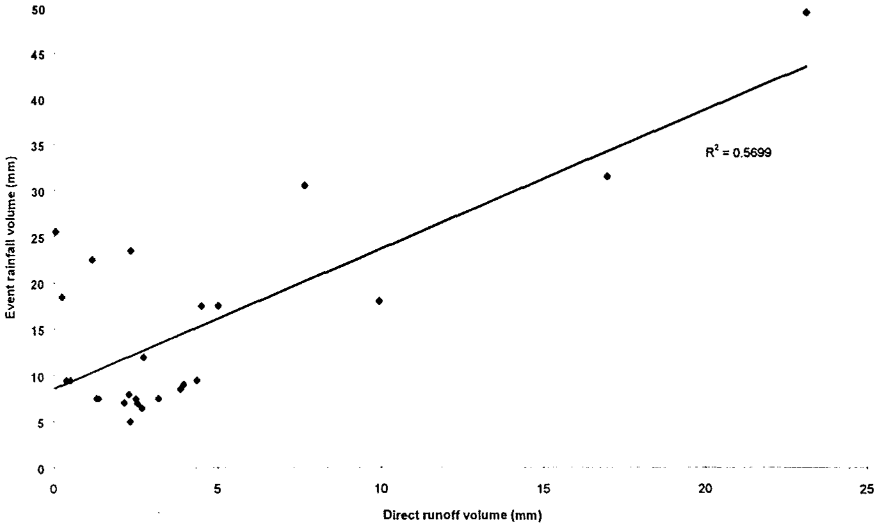


Figure 5-13 Correlation between event rainfall volume and direct runoff volume

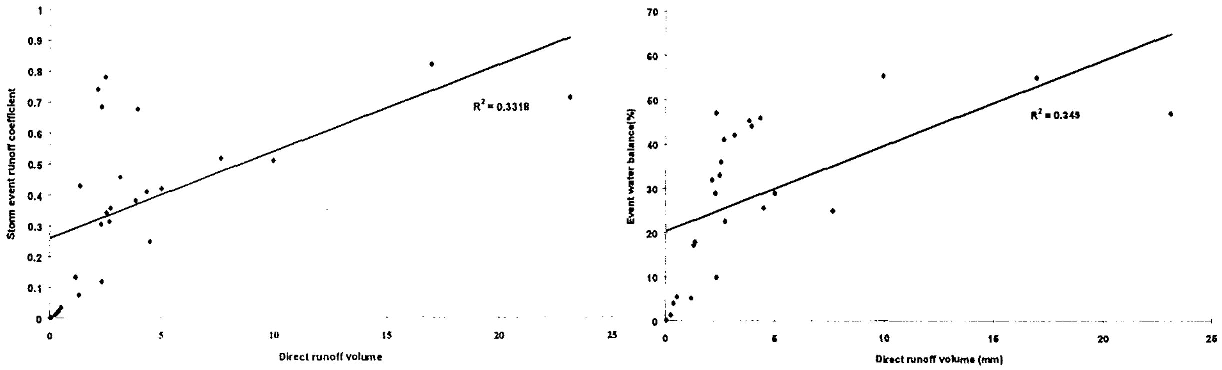


Figure 5-14 Correlations between event direct runoff volume with runoff coefficient and with water balance

Harris *et al*, (1994) and Haria *et al*, (1994) have described clay soils as being particularly prone to cracking from shrinkage during periods when the soil moisture content is low. This may occur after a period absent from rain or during a period in the growing season when the water demand of vegetation exceeds that readily available from the soil profile. In this situation, depending on the magnitude of the direct runoff volume, rain water would initially flow down into the soil column through the soil-shrinkage cracks as interflow and would generally be absorbed within the soil profile. As the direct runoff volume increases, the water moving through the shrinkage cracks would eventually pass into the drainage channels and contribute to the catchment discharge. With increasing direct runoff volume, eventually all the macro-pore and bio-pore interflow routes within the soil profile would be conducting water to the drainage channel, until a stage is reached where the direct runoff volume is of sufficient magnitude that it exceeds the drainage capacity of the soil profile and instead rapidly moves as overland runoff to the main drainage channel. Therefore, the greater the proportion of the direct runoff moving as unattenuated overland runoff, then the higher the water balance and the runoff coefficient.

However, with persistent rainfall, the soil eventually becomes saturated and expands, closing most of the macro-pore flow routes. In this state, the rate of rainwater drainage into and through the soil profile would be significantly reduced since it would be dependent on the hydraulic conductivity of the clay soil which is typically of the order of 1cm day^{-1}. In this state a relatively minor volume of direct runoff would rapidly generate and move as overland runoff and contribute to catchment discharge. This transition from soil hydrology based on macro-pore interflow routes to matrix flow may help to explain the two-tier appearance of the variation of the water balance and runoff coefficient during the course of the monitoring programme as shown in Figure 5-12.

In conclusion, the examination of the storm event hydrology has shown that the occurrence and amount of direct surface runoff was principally dependent on rainfall volume. Positive correlation between the rainfall-runoff lag and event duration showed that extended periods of direct surface runoff were associated with periods when the soil moisture deficit of the agricultural sub-catchment catchment was high. However, the volume of direct surface runoff was higher during periods when the soil moisture deficit was low which favoured higher water balance and runoff coefficient values. Also, the positive correlation of the direct runoff volume with water balance and the runoff coefficient suggest that the response of the agricultural sub-catchment to rainfall increased as the volume of direct surface runoff increased. Overall, the highest volume of direct surface runoff was most likely to occur and be efficiently generated during the wet winter season.

5.2.3 Monthly variation of the agricultural sub-catchment water balance

The monthly water balance values (for total runoff) for the agricultural sub-catchment from January 1992 to April 1993 are shown in Table 5-4 and Figure 5-15. The values show that during the winter months of the 1992/93, the monthly water balance for the agricultural sub-catchment peaked in excess of 700%. The event-based water balance values for the analysed hydrographs shown in Table 5-2 were derived from event rainfall and subsequent direct runoff and were within acceptable limits for small clay catchments. Therefore, the large monthly water balance values which include event and inter-event baseflow, suggest that the baseflow runoff from the agricultural sub-catchment was supplemented by a source of water from outside of the sub-catchment boundary.

Table 5-4 Monthly water balance for the agricultural sub-catchment from January 1992 to April 1993

Month	Rainfall (mm)	Runoff (mm)	Water Balance (%)
January	18.5	1.05	5.7
February	16.5	0.49	2.98
March	58	2.15	3.71
April	52	2.02	3.88
May	66.5	1.79	2.7
June	37.5	0.08	0.22
July	68	0.00	0.00
August	85.5	4.66	5.45
September	105.5	53.56	50.77
October	104.5	98.25	94.02
November	106.5	149	139.90
December	44.5	142.3	319.75
January	70.5	188.7	267.62
February	9.5	76	799.82
March	16	54	335.97
April	79.5	142	179.18

Examination of the 1:25,000 Ordnance Survey map for the area showed the presence of a spring (Posternlane Spring) at map reference TL 40/50 485 025 which almost exactly coincided with the flow path of the main drainage channel of the agricultural sub-catchment as shown on Figure 5-1. The presence of the ephemeral spring had also been confirmed by discussion with the farm manager of Sears Hall Farm.

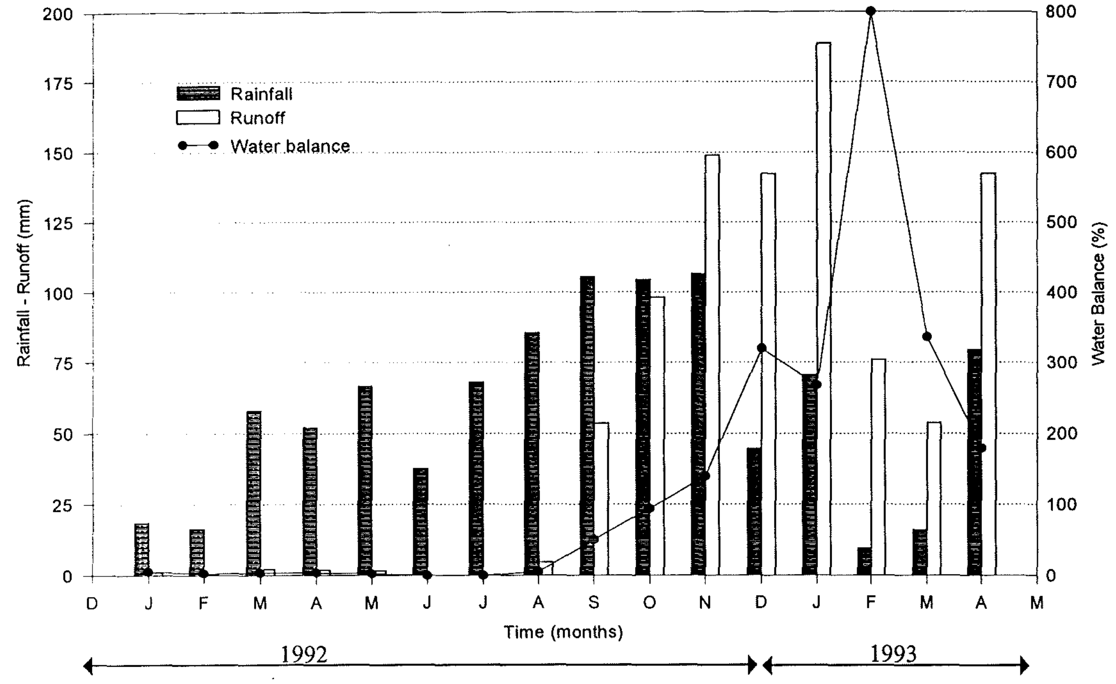


Figure 5-15 **Monthly water balance for the agricultural sub-catchment from January 1992 to April 1993.**

Assuming that the spring water was free of pesticide contamination, the concentration of any pesticide transported within storm runoff would have been diluted by the spring water supplement to the storm event baseflow. The extent of this dilution was almost impossible to measure without an extensive hydrogeological examination of the agricultural sub-catchment and the land surrounding it. Estimation would have required the identification of those areas outside the sub-catchment that contributed to the baseflow, the volume of rain received on these areas and the travel time between rainfall and appearance in the baseflow of the sub-catchment.

5.3 The urbanised catchment

The urbanised catchment covered an area of 150ha of which 99ha was characterised by residential development in addition to a nine hole golf course and a small industrial estate (see Section 4.2). The remaining area was made up of grassed and minor arable areas. Of the 150ha total catchment area, approximately 20ha was calculated to be totally impervious. This value was could not guarantee that there were no remaining illegal connections. The drainage department estimated that the flow contribution of those illegal connections it had not yet located was negligible.

Due to frequent surface water flooding in the North Weald village, a flood by-pass system was constructed in 1998 to divert high storm flows away from the centre of the village to a safe location, away from the inhabited area of the village (Section 4.2; Figure 4-1; Plate 4-3). The system was designed such that storm flows exceeding 400 $l\ s^{-1}$ would be diverted over a side-of-channel weir. However, from examination of the flow rates at Sites A and D, on occasions when the by-pass channel began to operate, it appeared that this threshold flow rate varied. This behaviour was discussed with EFDC and attributed to a combination of the sur-charging of the surface water sewers and the silting up of the main drainage channel stream bed adjacent to the by-pass side-of-channel weir.

5.3.1 Overview of the hydrological regime of the urbanised catchment

The flow monitoring of the main drainage channel at the outlet to the urbanised catchment was achieved through the continuous measurement of stage height over a concrete step-weir (see Section 4.3.2). Stage height was primarily measured using a Druk electronic hydraulic pressure transducer linked to an electronic data logger which was backed up by an Arkon pneumatic hydraulic pressure transducer. Unfortunately both transducers were prone to technical problems. The Arkon generally performed well and faithfully recorded stage height but was prone to intermittent jumping and jamming of its chart paper which meant the record it produced was discontinuous and where stage was recorded, errors were present in the time-base. The Druk was found to be more reliable than the Arkon and rarely failed to produce a continuous stage record with an accurate time-base. However, with time it was noticed that its response characteristics varied such that at different times a given head of water would produce a different output voltage.

Overall, this meant that compared to the flow record for agricultural sub-catchment, the record for the urbanised catchment was of poor quality and discontinuous. Therefore, it was impossible to produce a continuous flow record for the whole of the monitoring period as was achieved for the agricultural sub-catchment. However, it was possible to produce storm hydrographs for the events where pesticide samples were taken and these were also common to those analysed for the agricultural sub-catchment (Table 5-2). Fortunately, sufficient hydrographs were obtained to reasonably show how the rainfall-runoff characteristics of the urbanised catchment changed during the course of the sixteen month monitoring period.

During the course of the monitoring period it was observed that, unlike the agricultural sub-catchment, an inter-storm event baseflow was continually present at the monitoring station of the urbanised catchment. This behaviour is more typical of pervious catchments which allow infiltration that supports a baseflow and it illustrates the relatively low level of urbanisation within the North Weald catchment. Typically residential urbanised catchments are made up of 35% of impervious area compared to approximately 20% of the urbanised catchment at North Weald (Ellis pers comms, 1998).

5.3.2 Storm event hydrology

From the discontinuous flow record of the urbanised catchment, eleven hydrographs were characterised and analysed in the same way as those hydrographs obtained from the agricultural sub-catchment. The runoff for the urbanised catchment was isolated from the runoff for the agricultural sub-catchment by combining the runoff monitored at Site D with the by-pass flow and then subtracting the measured runoff from Site A. The dates of the examined storm events are shown in Table 5-5. In every case except for the event occurring on the 29th May 1992, the hydrographs produced were based on the Druk stage record. For the 29th May 1992 event, an Arkon stage record was available with an accurate time-base as the site was visited during the event and the chart recorder checked for time-base accuracy. For the remaining ten events, the Druk stage record had to be modified to take into account the spurious sensitivity of the transducer. Hydrographs produced from the raw Druk stage data appeared to be compressed along the flow axis. Therefore, the hydrograph flow peak was estimated and the raw stage data amended to decompress the resulting hydrograph such that its flow peak matched the estimated flow peak.

The hydrograph flow peak was estimated using the rational formula described in Section 5.2.2.1. Two peak flow values were calculated representing the impervious and pervious areas of the urbanised catchment. For the impervious area, a runoff coefficient of 1.0 was used and for the pervious grassed/wooded area the coefficient derived from the corresponding agricultural sub-catchment hydrograph analysis was used.

The determination of an overall estimated peak flow value was dependent on the shape of the hydrograph in question and also the magnitude of the corresponding hydrograph from the agricultural sub-catchment. For example, the hydrograph shown in Figure 5-17 shows an initial sharp distinct flow peak, characteristic of rapid runoff from impervious hard surface. The main peak was followed by minor peaks which may represent runoff from the pervious fraction of the catchment, which is characterised by a low runoff coefficient and a slow response. This scenario was probable due to the fact that the hydrograph from Site A was negligible (21 s^{-1} flow peak) and the corresponding calculated runoff coefficient for the hydrograph was very small (0.003). Therefore, it is logical to conclude that the major peak in the hydrograph in question is due solely to runoff from the impervious fraction of the urbanised catchment. The estimated flow peaks for the impervious and pervious fractions of the urbanised catchment using the rational formula were 55.51 s^{-1} and 21 s^{-1} respectively, which further confirms the interpretation of the hydrograph. As a result, the raw Druk data was amended to ensure the peak assigned to the impervious area had a maximum value of approximately 55.51 s^{-1}.

Figure 5-20 shows the opposite scenario where the runoff coefficient (0.4286) for the corresponding Site A hydrograph was significant enough for the calculated pervious flow peak to be comparable to the impervious flow peak. In this situation it was assumed that the response times of the pervious and impervious areas were close enough to summate the estimated values to give a single estimated flow peak. This assumption was strengthened since the hydrograph occurred as a single tailing peak which was more associated with runoff from pervious catchments than those dominated by impervious runoff.

Although the approach described above depended on a degree of subjective interpretation it was considered that it was the best option for rectifying the errors of the raw Druk data whilst not entailing excessive calculations that may have only marginally improved the flow peak estimate. The eleven hydrographs produced were analysed and examined using similar methods to those used for the analysis of the hydrographs recorded at Site A.

5.3.2.1 Baseflow separation using FSR method

Separation of baseflow from direct surface runoff was performed using the FSR method described in Section 5.2.2.1. Thus, where storm event hydrographs were made up of multiple peaks, the rainfall-runoff lag time was taken as the time between the rain centroid and the apex of the most significant peak.

5.3.2.2 Results of hydrograph analyses

The results of the hydrograph analyses are shown in Table 5-5. Due to the possible errors associated with the estimation of the hydrographs, the data shown in Table 5-5 was not subjected to linear regression analysis to aid interpretation and identify trends. Instead four hydrographs have been selected and described to show how the rainfall-runoff response of the urbanised catchment could vary during the course of the monitoring period, and also how the variation compared to the concurrent response of the agricultural sub-catchment.

Table 5-5 Results of selected hydrograph analysis of storm events recorded at the outlet of the urbanised catchment

JD	Date	RI	RV	ADP	LAG	PF	TR	BFV	DRV	PBFV	PR	WB	ED
106	15/4/92	2	7	-	70	55	0.63	0.29	0.35	45	55	7.4	23.5
119	28/4/92	3	18.5	36	45	161	3.89	1.11	2.78	29	71	15	24
122	1/5/92	3.5	9.5	60	70	178	1.98	0.58	1.4	29	71	14.8	11.5
150	29/5/92	6	25.5	643	100	330	17.4	5.59	11.8	32	68	46	13.5
276	2/10/92	5.5	31.5	50	140	408	7.74	2.9	4.84	37	63	69	16.5
294	20/10/92	9.5	49.5	214	51	1468	15.9	1.9	14	12	88	28	17.5
314	9/11/92	3	12	164	85	426	7.9	2.71	5.19	34	66	43	12.5
320	15/11/92	5	7.5	80	78	560	3.20	1.31	1.89	56	59	43	7.3
6	6/1/93	2	7.5	18	50	367	6.22	2.4	3.82	39	61	51	18
91	1/4/93	5	17.5	16	130	515	6.05	0.85	5.2	14	86	29.7	18.5
115	25/4/93	2.5	8	-	105	412	11.4	7.78	3.63	68	22	45	18

Where:

RI	Rainfall intensity (mm hr)	RV	Rainfall volume (mm)
LAG	Rainfall-runoff lag time (hrs)	PF	Peak flow rate (l s-1)
BFV	Baseflow volume (mm)	DRV	Direct runoff volume (mm)
TR	Total runoff volume (mm)	WB	Water balance (%)
ED	Event duration[direct runoff] (hrs)	PBFV	Percentage baseflow volume
PR	Percentage runoff volume	ADP	Antecedent dry period (hrs)

Figure 5-17 shows the hydrographs recorded at Sites A and D during a storm event occurring on 15/4/92. During this period, the North Weald catchment received less than half the average rainfall expected for the time of year (see Section 5.2.1). Hence the SMD of the soil fraction of the whole catchment surface area was high and consequently the runoff from such areas was extremely low as illustrated for the Site A hydrograph. Therefore, the sharp peak at 5:30 p.m. in the Site D hydrograph was very likely to represent rapid runoff from the impervious area of the urbanised catchment. The small but delayed contribution from the pervious area of the catchment was probably represented by the minor peak occurring approximately four hours after the main peak and two hours before the hydrograph peak recorded at Site A. Overall on this occasion it can be seen that the main runoff contribution was that from the impervious area within the urbanised catchment.

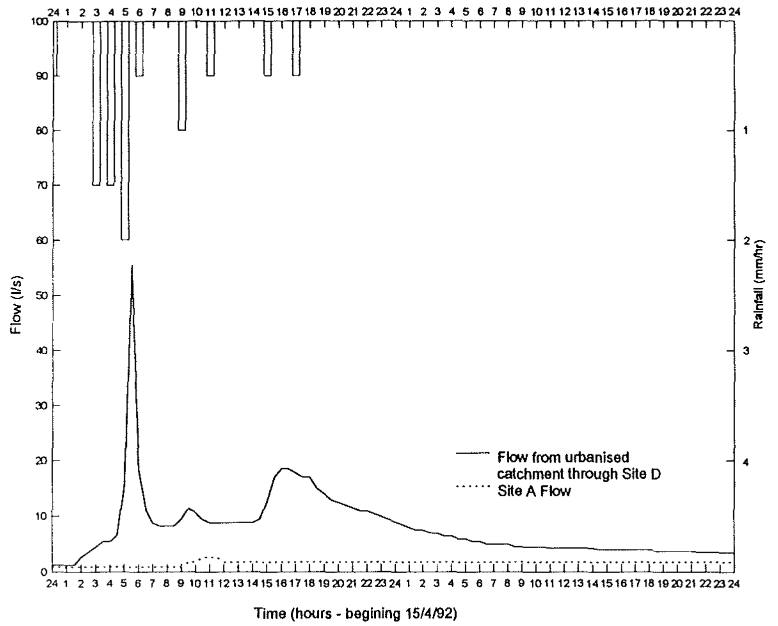


Figure 5-17 **Hydrographs for the storm event occurring on 15/4/92 showing rainfall and runoff from the urbanised catchment and the agricultural sub-catchment**

During the Spring of 1992, the runoff coefficient of the pervious soiled areas of the North Weald catchment continued to be kept low by the less-than-average rainfall and the increased demands of evapotranspiration resulting from the rise in seasonal temperature which promoted the onset of the growing season. Figure 5-18 shows the hydrographs recorded at Sites A and D during a storm event that occurred on 29/5/92. The hydrograph recorded at Site A was barely noticeable and had an associated runoff coefficient of 0.0022. Hence the hydrograph recorded at Site D was exclusively dominated by runoff from the impervious area of the urbanised catchment. The shape of the hydrograph was typical of runoff from impervious hard surfaces which provide the minimum of infiltration and buffering and hence rapidly produce sharp peaky hydrographs in response to rainfall (Shaw, 1991; Kiely, 1997). The absence of any tailing and the rapidity with which the flow returned to a value close to the pre-event level shows that the impervious area of the urbanised catchment provided very little rainfall storage.

In the autumn of 1992, the SMD of the pervious soiled areas of the North Weald catchment decreased as the evapotranspiration demands of senescent vegetation subsided and additional rainfall occurred. As a result of these factors, the runoff coefficient of the pervious soiled areas of the catchment increased to allow the generation of significant volumes of surface runoff during storm events.

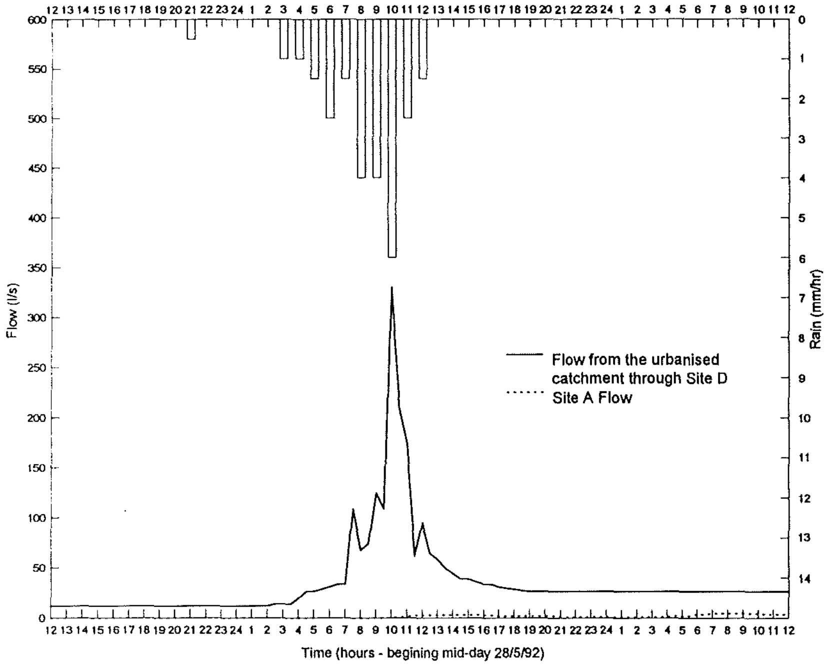


Figure 5-18 Hydrographs for the storm event occurring on 29/5/92 showing rainfall and runoff from the urbanised catchment and the agricultural sub-catchment

Figure 5-19 shows hydrographs recorded at Sites A and D during a storm event that occurred on 20/10/92. The hydrograph recorded at Site A was significant, and had an associated runoff coefficient of 0.2716. Hence, the hydrograph recorded at Site D was a combination of runoff from the impervious and pervious areas of the urbanised catchment. The less peaky, more rounded shape of the hydrograph suggested a considerable runoff contribution from the pervious area of the urbanised catchment. The absence of significant hydrograph tailing compared to that shown by the hydrograph recorded at Site A may be explained by the improved sub-soil drainage structure associated with grassed areas when compared to tilled bare soil (Rose *et al*, 1991). For the pervious grassed areas of the urbanised catchment this may have led to a greater proportion of rainfall infiltrating to the ground water, whereas in the agricultural sub-catchment, infiltration may have been impeded through the disruption of the sub-soil by the recent post-harvest tillage.

The second minor hydrograph peak was probably produced in response to the 3.5mm of rainfall that occurred at around 11:00am.

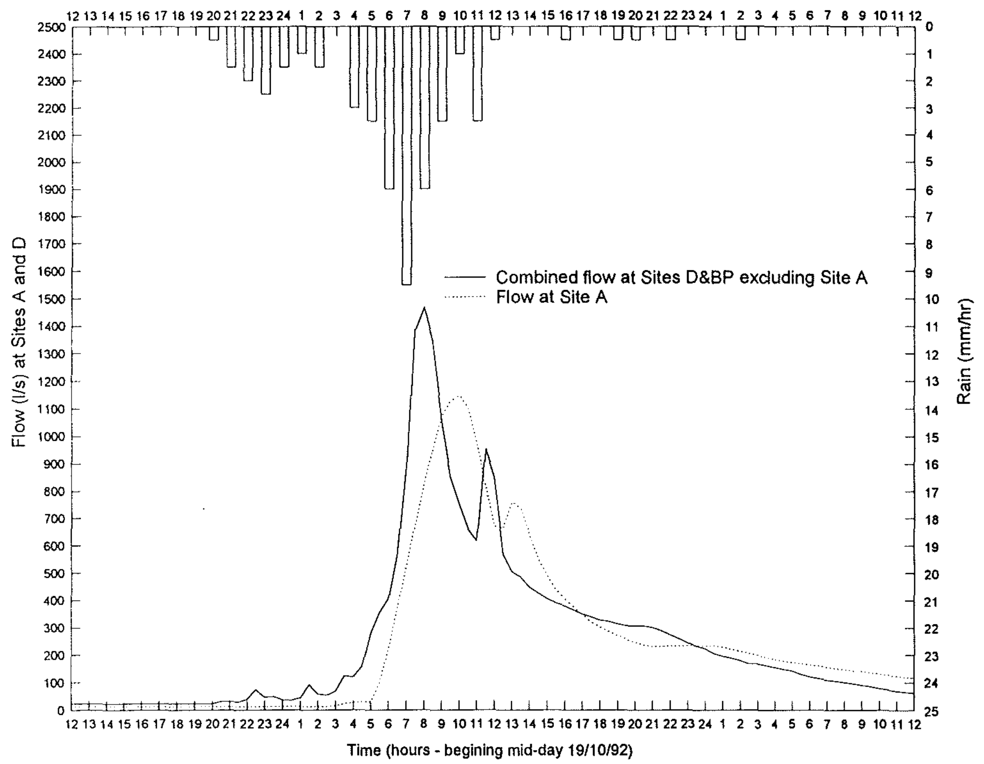


Figure 5-19 Hydrographs for the storm event occurring on 20/10/92 showing rainfall and runoff from the urbanised catchment and the agricultural sub-catchment

In the Winter of 1992, the North Weald catchment received above average rainfall which in some places probably brought the water table close to the land surface. This was the case for much of the bare-soiled arable portion of the agricultural sub-catchment (Plate 4-4) which encouraged the generation of overland flow during storm events. Figure 5-20 shows hydrographs recorded at Sites A and D during a storm event that occurred on 15/11/92. Here, the hydrograph recorded at Site D almost replicates that recorded at Site A both in shape, magnitude and also timing with coincident peaks being observed. The early peak of the Site A hydrograph was probably due to the rapid runoff from bare saturated or near saturated soil. The early minor peak of the hydrograph may represent rapid runoff from a minor sub-catchment of the impervious area, close to the monitoring station.

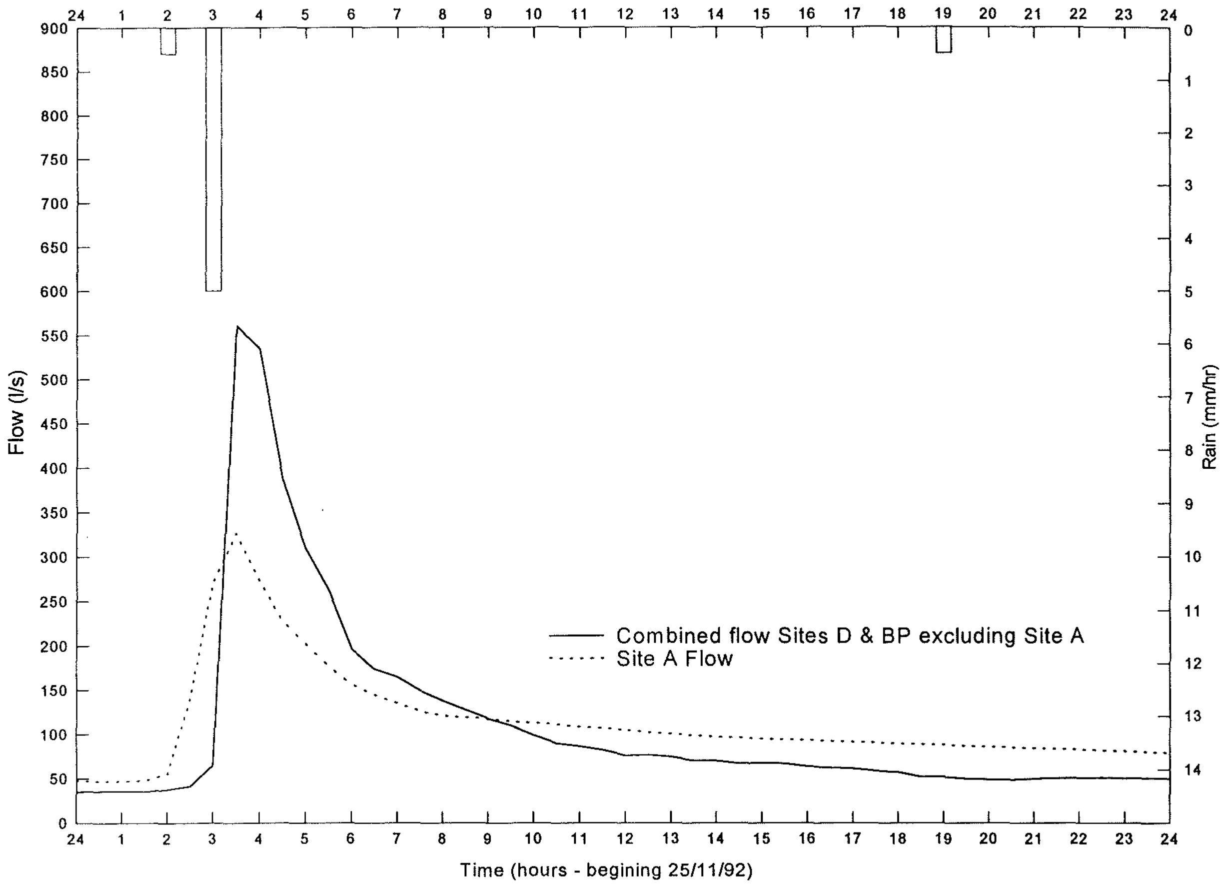


Figure 5-20 Hydrographs for the storm event occurring on 15/11/92 showing rainfall and runoff from the urbanised catchment and the agricultural sub-catchment

The examination of the four hydrographs recorded during the monitoring period at Site D has shown how the morphology of the hydrograph was dependent on the extent to which the impervious area of the urbanised catchment contributed to the overall runoff process. Depending on the time of year, the hydrograph varied from that which represented runoff from hard-surfaces to that which was more typical of runoff from pervious soil-based catchments.

The results of the analyses of the eleven hydrographs recorded at Site D during the course of the monitoring period are shown in Table 5-5. A comparison of the hydrograph components with those of the corresponding hydrographs recorded at Site A, essentially summarise the main differences between the hydrology of the agricultural sub-catchment and the urbanised catchment. Generally, for the same storm event, the water balance and percentage direct runoff were higher with less seasonal variability at Site D. Further, for a given storm the event duration and rainfall-runoff lag time were generally shorter although there were instances during wettest part of the winter where the Site A hydrograph peaked marginally before that of Site D. This probably occurred due to the more rapid movement of overland runoff from the saturated bare soil of the arable portion of the agricultural sub-catchment compared to the runoff from the urbanised area which may have been impeded by sur-charging in the storm sewer network.

Overall the nature of the hydrographs recorded at Site D exhibit the typical features of urban hydrology which are dictated by impervious surfaces with low infiltration capacity and storage potential resulting in the rapid and efficient response to rainfall. Other characteristics are sharp peaky hydrographs, relatively short event-duration times, higher water balance and percentage runoff values. To some extent this agrees with the work of Corbett *et al*, (1997) who compared the surface hydrology of urban and forested catchments and found that on average the water balance of the urban catchment was 14.5% higher than that of the forested catchment and that for urban catchment, runoff volumes were governed by the level of total impervious area.

CHAPTER SIX

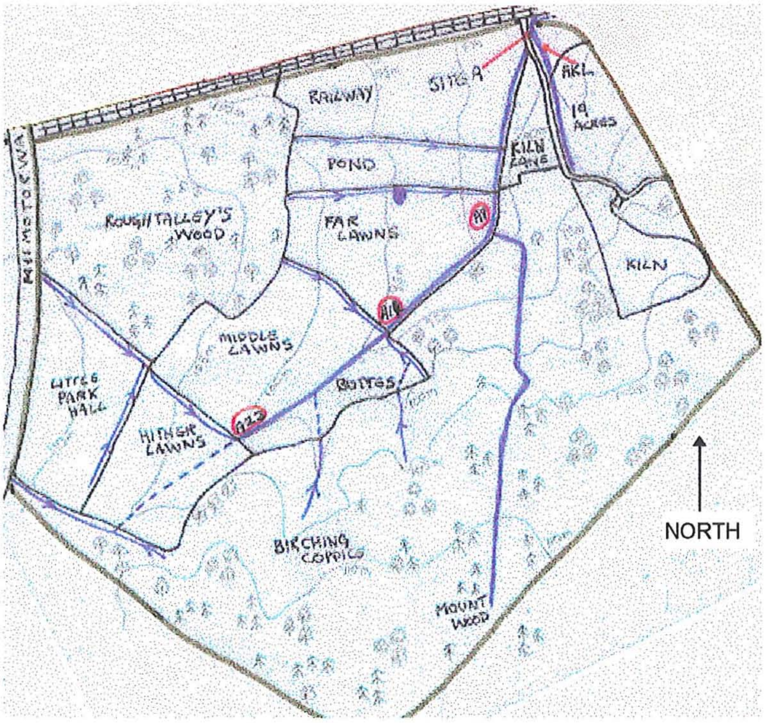
6. Pesticide runoff in the agricultural sub-catchment

This chapter provides details of the field management including the pesticide applications made to the agricultural sub-catchment together with descriptions of the storm events sampled during the monitoring period. The experiments carried out within the agricultural sub-catchment had (strong) similarities to the Rosemaund study (Williams *et al*, 1995) which has been referred to in Chapter 3, although a major difference was the fact that the Rosemaund site was owned and operated by the Ministry of Agriculture, Fisheries and Food, which funded the overall project. The benefits of such an arrangement allowed the careful planning and control of experiments and allowed complete access to the history of the agrochemicals applied to the catchment. In the case of the North Weald agricultural sub-catchment, the experiments were carried out at the discretion of the private land owners and although every effort was made to assemble a complete data base of the agrochemicals applied to the sub-catchment, there was no absolute guarantee that every application was identified.

The monitoring period approximately covered the 1991/92 and 1992/93 winter crop growing seasons which as discussed in Section 5.2 were characterised by lower- and higher-than-average rainfall respectively. For the 1991/92 growing season, the main herbicide application was made to the crop of winter barley and wheat during October and November 1991. For the 1992/93 growing season, the main herbicide application was made during early February 1993. Normally the application would have been made during the autumn of 1992 but during this period the bare soil was too waterlogged to allow tractor access to the fields (Plate 4-4).

6.1 Pesticide applications and field management within the agricultural sub-catchment

Figure 6-1 shows a schematic plan of the North Weald catchment including the location of the arable fields and the position of the main and minor drainage channels in the agricultural sub-catchment. The figure also shows the location of the automatic monitoring site (site A) and the positions of manual sampling sites.



Note:

- The main drainage ditches are represented by solid blue lines and the minor ditches represented by blue arrowhead lines; sub-soil drains are shown by a dashed blue line.

- The areas (ha) of the fields in the agricultural sub-catchment are as follows:

Sears Hall Farm:-	Little Park Hall	7.85	Hither Lawns	6.77	Middle Lawns	8.99
	Buttes	3.33	Far Lawns	9.47	Pond	4.51
Cold Hall Farm:-	19 Acres	4.25	Kiln	3.6		

- The location of Site A automatic sampling station is indicated with a red line. The location of the manual sampling points 'A9', 'A19', and 'A23' are shown with red circles. For manual sampling site descriptions see Table 6-5.

Figure 6-1 Schematic plan of the North Weald catchment showing the location of the arable fields and drainage systems in the agricultural sub-catchment

The details of the major pesticide applications within the agricultural sub-catchment before and during the course of the monitoring programme are given in Table 6-1 (for isoproturon), Table 6-2 (for chlorotoluron) and Table 6-3 (for simazine and mecoprop). This application data was compiled through liaison with the farm managers responsible for the management of the arable land within the boundaries of the agricultural sub-catchment. West Essex Farmers Agronomy Ltd were also consulted on agrochemical usage; the unit advised farmers in the Epping area on best management practice for the production of arable crops. The tabulated pesticides are all classified as herbicides and they were generally used within crop production to control grasses and broad-leafed weeds. At North Weald they were applied to protect winter wheat, winter barley and winter beans; the herbicides were normally applied soon after the winter cereal was drilled in the autumn and if necessary during early spring. Typical active ingredient application rates (kg ha^{-1}) for simazine, atrazine, chlorotoluron, isoproturon and mecoprop were 1.15, 2.75, 2.5 and 0.6 respectively. All herbicide applications were made using tractor mounted (herbicide) low-volume spraying equipment. Himel *et al* (1990) suggest that 3-5% of the herbicide applied as a spray may be lost due to drift. Since, in practice, it was very difficult to estimate the extent of drift loss, it was assumed to be negligible such that 100% of the herbicide applied was deposited on the agricultural sub-catchment. The herbicides applied to the agricultural sub-catchment were the most widely used pesticides in the UK in arable agriculture (see Section 2.4).

Table 6-1 shows that in 1990, 1991, and 1993 the arable portion of the agricultural sub-catchment received 80.405, 60.780, and 39.692 kg of isoproturon respectively.

Table 6-1 Isoproturon applications to the agricultural sub-catchment (1990-93)

Date of application	Field	Crop	Application area (ha)	Application rate (lha^{-1})	a.i. concentration (gl^{-1})	Mass (kg)
4/9/90	LPH	WW	7.85	5	500	19.625
	HL	OSR	6.77	5	500	16.925
	ML	OSR	8.99	5	500	22.475
	B	OSR	3.33	5	500	8.325
11/11/90	FL	WW	9.47	1	500	4.735
	P	WW	4.51	1	500	2.255
	RF	WW	10.25	1	500	5.125
	KL	WW	1.88	1	500	0.940
						Σ 80.405
28/10/91	FL	WBAR	9.47	1	500	4.735
	P	WBAR	4.51	1	500	2.255
	RF	WBAR	10.25	1	500	5.125
	KL	WBAR	1.88	1	500	0.940
6/11/91	HL	WW	6.77	5	500	16.925
	B	WW	3.33	5	500	8.325
16/11/91	ML	WW	8.99	5	500	22.475
						Σ 60.780
3/2/93	LPH	WW	7.85	4.2	500	16.485
	HL	WW	6.77	4.2	500	14.217
	ML	WW	8.99	2	500	8.99
						Σ 39.692

LPH = Little Park Hall, HL = Hither Lawns, ML = Middle Lawns, B = Buttes, FL = Far Lawns, P = Pond, RF = Railway Field, KL = Kiln Lane, WW = Winter wheat, OSR = Oil seed rape, WBAR = Winter barley, a.i. = active ingredient.

The decreasing amounts applied with time reflect decreasing areas of cereal production rather than reduced application rates, apart from Middle Lawns in 1993 where there was a reduced rate of application. The sub-catchment did not receive an isoproturon application during the autumn/winter months of 1992 because as discussed in Section 5.2.1, at this time the catchment received higher-than-average rainfall and consequently the bare soil was too water-logged to allow tractor access for herbicide spraying. Table 6-2 shows that in 1990 and 1991, the agricultural sub-catchment received 71.801 and 78.330 kg of chlorotoluron respectively. In this case the increase in the amount applied in 1991 was due to a marginally increased application rate of chlorotoluron. The 1991 application of chlorotoluron was the last made to the agricultural sub-catchment during the period of the monitoring programme. In the UK Pesticide Guide, Ivens (1991) describes chlorotoluron as a contact and residual acting urea herbicide. Therefore, although unconfirmed, the decision not to make further applications of chlorotoluron may have been taken as a precaution to prevent damage to the following 1992 crop. Riley and Eagle (1990) describe the potential risk to a succeeding crop from herbicide residues. This depends on the persistence of the herbicide, the susceptibility of the following crop to the residues and the position of the residues in the soil in relation to the seed and root system. As the residues tend to be near the surface, the effect on seeds and young roots can be significant. Table 6-3 shows that in late November 1991 the agricultural sub-catchment received an application of 9.027 kg of simazine to a crop of winter beans only sown in Little Park Hall field. The control of annual dicotyledons and annual grasses was by use of simazine rather than isoproturon or chlorotoluron which would have damaged the crop. Table 6-3 also shows that in November 1991, Middle Lawns received 5.394 kg of mecoprop and in April 1992 Kiln and Nineteen Acre fields received 2.160 kg and 2.550 kg of mecoprop respectively. According to the Advisory Committee on Pesticide labelling, mecoprop is normally used to control annual dicotyledons and cleavers that are competing with the crop, typically winter wheat, between the seedling and young plant stage. This explains the application during April 1992 when the winter wheat drilled during the previous autumn would have been at the young plant stage. The application during November 1991 was probably due to the dry mild 1991/92 winter which would have encouraged the early growth of weeds.

Table 6-2 Chlorotoluron application to the agricultural sub-catchment (1990-93)

Date of application	Field	Crop	Application area (ha)	Application rate (lha^{-1})	a.i. (gl^{-1})	Mass applied (kg)
11/11/90	FL	WW	9.47	5.5	500	26.042
	P	WW	4.51	5.5	500	12.402
	RF	WW	10.25	5.5	500	28.187
	KL	WW	1.88	5.5	500	5.170
						Σ 71.801
28/10/91	FL	WBAR	9.47	6	500	28.410
	P	WBAR	4.51	6	500	13.530
	RF	WBAR	10.25	6	500	30.750
	KL	WBAR	1.88	6	500	5.640
						Σ 78.330

Table 6-3 Simazine and Mecoprop applications to the agricultural sub-catchment (1991-93)

Pesticide applied	Date of application	Field	Crop	Application area (ha)	Application rate (lha^{-1})	a.i. (gl^{-1})	Mass (kg)
Simazine	28/11/91	LPH	WB	7.85	2.3	500	9.027
Mecoprop	16/11/91	ML	WW	8.99	1	600	5.394
Mecoprop	14/4/92	K	WW	3.6	1	600	2.160
		N	WW	4.25	1	600	2.550
							Σ 4.710

K = Kiln, N = Nineteen acre, WB = Winter beans

Note only 55% of Nineteen acre field was in the agricultural sub-catchment

6.1.1.1 The properties of the pesticides detected in runoff from the agricultural sub-catchment

Although shown in Section 4.4.1, the properties of the herbicides detected in runoff from the agricultural sub-catchment are shown in Table 6-4 for ease of reference. The herbicides that are listed reflect the compounds that were applied to the agricultural sub-catchment except for atrazine and mecoprop. The detection of atrazine was not linked to any known application within the agricultural sub-catchment, and as discussed later in the Chapter, its detection was considered to be the result of non-agricultural applications made to the M11 motorway which bordered the southern boundary of the sub-catchment. Based on the two literature values for the half-life of chlorotoluron, a value of 140 days was chosen for the North Weald catchment. For isoproturon a value of 55 days was selected. This is the same value as that used by Harris *et al* (1994) for their work on clay-soiled-field-plot at Brimstone Farm, Oxfordshire.

It should be noted that K_{OC} values listed in Table 6-4 can be derived from K_{OW} from the relationship described on page 53. In this instance the K_{OC} values used to interpret pesticide behaviour are empirical values quoted from the literature. Had the K_{OC} values used, been derived from K_{OW} , the interpretation of pesticide behaviour based on K_{OC} would have been significantly different from that arrived at through the use of the empirically obtained K_{OC} values. Empirically obtained K_{OC} values were used since they were obtained from studies similar to that at North Weald and therefore were considered to be more reliable than those derived from K_{OW}.

Table 6-4 Properties of pesticides detected in runoff from the agricultural sub-catchment

Pesticide	M.W.	m.p (°C).	Aqu.sol. (mg/l)	Vap.pre (mPa)	Log K_{ow}	K_{oc}	$t_{1/2\ (SOIL)}$	Ref.
Simazine	201.7	225-227	5	810.10^{-6}	1.95	130	60	1, 2
Chlorotoluron	212.7	147-148	70	0.017	2.29	175^{6},	135^{6},143^{4}	1, 3
Atrazine	215.7	175-177	30	0.04	2.34	100	60	1, 2
Isoproturon	206.3	155-156	55	0.0033	2.24	107^{4}	6-28^{5}, 20^{6} , 30^{7}, 46^{2},	1, 4

Note: General data for each pesticide is referenced in the 'Ref' column; more specific references are marked with superscript

1. Worthing & Hance (1991) 2. Wauchope *et al* (1992) 3. Canton *et al* (1991) 4. Fielding *et al* (1992)
5. Tomlin (1994) 6. Fielding *et al* (1994) 7. Johnson *et al* (1995) 8 Harris *et al*, 1994

Key: Log K_{ow} Logarithm of octanol/water partition coefficient; K_{oc} Organic carbon/water partition coefficient
$t_{1/2\ (SOIL)}$ Half life due to biochemical decay in soil

6.2 Results of storm event monitoring for 1992

The results discussed in this section cover the 1991/92 crop growing season for the agricultural sub-catchment. The principal herbicide applications of isoproturon, chlorotoluron, simazine, and mecoprop were made to the agricultural sub-catchment during October and November of 1991 (Tables 6-1, 6-2, and 6-3). First shown in Chapter five, Figures 6-2, 6-3, and 6-4 show the rainfall and runoff from the agricultural sub-catchment during the 1992 monitoring period. The storm events which were sampled are identified with the Julian day on which the hydrograph occurred, and also the storm-event water balance based on direct surface runoff. The periods between the 1991 autumn herbicide applications, to the end of 1991 are not shown. During this period of below-average rainfall, the soil-moisture deficit of the agricultural sub-catchment was high and a permanent baseflow was absent. Two very minor events occurred with a peak flow rate of 2.8 ls^{-1}. The first event of sufficient magnitude to trigger the automatic sampler at site A occurred on 1/5/92 (Julian day 122), approximately 6-7 months after the herbicide application (Figure 6-3). Prior to this event, the dry period from January to April 1992 remained relatively event-free with only three minor events occurring; the largest with a flow rate of 17 ls^{-1} occurred at the end of March 1992 (Figure 6-2). The height of the sampler trigger at site A was set too high to be activated by the storm events occurring during this period. The criteria for setting trigger height above the gauging weir was a balance between the requirement to sample the first significant post-application storm event and the precaution not to have the sampler activated unnecessarily which may have exhausted the sampling capacity immediately prior to a significant storm event. The sampler could have been activated unnecessarily, for example, by a very minor storm event or natural disturbance of the water surface caused by a falling branch or a wild animal.

As shown in Figure 6-2, the period after the storm event on 1/5/92 to the storm event on 13/8/92 remained almost entirely absent of storm runoff episodes despite regular rainfall events. This was probably due to a significant soil-moisture deficit in the agricultural sub-catchment caused by the evapotranspiration water demand of vegetation, including the cereal crops, during the height of the growing season. Interestingly, the first significant rainfall that occurred after the harvest of the cereal crops generated a runoff event with the highest flow rate since the herbicide applications approximately nine months earlier; this probably reflected the extra volume of effective rainfall that was made available by the absence of crop interception.

As the monitoring period progressed into autumn and winter 1992, lower temperature, senescent vegetation and bare arable soil allowed sufficient increase in the soil-moisture content of the agricultural sub-catchment to support a permanent baseflow and the relatively efficient generation of surface runoff during rainfall event. Figure 6-4 shows the storm events that were sampled during this period which are identified with the Julian day on which the hydrograph occurred and also the storm-event water balance based on direct-surface runoff.

Monitoring results will be discussed according to the chemical type of the herbicide as this approximately corresponds to the differing levels of pesticide application to the agricultural sub-catchment. During the period of the monitoring programme, manual samples were taken during non-storm conditions to supplement the samples taken during storm events (Table 6-6).

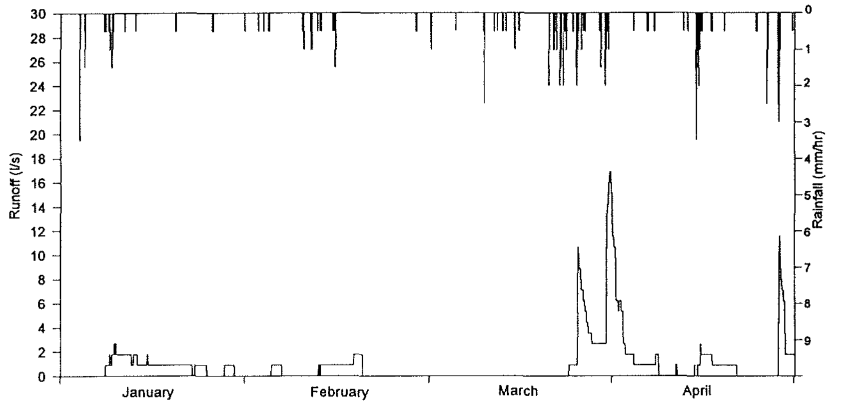


Figure 6-2 Rainfall and runoff for the agricultural sub-catchment between January and April 1992 (no storm events were sampled at site A during this period).

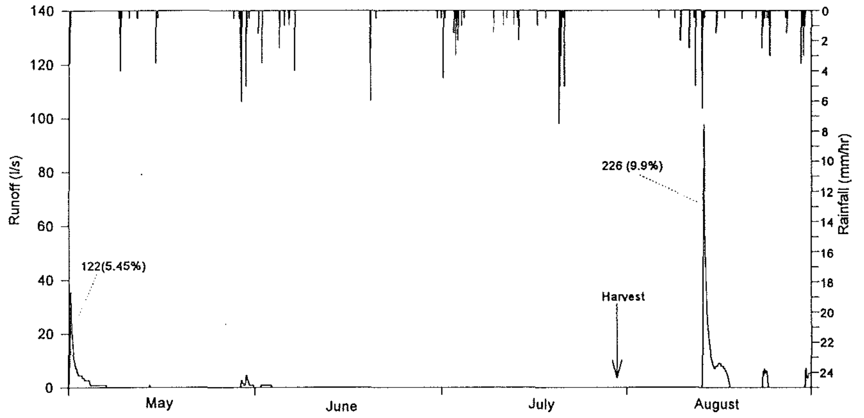


Figure 6-3 Rainfall and runoff for the agricultural sub-catchment between May and August 1992 showing storm events monitored at site A which are labelled with the Julian day on which the hydrograph occurred and also the storm-event water balance based on direct-surface runoff.

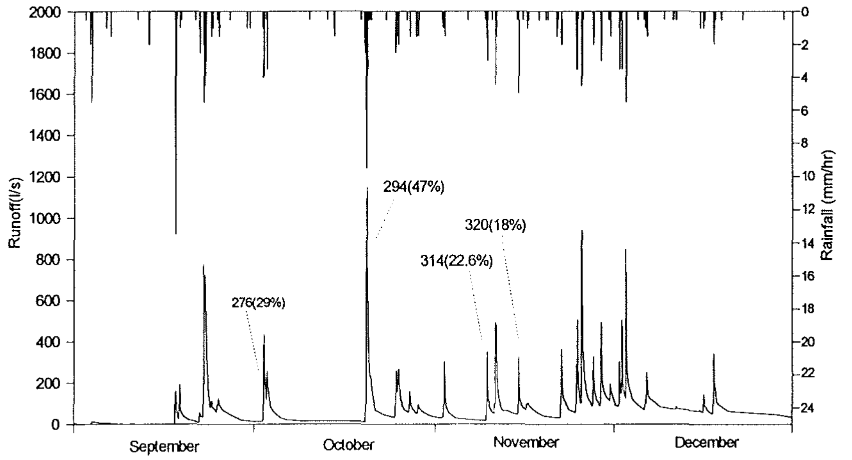


Figure 6-4 Rainfall and runoff for the agricultural sub-catchment between September and December 1992 showing storm events monitored at site A which are identified with the Julian day on which the hydrograph occurred and also the storm event water balance based on direct surface runoff

Table 6-5 lists the storm events automatically sampled during 1992, the table shows the date and the corresponding Julian Day date

Table 6-5 Storm events automatically sampled during 1992

Date	Julian Day	Date	Julian Day
1/5/92	122	20/10/92	294
13/8/92	226	9/11/92	314
2/10/92	276	15/11/92	320

During the non-storm conditions the flow leaving the agricultural sub-catchment would have been entirely composed of baseflow runoff and therefore the data from the manual samples showed the concentration of pesticides present in the baseflow and also provided a reference point from which to assess the pesticide concentrations during storm events. The discussion of the monitoring results begins with the results for the manual sampling and then in turn discusses the results for the sampled storm events.

6.2.1 Results of manual sampling

6.2.1.1 Chlorotoluron and isoproturon

As shown in Tables 6-1 and 6-2 the application of isoproturon (60.780 kg) to the agricultural sub-catchment was made between 28/10/91 (Julian day [JD] 301) and 16/11/91 (JD 320) and the application of chlorotoluron (78.330) was made on 28/10/91 (JD 301). Due to the dry 1991/92 winter, the first significant storm event sampled did not occur until 1/5/92 (JD 122) which was 167-186 days after the isoproturon application and 186 days after the chlorotoluron application.

Prior to the 1/5/92 event, manual samples were taken from site A and at various points along the main drainage channel on 6/3/92 (JD 66) which was 111-130 days after the isoproturon application and 130 days after the chlorotoluron application. The results are shown in Table 6-6. The concentrations of isoproturon and chlorotoluron at site A were 0.31 and 0.19 μgl^{-1} respectively; at site A9 the concentrations were 0.46 and 0.26 μgl^{-1} respectively; at site A14 the concentrations were 1.44 and *non-detectable* respectively; and at site A23 the concentrations were 0.48 and 0.41μgl^{-1} respectively (see Figure 6-1 for location of sampling sites). On the basis of the relative amounts of pesticide that were initially applied, the concentrations found in the manual samples were the reverse of what may have been forecast considering that although more chlorotoluron was applied (78.330kg) than isoproturon (60.780kg), the concentrations of isoproturon were consistently higher than those of chlorotoluron. However, this behaviour can be explained through consideration of the physico-chemical properties of the two compounds. As shown in Table 6-4, compared to chlorotoluron, isoproturon was more likely to leach and be detected at higher concentrations since it was less likely to retained by the organic matter content of the soil matrix, due to its lower K_{oc} value. Interestingly, the detection of chlorotoluron at manual sampling site A23 was unexpected since it was applied to fields that drained north-easterly away from this point, in the direction of the lower end of the agricultural sub-catchment. Its detection was either as a result of an accidental spillage or the result of a chlorotoluron application prior to autumn 1990. If the detection was the result of an application of chlorotoluron made before autumn 1990, this would show that whenever the application was made, it produced significant residue concentrations in the baseflow drainage water for at least 481 days after the application.

Table 6-6 Results of the 1992 manual sampling

Date	Location	Flow (l/s)	Pesticide concentration (µg/l)			
			Simazine	Atrazine	Chlorotoluron	Isoproturon
6/3/92	Site A	0.5	0.30	0.39	0.19	0.31
	A9	<0.1	0.30	0.16	0.26	0.46
	A14	<0.1	0.31	0.18	nd	1.44
	A23	<0.1	0.13	0.13	0.41	0.48
25/3/92	Site A	1.9	0.23	0.19	0.17	0.19
8/4/92	Site A	1.5	0.12	0.07	0.06	0.14
29/5/92	Site A	2.8	0.53	0.54	0.16	0.13

Key; (see Figure 5-1 for location references)
Site A: Outlet of agricultural sub-catchment.
A14: Main drainage ditch, 1 metre down stream of junction of Far Lawns and Middle Lawns
A9: Main drainage ditch, 5 metres upstream of junction of Pond and Far Lawns.
A23 Outlet of main drain from Hither Lawns.

This behaviour may have been a consequence of the relatively long half-life of chlorotoluron ($t_{1/2}$ 140 days). The high concentration of isoproturon detected at manual sampling site A14 may be explained by its late application (16/11/92) to Middle Lawns which was in close proximity to the sampling point. This would have therefore minimised the dilution of any field drainage water leaving Middle Lawns with less contaminated drainage water from elsewhere.

Manual samples were also taken from the agricultural sub-catchment on 25/3/92 (JD 84) and 8/4/92 (JD 99). For those taken on 25/3/92 from site A, the isoproturon concentration was 0.19μgl^{-1} and the chlorotoluron concentration 0.17μg.l^{-1}. The manual samples taken on 8/4/92 (JD 99) were also only from site A. The concentrations of isoproturon and chlorotoluron were 0.14μgl^{-1} and 0.06μgl^{-1} respectively. As for the samples taken on 6/3/92, the isoproturon concentration was double that of chlorotoluron which was again probably due to the lower leaching tendency for chlorotoluron compared to isoproturon due to its higher K_{oc} value.

The manual samples taken on 29/5/92 (JD 150) were from site A during the course of a storm event. Despite 25.5 mm of rain falling with a peak intensity of 6 mmhr^{-1}, the runoff hydrograph only peaked at 2.8 ls^{-1}; the very low water balance (0.19%) was probably caused by excessive evapotranspiration demands on the soil water which would have produced a very high soil moisture deficit. The concentrations of chlorotoluron and isoproturon were 0.16 and 0.13 μg l^{-1} respectively. The higher chlorotoluron value may have reflected its greater half-life (140 days) compared to isoproturon (30 days) which, although more likely to leach, may have begun to become depleted in the soil column.

6.2.1.2 Mecoprop, simazine and atrazine

On 6/3/92, manual samples were taken from site A and at various points along the main drainage channel. This was 98 days after the simazine application and 110 days after the mecoprop application. Application details for atrazine were unavailable but it was very unlikely that it was applied agriculturally since it was only used for the control of weed amongst maize which was, and still is, a very minor crop in the UK. It was more likely that the detection of atrazine within the agricultural sub-catchment was the result of non-agricultural application to the M11 motorway which defined the southern boundary of the agricultural sub-catchment (Figure 6-1). The results of the manual sampling are shown in Table 6-6. Due to technical problems, mecoprop was not determined. The concentrations of simazine and atrazine at site A were 0.30μgl^{-1} and 0.39μgl^{-1} respectively; at site A9 the concentrations were 0.30μgl^{-1} and 0.16μgl^{-1} respectively; at site A14 the concentrations were 0.31μgl^{-1} and 0.18μgl^{-1} respectively; and at site A23 the concentrations were both 0.13μgl^{-1}. The detection of simazine at all sites was consistent with the November 1991 application to Little Park Hall field. The reduced concentration at site A23 was probably caused by the majority of the drainage water originating from Hither Lawns which had not received a simazine application. The detection of atrazine was not connected with any known agricultural applications. Its presence was probably the result of an application made to the M11 motorway. The higher concentration of atrazine detected at site A may be explained by its possible application to the area surrounding a British Gas pumping station located approximately ten metres west of this site. It was possible that if atrazine had been applied to the minor gravelled areas (10m^2) around the station, surface drainage from it could have entered the main drainage channel and passed through to site A.

The detection of simazine and atrazine in manual samples taken on 24/3/92 and on 8/4/92 showed a reduction in concentration from 0.23μgl^{-1} to 0.12μgl^{-1} for simazine and from 0.19μgl^{-1} to 0.07μgl^{-1} for atrazine over a time period of 15 days. The sources of simazine and atrazine were probably the same as those described for the earlier manual sample. The manual sample taken on 29/5/92 which was obtained during a very minor event with a maximum flow rate of 2.8ls^{-1} gave a simazine concentration of 0.53μgl^{-1} and an atrazine concentration of 0.54μgl^{-1}. The simazine concentration was approximately 5 times greater than the isoproturon concentration despite approximately seven times more isoproturon having been applied to the agricultural sub-catchment (Tables 6-1and 6-3). Simazine and isoproturon have similar soil retention tendencies and half-life values, therefore the differing concentrations may possibly be explained by a further source of simazine from the British Gas pumping station.

6.2.2 Results for the storm event on 1/5/92 (Julian Day 122)

The following sub-sections describe the pattern of occurrence of chlorotoluron, isoproturon, simazine and atrazine determined in samples collected automatically during the storm event. Seventeen days prior to the event mecoprop was applied to Kiln and Nineteen Acre fields of Cold Hall Farm; analysis for mecoprop was carried out on samples 1, 2, 3, 5, 7 and 10 with the result that no detections were made. This was attributed to its very short half-life of 3.6 days

(Nicholls *et al*, 1993) and the relatively minor amount applied. Due to degradation, it was considered very unlikely that mecoprop would be detected in subsequent sample sets, therefore in order to conserve analysis time and laboratory resources, a decision was taken to omit mecoprop from the analysis suite for all other automatic and manual samples taken during the remainder of the monitoring programme.

6.2.2.1 Chlorotoluron and isoproturon

Figure 6-5 shows the first sampled storm event that occurred, on 1/5/92 (JD 122), after the autumn 1991 application of isoproturon and chlorotoluron to the agricultural sub-catchment. Specifically, the Figure shows the rainfall intensity (mm/hr) measured by the rain gauge (for location see Figure 5-1), and the subsequent increase and decrease in runoff (hydrograph) flow rate (l/s); superimposed on the hydrograph is shown the variation of chlorotoluron and isoproturon concentrations determined from the automatic samples taken during the duration of the event. Also shown are the respective flux curves—the products of flows and herbicide concentrations. The event occurred 167-186 days after the isoproturon application and 186 days after the chlorotoluron application. Following an initial flow rate of 2ls^{-1}, the event hydrograph peaked at 35.55ls^{-1} after 9.5mm of rain fell on the agricultural sub-catchment at a maximum intensity of 3.5mmhr^{-1}. During the course of this event, twenty-one samples were taken. The concentration of the first sample, taken as the sampler was triggered at the onset of the event, showed equal isoproturon and chlorotoluron concentrations of 0.1μgl^{-1}. The second sample, taken one hour later, showed the highest concentrations detected over the entire event with isoproturon and chlorotoluron concentrations of 1.0μgl^{-1} and 0.79μgl^{-1} respectively. These are approximately 7 and 11 times higher than the manual sample baseflow concentrations determined on 8/4/92. The peak concentrations occurred 1.5 hours before the peak of the hydrograph. Similar isoproturon behaviour was observed by Williams *et al* (1995) in runoff during storm events monitored at the Rosemaund catchment. This was described as being indicative of the rapid movement of isoproturon to the main drainage channel via by-pass flow channels passing through the soil column. This type of soil hydrology agrees well with that proposed for this period of the monitoring programme (see Section 5.2.2). The subsequent samples showed the concentrations of isoproturon and chlorotoluron decaying in an exponential manner along with the recession of the event hydrograph.

The last few samples collected towards the end of the storm event showed a small rise in concentration for both herbicides. The hydrograph analysis of the event, involving the separation of direct runoff from baseflow, showed that it was at this time during this event that direct runoff ceased and that the major runoff component was an elevated level of baseflow including delayed interflow (see Section 5.2.2). The slight increase in chlorotoluron and isoproturon concentration suggests that as well as being predominantly transported in the surface runoff—primarily composed of shallow interflow and preferential flow through soil macropores—a fraction of the two herbicides may have been transported in delayed interflow.

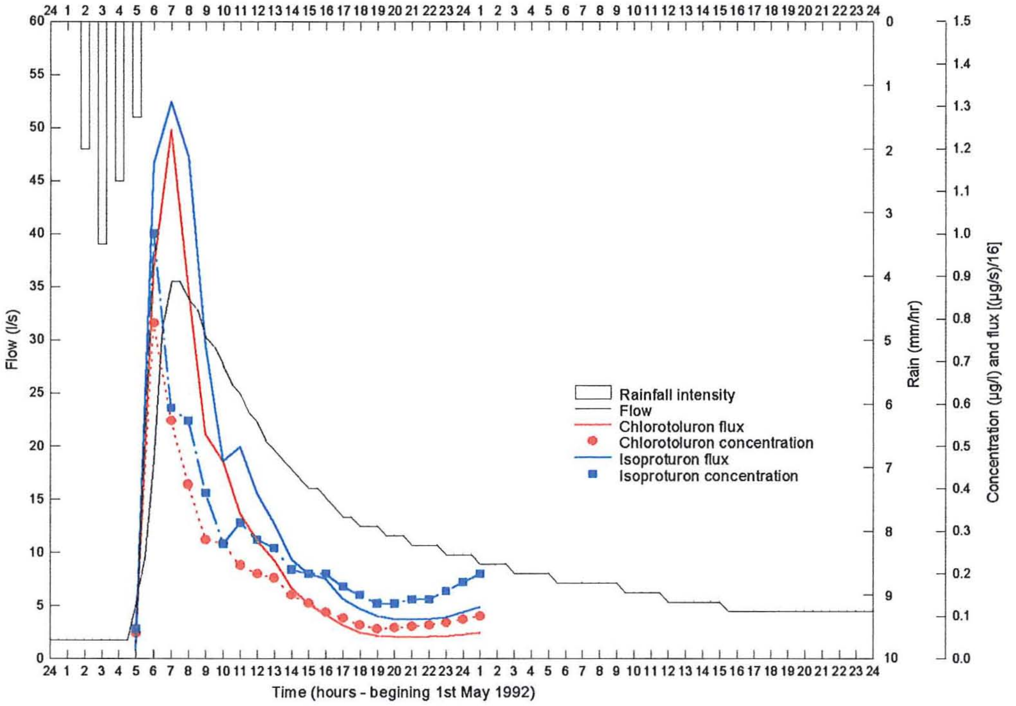


Figure 6-5 Chlorotoluron and isoproturon concentrations (µg/l) and fluxes ((µg/s)/16) at site A during the storm event occurring on 1/5/92 (JD 122) (Rainfall intensities (bar chart) and storm runoff also shown)

The maximum chlorotoluron and isoproturon flux values were 19.9µg/s and 20.9µg/s which both occurred approximately 30 minutes before the peak hydrograph flow rate. The integration of the hydrograph and pesticide flux-curves showed that during the sampling period of the event, 0.43g and 0.33g of isoproturon and chlorotoluron respectively were transported in the $1.216x10^6$ litres of event runoff. The amounts of herbicide removed correspond to application losses of 0.00072% and 0.00043% respectively. The event mean concentrations for isoproturon and chlorotoluron were calculated at 0.34μgl^{-1} and 0.25μgl^{-1} respectively for total runoff and 0.49μgl^{-1} and 0.37μgl^{-1} respectively, based on direct runoff. The relative magnitude of the event mean concentrations was the inverse of the amounts of the two herbicides applied (Tables 6-1 and 6-2), and similar to that of the concentrations detected in the manual samples taken prior to the storm event. As discussed previously, this behaviour was probably due to the higher K_{oc} value of chlorotoluron, which reduced its availability for leaching when compared to isoproturon.

6.2.2.2 Simazine and atrazine

The simazine and atrazine concentrations detected during the storm event of 1/5/92 (JD 122) are shown in Figure 6-6 together with the corresponding herbicide fluxes and the relevant hydrological data. This storm event occurred 155 days after the simazine application; no information was available on atrazine applications. The integration of the herbicide-flux curves showed that during the sampling period of the event, 0.265g and 0.133g of simazine and atrazine respectively were transported during the event runoff. The weight of simazine removed corresponded to an application loss of 0.0029%. The event mean concentrations, based on direct runoff only, were 0.28μgl^{-1} for simazine and 0.15μgl^{-1} for atrazine.

The concentration of simazine in the first sample was 0.11μgl^{-1} which gradually increased to a peak concentration of 0.29μgl^{-1} approximately one hour after the hydrograph peak. The concentrations in the subsequent samples decreased to 0.16μgl^{-1} and then increased late in the event to a second peak at a concentration of 0.27μgl^{-1}. After this point the concentration gradually decreased and then increased late in the event to a value of 0.28μgl^{-1}. During the latter stages of the event, like chlorotoluron and isoproturon, the concentration of simazine also increased, suggesting that it too may have also been transported in delayed interflow. The variation in the atrazine concentrations during the event showed a markedly different pattern. The highest concentration of 0.21μgl^{-1} was detected in the first sample and with the rise of the storm hydrograph, the concentration in the following sample decreased to 0.11μgl^{-1}. The next two samples showed the concentration rising to a minor peak at 0.14μgl^{-1} that coincided with the hydrograph peak. The following sixteen hours saw the atrazine concentration progressively decrease in a linear manner to 0.06μgl^{-1}. The decrease in the atrazine concentration with the onset of the storm event runoff suggests that the herbicide may have been transported in the baseflow, since at the time this runoff component would have been diluted with increasing volumes of surface runoff. The maximum simazine and atrazine flux values were 9.8μg/s and 4.9μg/s respectively; the simazine flux peak occurred one hour after the hydrograph peak, whilst the atrazine peak coincided with the hydrograph peak.

The temporal pattern of the simazine concentrations was somewhat different to those of chlorotoluron and isoproturon. Although the three herbicides were applied to the agricultural sub-catchment during approximately the same period, chlorotoluron and isoproturon produced significant concentration peaks approximately one hour before the hydrograph peak whereas simazine produced a minor but broader peak approximately one hour after the hydrograph peak.

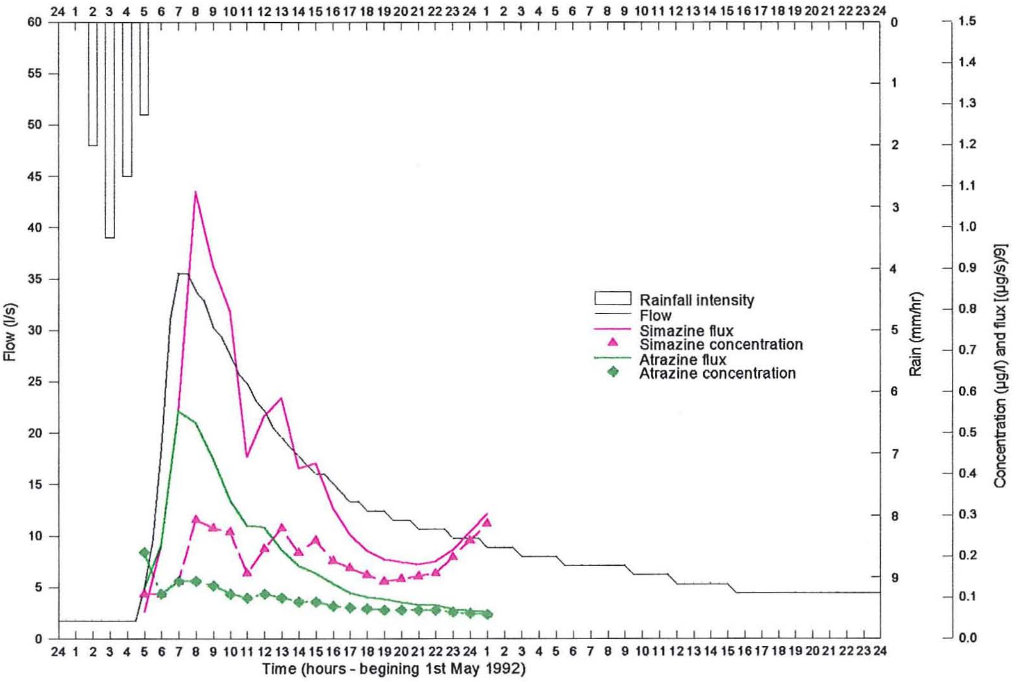


Figure 6-6 Atrazine and simazine concentrations (μg/l) and fluxes ((μg/s)/9) at site A during the storm event occurring 1/5/92 (JD 122) (Rainfall intensities (bar chart) and storm runoff also shown)

The difference in behaviour between the two herbicide types probably came about as the result of a more widespread application of chlorotoluron and isoproturon throughout the fields of the agricultural sub-catchment, compared to the relatively minor application of simazine (9.027 kg compared to 28.330kg and 60.780kg) to Little Park Hall field which was at the farthest point from the monitoring station at site A.

6.2.3 Results for the storm event on 13/8/92 (Julian Day 226)

6.2.3.1 Chlorotoluron and isoproturon

The second event to be automatically sampled during 1992 occurred on 13/8/92 (JD 226) which was 271-290 days after the isoproturon application and 290 days after the chlorotoluron application. The event occurred after 23.5 mm of rainfall, with a maximum intensity of 6.5mmhr^{-1}, had fallen producing a hydrograph with a peak flow rate of 97.7ls^{-1}. The isoproturon and chlorotoluron concentrations and fluxes are shown in Figure 6-7 together with the flow and rainfall data.

According to information from the farm manager responsible for most of the arable land in the agricultural sub-catchment, it was planned that a number of fields would receive an application of isoproturon and chlorotoluron during late October 1992. Therefore, it was decided to reduce the number of samples analysed from storm events occurring before the application in order to conserve laboratory resources for the extensive analysis of storm event samples occurring after the application which, it was considered, would produce more important data. Therefore, of the 12 samples taken during the 13/8/92 event, only three samples were analysed. Following consideration of the pattern of the 1/5/92 event pollutograph, these samples were chosen to represent the peak pesticide concentration and those at the beginning and end of the storm event. The first sample had isoproturon and chlorotoluron concentrations of 0.13μgl^{-1} and 0.81μgl^{-1}; the second sample (which coincided with the peak hydrograph) had concentrations of 0.29μgl^{-1} and 1.47μgl^{-1}; and the third sample had concentrations of 0.15μgl^{-1} and 0.33μgl^{-1}, respectively. The integration of the hydrograph and pesticide flux curves showed that during the sampling period of the event, 0.60g and 2.67g of isoproturon and chlorotoluron respectively were removed in 4.41×10^6 litres the event runoff. These weights correspond to application losses of $9.8 \times 10^{-4}\%$ and $3.4 \times 10^{-3}\%$ respectively. The event mean concentrations, based on total runoff, for isoproturon and chlorotoluron were calculated at $0.23\mu gl^{-1}$ and $1.03\mu gl^{-1}$ respectively; those based on direct runoff only, were calculated at $0.24\mu gl^{-1}$ and $1.09\mu gl^{-1}$ respectively. The maximum flux values for chlorotoluron and isoproturon were 130.6µg/s and 26.4µg/s occurring 30 minutes before and coincidentally with the hydrograph peak respectively. In this instance less confidence is associated with the assignment of the position and magnitude of the flux curves due to the limited number of samples analysed to represent herbicide concentration variation during the period of the storm event. The flux curves illustrated in Figure 6-7 were produced by multiplying the interpolated values between the three herbicide concentration data points shown, with the concurrent flow rate values.

From the data it is apparent that the levels of the isoproturon and chlorotoluron concentrations had reversed compared to the respective concentrations monitored in the previous storm event (1/5/92) and in the manual samples taken following pesticide application. The reversal in the magnitude of concentrations probably occurred due to the shorter half-life of isoproturon (assumed to be 55 days) compared to that of chlorotoluron (assumed to be 140 days). During the period of time elapsed between event 122 and event 226 it was possible that the affect of the respective half-life values was superseded by that of the respective K_{oc} values in determining the relative magnitudes of the event mean concentration values of the two herbicides.

Also, it is apparent that the isoproturon event mean concentration had decreased by approximately 50% in comparison to that for the event on 1/5/92, and the chlorotoluron event mean concentration had increased by approximately 400%. Rather than the chlorotoluron event mean concentration decreasing with time as would be generally expected due to the effect of micro-biological degradation, it appeared to have increased. A possible explanation for this is explained in the next paragraph.

Most of the period since the 1991 autumn application of the chlorotoluron was characterised by lower-than-average rainfall that was unable to sustain a permanent baseflow from the agricultural sub-catchment (Section 5.2.1) and which probably had a significant soil-moisture deficit producing dry soil conditions. In this state, chlorotoluron molecules may have bound to easily accessible soil adsorption sites that would have normally been blocked by water molecules, in effect increasing the chlorotoluron soil partition coefficient.

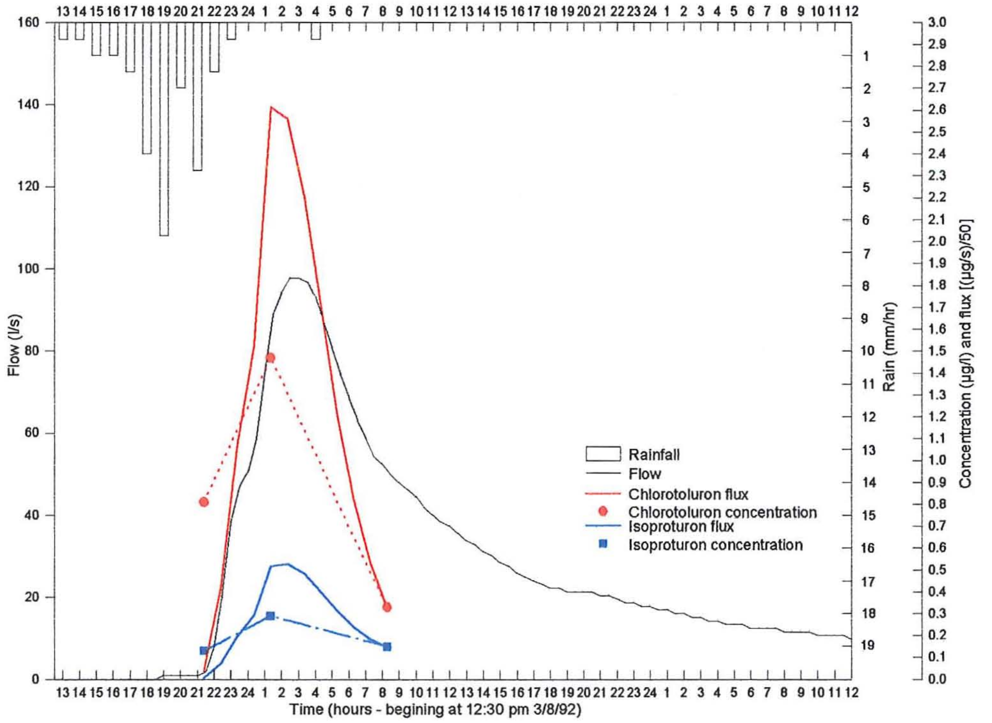


Figure 6-7 Chlorotoluron and isoproturon concentrations and fluxes at site A during a event occurring 13/8/92 (JD 226) (Rainfall intensities (bar chart) and storm runoff also shown)

As the soil moisture deficit of the arable fields of the agricultural sub-catchment began to decrease, due to reduction in water demand brought about by the harvesting of the winter cereal in late July 1992, the bound chlorotoluron molecules may have been displaced back into the soil water by the greater abundance of water molecules. This would have had the effect of creating a fresh reservoir of chlorotoluron, available for leaching by infiltrating rainwater. Similar behaviour of non-polar pesticides adsorbed by the active sites of dry soil has been described by Koskinen and Harper (1990) and Ng *et al* (1995).

6.2.3.2 Simazine and atrazine

The simazine and atrazine concentrations detected during the storm event on 13/8/92 (JD 226) are shown in Figure 6-8. The event occurred 259 days after the simazine application. As was the case for chlorotoluron and isoproturon previously described, the flux curves illustrated in Figure 6-8 were produced by multiplying the interpolated values between the three herbicide concentration data points shown, with the concurrent flow rate values The simazine and atrazine flux curves peak at values of 32μg/s and 13μg/s respectively; the simazine peak occurred 60 minutes after the hydrograph peak and the atrazine peak coincided with it. Again, the level of confidence associated with the position and magnitude of the two flux curves was less compared to the event on 1/5/95, because it was derived from the concentration and flow data of three samples. The integration of the hydrograph and herbicide flux curves showed that during the sampling period of the event, 0.845g and 0.317g of simazine and atrazine respectively were transported in the event runoff. The amount of simazine removed from the catchment corresponded to an application loss of 9.3×10^{-3}%. The event mean concentrations, based on direct runoff only, were $0.34 \mu g l^{-1}$ for simazine and $0.13 \mu g l^{-1}$ for atrazine.

Atrazine and simazine were both detected in the three samples taken from the collected set of 12 samples to represent the beginning, peak flow and end of the event. For simazine, the first sample had a concentration of $0.17 \mu g l^{-1}$, the second analysed sample which was taken one hour before the hydrograph peak had a concentration of $0.20 \mu g l^{-1}$, and the third taken seven hours after the hydrograph peak had a concentration of $0.60 \mu g l^{-1}$. The simazine concentration increases throughout the event (Figure 6-8) and, although an interpretation based on three samples must be treated with some caution, it appeared that the simazine concentration increased as the direct runoff contribution to the total runoff subsided and therefore this herbicide may have been transported in delayed interflow passing through the soil column. Conversely, the atrazine concentration decreased in a linear manner during the course of the event from of $0.17 \mu g l^{-1}$ in the first sample to $0.07 \mu g l^{-1}$ in the final analysed sample. The atrazine showed similar behaviour to the previous event (1/5/92), in that it appeared to be transported in the baseflow runoff.

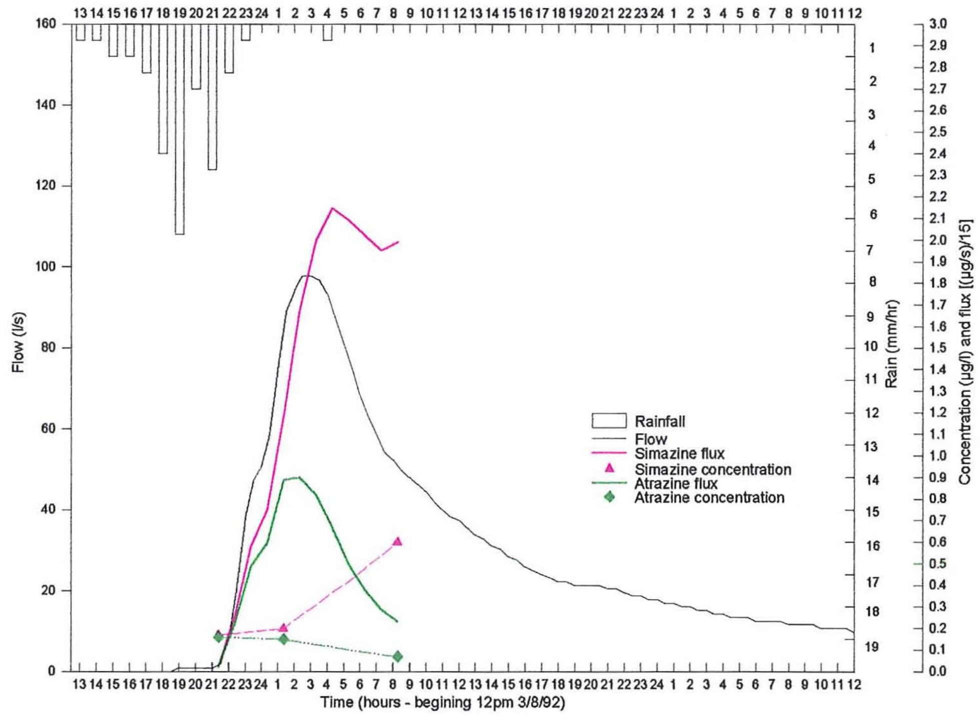


Figure 6-8 Atrazine and simazine concentrations and fluxes at site A during an event occurring 13/8/92 (JD 226) (Rainfall intensities (barchart) and storm runoff also shown)

6.2.4 Results for the storm event on 2/10/92 (Julian day 276)

6.2.4.1 Chlorotoluron and isoproturon

During the autumn of 1992 a permanent baseflow was established leaving the agricultural sub-catchment which was sustained by regular seasonal rainfall and lower rates of evapotranspiration as the growing season moved into senescence. Figure 6-9 shows details of a storm event that occurred on 2/10/92 during this period and which took place 321-340 days after the isoproturon application and 340 days after the chlorotoluron application. The event occurred after 17.5mm of rainfall, with a peak intensity of 4mmhr^{-1}, had fallen on to the agricultural sub-catchment producing a maximum flow rate of 434ls^{-1}. The initial event was shortly followed by a further 7mm of rain, with a peak intensity of 3.5mmhr^{-1}, which produced a peak flow rate of 256ls^{-1}. Of the 21 samples collected during the event, four samples were selected for analysis to represent the first peak concentration of isoproturon and chlorotoluron as well as those at the beginning and during the recession of the event. The first sample contained isoproturon and chlorotoluron concentrations of 0.13μgl^{-1} and 1.29μgl^{-1} respectively; the second sample (which coincided with the peak flow) contained 0.18μgl^{-1} and 1.62μgl^{-1} respectively; the third sample contained 0.27μgl^{-1} and 0.47μgl^{-1} respectively; and the fourth sample contained 0.19μgl^{-1} and 0.65μgl^{-1} respectively. The flux curves were produced in the same manner as those for event 226. The chlorotoluron and isoproturon flux curves peaked at 673.73μg/s and 82.58μg/s respectively, both coinciding with the peak flow rate. The integration of the hydrograph and herbicide flux-curves showed that during the sampling period of the event, 3.36g and 15.66g of isoproturon and chlorotoluron respectively were transported from the catchment in 10.99x10^{6} litres of runoff. These amounts of herbicide correspond to application losses of 5.5x10^{-3}% and 1.9x10^{-2}% respectively. The event mean concentrations, based on total runoff, for isoproturon and chlorotoluron were 0.21μgl^{-1} and 0.98μgl^{-1} and those based on direct runoff only were 0.28μgl^{-1} and 1.28 μgl^{-1} respectively.

The concentration of chlorotoluron in the first sample taken at the onset of the event was approximately 60% higher than in the first sample of the event occurring on 13/8/92. Also the chlorotoluron concentration in the sample selected to represent the peak concentration was approximately 10% higher than that for the same sample from the event on 13/8/92. Further, the event mean concentration of chlorotoluron, based on direct runoff only, was higher than for the latter storm event. The baseflow of the runoff leaving the agricultural sub-catchment was probably augmented by spring water fed by a source from outside of the sub-catchment (see Section 5.2.3). Therefore, to remove the effect of unknown dilution factors it was considered that the comparison of event mean concentrations based only on direct runoff volumes was more meaningful than that based on total runoff volumes supplemented with unknown quantities of spring water.. As was also the case for the event on 13/8/92, the higher chlorotoluron concentrations were probably occurring as a result of the displacement of adsorbed chlorotoluron molecules from soil particle surfaces by water molecules, as the soil moisture content of the agricultural sub-catchment gradually increased due to the above average rainfall and subsiding soil water demands from sub-catchment evapotranspiration.

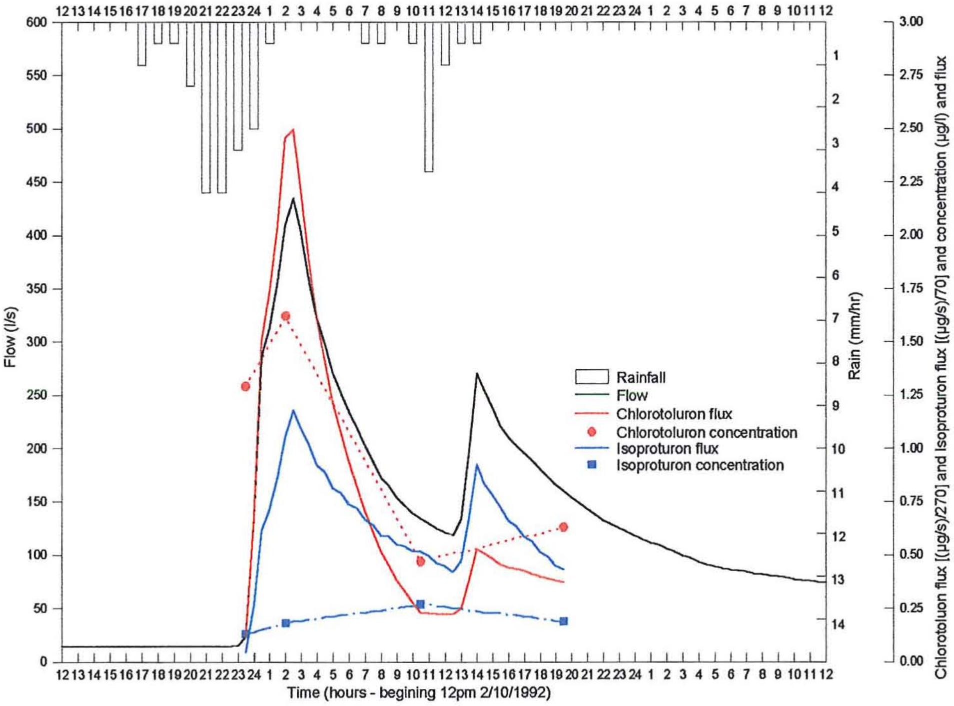


Figure 6-9 Chlorotoluron and isoproturon concentrations and fluxes at site A during the storm event occurring on 2/10/92 (JD 276). (Rainfall intensities (bar chart) and storm runoff also shown)

6.2.4.2 Simazine and atrazine

The temporal variations in simazine and atrazine concentrations and fluxes detected during the storm event on 2/10/92 (JD 276) are illustrated in Figure 6-10. The event occurred 309 days after the simazine application. Again, the flux curves were produced in the same manner as described for chlorotoluron and isoproturon for this event. The simazine and atrazine flux curves peaked at 44.77µg/s and 14.45µg/s respectively; the simazine peak occurred 30 minutes after the hydrograph peak, whereas the atarzine peak occurred 15 hours after the hydrograph peak due to is late detection during the storm event. The integration of the hydrograph and herbicide-flux curves showed that during the sampling period of the event, 3.261g and 0.362g of simazine and atrazine respectively were transported in the event runoff. The simazine weight corresponded to an application loss of $3.6\text{x}10^{-2}$%. The event mean concentrations, based on direct runoff only, were 0.26μgl^{-1} for simazine and 0.07μgl^{-1} for atrazine.

Simazine was detected in all the four samples taken from the sample set to represent the beginning, peak and end of the event, and atrazine was detected only in the last two. For simazine, the first sample had a concentration of 0.15μgl^{-1}, the second sample which coincided with the hydrograph peak had a concentration of 0.9μgl^{-1}, the third taken eight hours after the hydrograph peak had a concentration of 0.27μgl^{-1}, and the fourth sample taken seventeen hours after the first hydrograph peak had a concentration of 0.33μgl^{-1}. As shown in Figure 6-10, after an initial decrease, the simazine concentration increases throughout the two consecutive rainfall events. Any interpretation based on four samples covering two hydrographs must be treated with some caution.

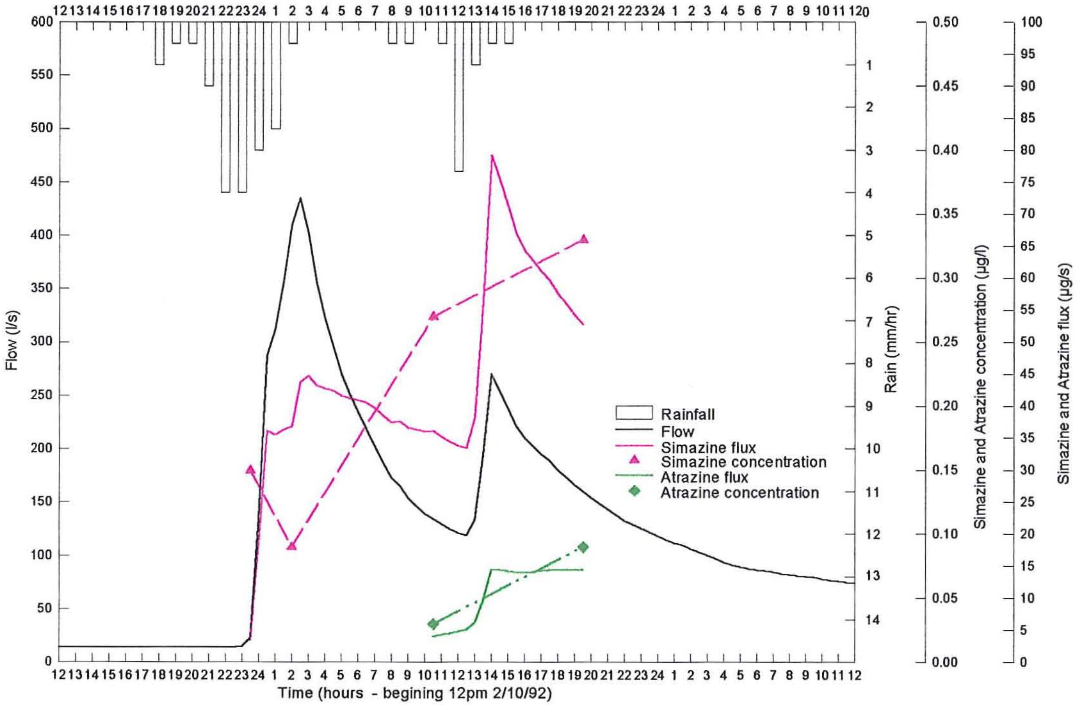


Figure 6-10 Atrazine and simazine concentrations and fluxes at site A during the storm event occurring on 2/10/92 (JD 276) (Rainfall intensities (bar chart) and storm runoff also shown)

However, during the first hydrograph peak, based on the first three samples, it appeared that the simazine concentration increased as the direct runoff contribution to the total runoff subsided and therefore may have been transported in delayed interflow passing through the soil column. A similar decrease in simazine concentration followed by a recovery may have occurred between samples three and four, however without the missing concentration data it would be difficult to suggest this behaviour with any certainty. Atrazine was detected in the last two samples at concentrations of 0.03μgl^{-1} and 0.09μgl^{-1}. The behaviour of atrazine during the two previous storm events suggested that it was transported in the baseflow component of the runoff. The absence of atrazine in the first two samples that were taken during the course of the first hydrograph, suggested that during this period the atrazine present in the baseflow was diluted by the increasing volume of direct runoff, to a level below the detection limit of the analytical method. As the storm event proceeded, infiltrating rainwater may have replenished and increased the baseflow contribution to the total runoff and hence the concentration of atrazine in the runoff. achieved detectable levels

6.2.5 Results for the storm event on 20/10/92 (Julian day 294)

6.2.5.1 Chlorotoluron and isoproturon

Figure 6-11 shows details of a storm event that occurred on 20/10/92 (JD 294) which was 339-358 days after the isoproturon application and 358 days after the chlorotoluron application. The event occurred after 49.5mm of rainfall, with a peak intensity of 9.5$mmhr^{-1}$, had fallen on to the agricultural sub-catchment producing a maximum flow rate of 1148ls^{-1}. In respect of rainfall volume, rainfall intensity, and peak runoff, this event was the largest one recorded during the course of the monitoring program. Of the 21 samples taken during the event, four samples were selected for analysis to represent the peak pesticide concentrations as well as those at the beginning and end of the event. Analysis of the samples revealed only the detection of chlorotoluron; the absence of isoproturon was probably the result of the high dilution factor of the runoff volume in conjunction with a relatively minor soil residue level due to its shorter half-life compared to chlorotoluron. The first sample had a chlorotoluron concentration of 0.41μgl^{-1}; the second sample contained 0.62μgl^{-1}; the third sample contained 0.73μgl^{-1}; and the fourth sample contained 0.40μgl^{-1}. The chlorotoluron flux curve peaked at 830.27μg/s and occurred approximately 30 minutes before peak hydrograph flow. The integration of the hydrograph and flux curves showed that during the sampling period of the event, 16.85g of chlorotoluron was removed from the catchment corresponding to an application loss of 2.2×10^{-2}%. The event mean concentration, based on direct runoff only, was 0.63μgl^{-1}. Compared to the chlorotoluron event mean concentration of the previous event (2/10/92, 1.28μgl^{-1}) and the following event (9/11/92, 1.15μgl^{-1}, Section 6.2.6.1), this value was approximately 50% lower. This behaviour may be explained by the greater dilution of the leached chlorotoluron that occurred during the event due to the large volume of runoff generated (44.37×10^{6} litres). It was probable that the large volume of runoff may have counteracted any increase in chlorotoluron leaching that may have resulted from the high intensity of the rainfall (Johnson (1995).

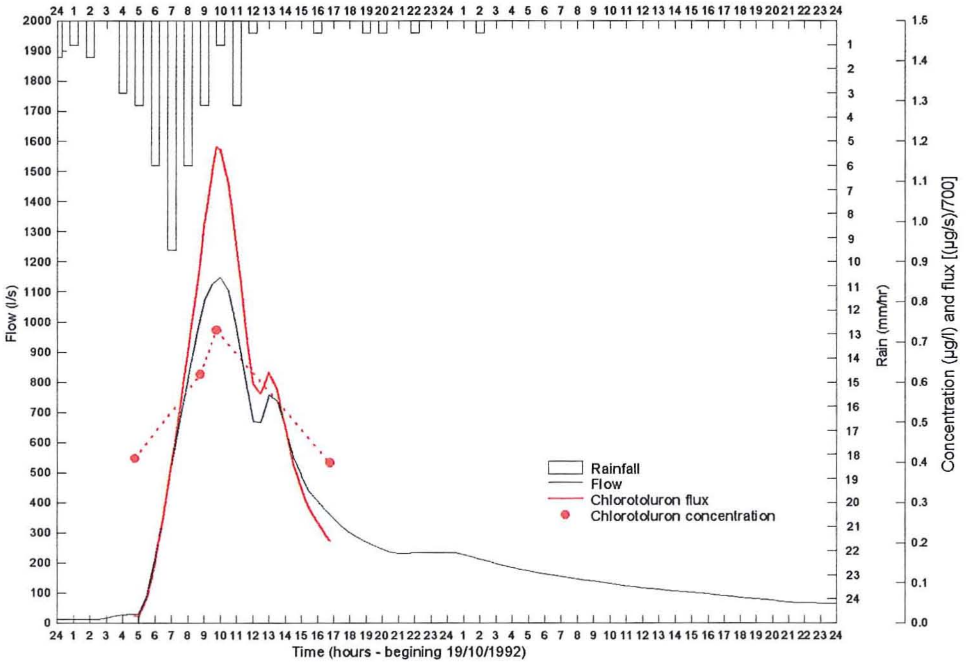


Figure 6-11 Chlorotoluron concentrations and fluxes at site A during the storm event occurring 20/10/92 (JD 294) (Rainfall intensities (bar chart) and storm runoff also shown)

6.2.5.2 Simazine and atrazine

The simazine and atrazine concentrations and fluxes detected during the storm event on 20/10/92 (JD 294) are shown in Figure 6-12. The event occurred 327 days after the simazine application. The integration of the hydrograph and herbicide-flux curves showed that during the sampling period of the event, 2.861g and 1.625g of simazine and atrazine respectively were transported in the event runoff. The simazine and atrazine flux curves peaked at 126.33μg/s and 72.2μg/s respectively. The simazine peak coincided with the peak flow rate and the atrazine peak occurred 60 minutes after the flow peak; the position and magnitude of the flux-curves should be treated with some caution since they were derived from three and four samples respectively. The measured weight of simazine corresponded to an application loss of $3.1\times10^{-2}\%$. The event mean concentrations, based on direct runoff only, were $0.1\mu gl^{-1}$ for simazine and $0.08\mu gl^{-1}$ for atrazine.

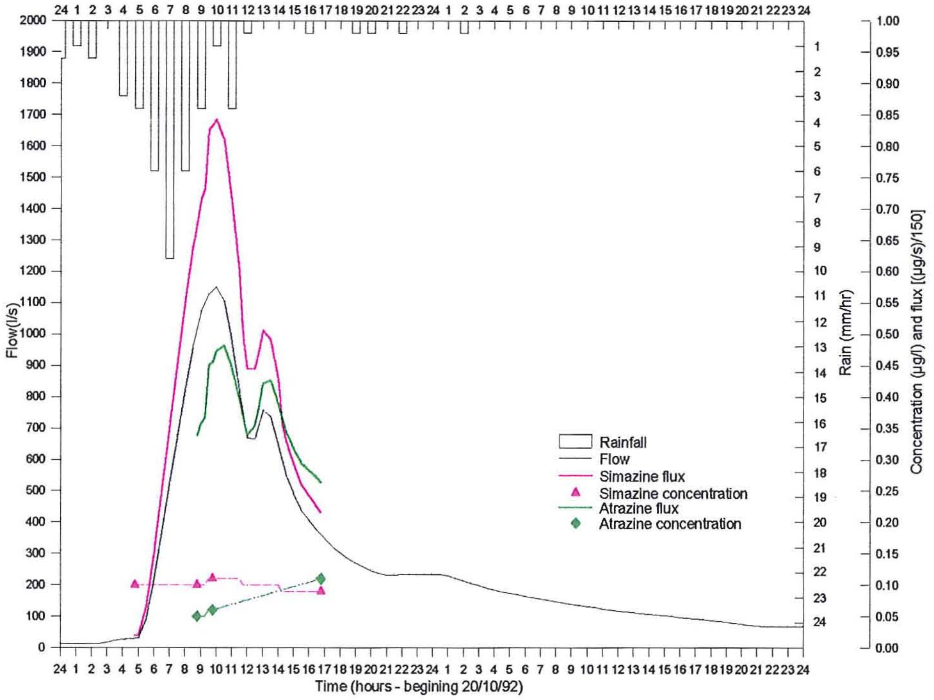


Figure 6-12 Atrazine and simazine concentrations and fluxes at site A during the storm event occurring on 20/10/92 (JD 294) (Rainfall intensities (bar chart) and storm runoff also shown)

Simazine was detected in all the four samples taken from the sample set to represent the beginning, peak and end of the event, and atrazine was detected only in the last three. For simazine, the first sample had a concentration of 0.11μgl^{-1}, the second sample which occurred one hour before the hydrograph peak had a concentration of 0.10μgl^{-1}, the third that coincided with the hydrograph peak had a concentration of 0.11μgl^{-1}, and the fourth sample taken seven hours after the hydrograph peak had a concentration of 0.09μgl^{-1}. For atrazine, the second sample had a concentration of 0.05μgl^{-1}, the third sample had a concentration of 0.06μgl^{-1}, and the fourth sample a concentration of 0.09μgl^{-1}. The concentrations for both simazine and atrazine were very low and at this level associated with significant error, therefore interpretation must be treated with caution. All that can be suggested is that both simazine and atrazine did not appear to respond to the increased flow of the hydrograph which indicates that transport during the event may have been associated with the baseflow and delayed interflow components of the total runoff.

6.2.6 Results for the storm event on 9/11/92 (Julian day 314)

6.2.6.1 Chlorotoluron and isoproturon

Figure 6-13 shows the details of a storm event that occurred on 9/11/92 (JD 314) which was 359-378 days after the isoproturon application and 378 days after the chlorotoluron application. The event occurred after 12mm of rainfall, with a peak intensity of 3mmhr^{-1}, had fallen onto the agricultural sub-catchment producing a maximum flow rate of 350ls^{-1}. Of the 21 samples taken during the event, seven samples were selected for analysis to represent the peak pesticide concentrations as well as those during the earlier and later parts of the event. Except for one sample, the analyses revealed only the detection of chlorotoluron which was similar to the previous sampled event of 20/10/92. The absence of isoproturon in the samples probably reflected its relatively short half-life of ~55 days compared to 140 days for chlorotoluron. The chlorotoluron flux curve peaked at 780μg/s and coincided with the hydrograph peak. The integration of the hydrograph and chlorotoluron-flux curves showed that during the sampling period of the event, 3.63g of chlorotoluron was transported in 7.088x10^{6} litres of event runoff.

This weight corresponded to an application loss of $4.6\text{x}10^{-3}$%. The event mean concentration, based on direct runoff only, was $1.15\mu gl^{-1}$. The first sample had a chlorotoluron concentration of $1.26\mu gl^{-1}$; the second sample, coinciding with the hydrograph peak, contained the maximum chlorotoluron concentration of $2.23\mu gl^{-1}$ and also the only detection of isoproturon at $0.08\mu gl^{-1}$. In the following hour the chlorotoluron concentration in the next two samples decreased to approximately 0.45µg/l and the concentration in the last sample, taken later was 0.14µg/l. This behaviour of chlorotoluron was significantly different from that during the event of 1/5/92, where the peak in chlorotoluron concentration occurred one hour before the hydrograph peak and then declined in a much-slower exponential manner. The apparent difference in the behaviour of chlorotoluron was probably due dilution exhaustion of the herbicide source.

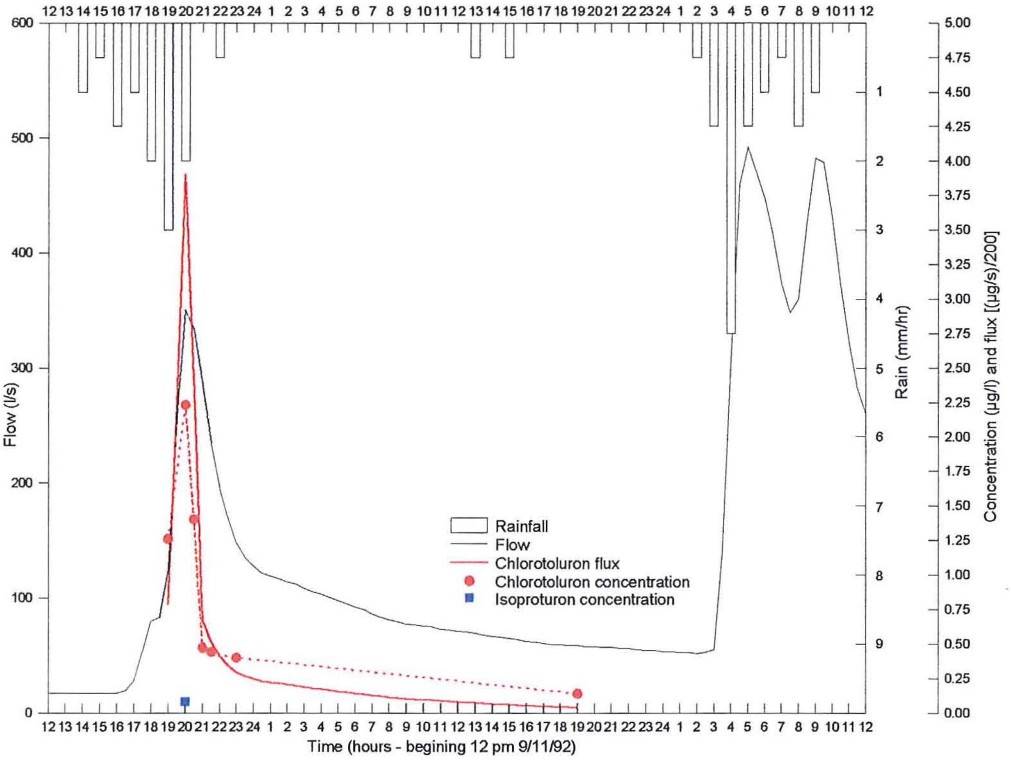


Figure 6-13 Chlorotoluron and isoproturon concentrations and fluxes at site A during the storm event occurring on 9/11/92 (JD 314) (Rainfall intensities (bar chart) and storm runoff also shown)

6.2.6.2 Simazine and atrazine

The simazine and atrazine concentrations and fluxes detected during the storm event of 9/11/92 (JD 314) are shown in Figure 6-14. The event occurred 347 days after the simazine application. The peak simazine and atrazine flux values were 43µg/s and 10.5µg/s respectively, the simazine peak coincided with the hydrograph peak whilst the atrazine peak occurred 30 minutes earlier. The integration of the hydrograph and herbicide flux curves showed that during the sampling period of the event, 0.478g and 0.040g of simazine and atrazine respectively were transported in the event runoff. The simazine weight corresponded to an application loss of $5.3x10^{-3}\%$. The event mean concentrations, based on direct runoff only, were $0.12\mu gl^{-1}$ for simazine and $0.04\mu gl^{-1}$ for atrazine.

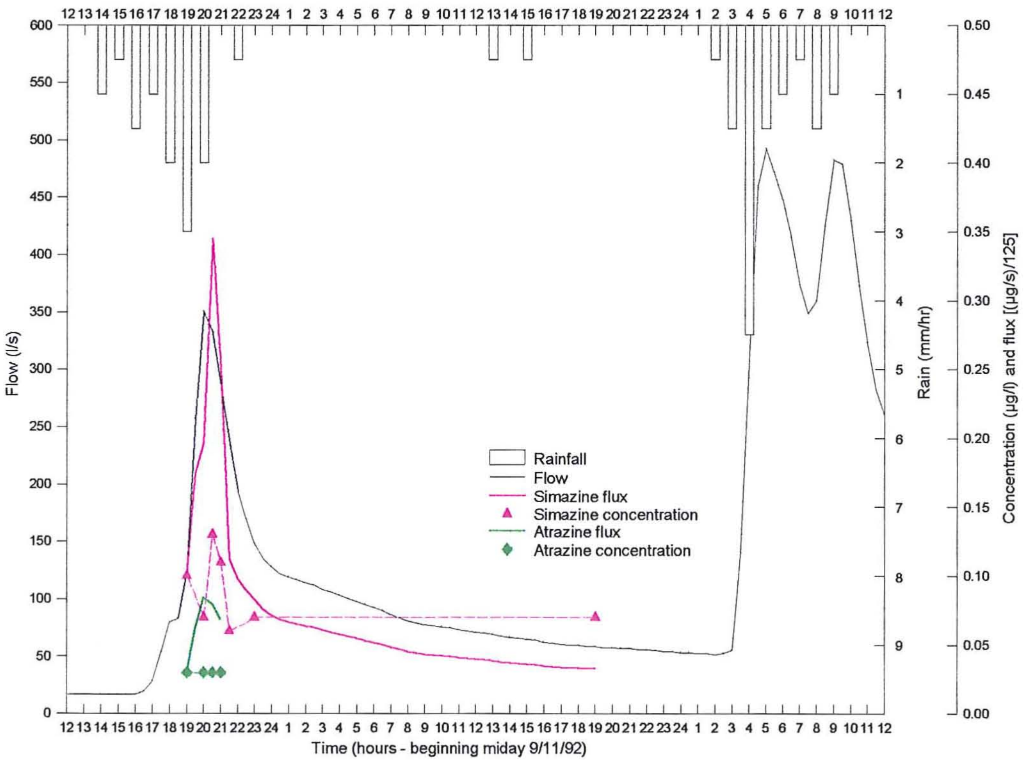


Figure 6-14 Atrazine and simazine concentrations and fluxes at site A during the storm event occurring on 9/11/92 (JD 314) (Rainfall intensities (bar chart) and storm runoff also shown)

Simazine was detected in seven of ten samples taken from the sample set of nineteen samples to represent the beginning, peak and end of the event, and atrazine was detected in the first four. For simazine, the first sample had a concentration of 0.10μgl^{-1}; the second sample which coincided with the hydrograph peak had a concentration of 0.07μgl^{-1}; the third sample occurred one hour after the hydrograph peak and had the maximum concentration of the data-set at 0.13μgl^{-1}. The subsequent samples showed the concentration decreasing to 0.07μgl^{-1} three hours after the hydrograph peak, with the last sample occurring twenty-four hours after the hydrograph peak also recording this concentration. For atrazine, the first four samples all had a concentration of 0.03$\mu g\ l^{-1}$, which is theoretically below the detection limit of 0.05μgl^{-1}. However, in this instance the detection was confirmed by the UV scans from the HPLC photo-diode-array detector. As in the case of the previously sampled storm event, the concentrations of both simazine and atrazine were very low and at this level associated with significant error, therefore interpretation must be treated with caution. Unlike the event on 20/10/92, simazine data show a small peak occurring one hour after the hydrograph peak. The very low atrazine concentrations remained constant throughout the peak of the hydrograph, and as previously suggested, probably represents transport in the baseflow runoff component. The detection of simazine and atrazine during this event were the last to be observed during the course of the monitoring program.

6.2.7 Results for the storm event on 15/11/92 (Julian day 320)

6.2.7.1 Chlorotoluron and isoproturon

Figure 6-15 shows the chlorotoluron concentration and flux curve for the storm event that occurred on 15/11/92 (JD 320) which took place 384 days after the chlorotoluron application. The event occurred after 7.5mm of rainfall, with a peak intensity of 5$mmhr^{-1}$, had fallen onto the agricultural sub-catchment producing a maximum flow rate of 326ls^{-1}. All of the 21 samples taken during the event were analysed, however as shown in Figure 6-15, chlorotoluron was only detected in the first five samples. Isoproturon was not detected in any of the samples taken during this event or from the following monitored event on 6/1/93. This was probably the result of in-situ degradation and off-site loss which reduced the isoproturon concentration to below the detection limit. The chlorotoluron flux curve peaked at a value of 298µg/s, occurring 30 minutes after the hydrograph peak.

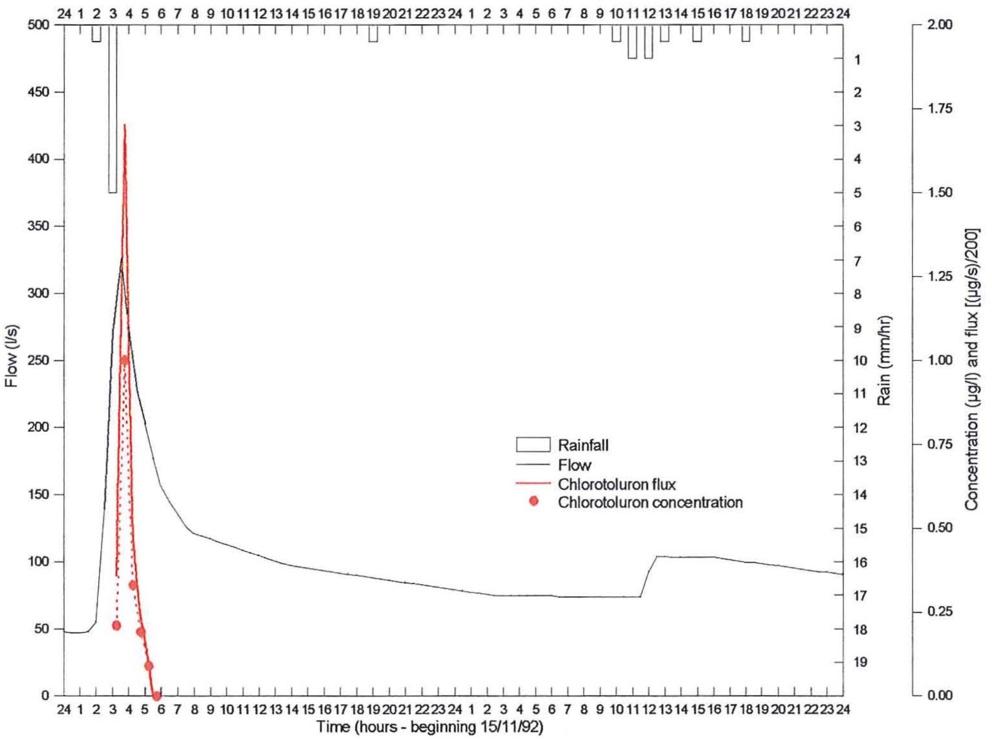


Figure 6-15 Chlorotoluron concentration and flux at site A during the storm event occurring on 15/11/92 (JD 320) (Rainfall intensities (bar chart) and storm runoff also shown)

The integration of the hydrograph and chlorotoluron flux curves showed that during the sampling period of the event, 0.83g of chlorotoluron was transported in 4.256×10^6 litres of event runoff which corresponded to an application loss of 1.1×10^{-3}%. The event mean concentration, based on direct runoff only, was 0.79µgl^{-1}. The first sample had a chlorotoluron concentration of 0.21µgl^{-1}, whereas the second sample, coinciding with the hydrograph peak, contained the maximum chlorotoluron concentration of 1.00µgl^{-1}. In a similar pattern to the 314 event (Figure 6-13), in the two-hour period following the maximum concentration the chlorotoluron level decreased rapidly and can similarly be explained by dilution exhaustion of the herbicide source.

6.3 Results of storm event monitoring for 1993

The results discussed in this section cover the 1992/93 crop-growing season for the agricultural sub-catchment. Only isoproturon was applied and the principal application of this herbicide was made to the agricultural sub-catchment during early February 1993 rather than during the 1992 autumn due to the water-logged soil present during that period; details of the isoproturon application are given in Table 6-1. Figure 6-16 shows the rainfall and runoff from the agricultural sub-catchment during the 1993 monitoring period (January-April) and identifies the storm events that were sampled. Early in January 1993, the farm manager of Searls Hall Farm stated that a major isoproturon application was imminent and its timing was dependent upon the soil of the agricultural sub-catchment being sufficiently dry to allow tractor access. Therefore, other than analyses of samples taken during the storm event on 6/1/93, to conserve laboratory resources a decision was taken to defer further monitoring and analyses until after the isoproturon application.

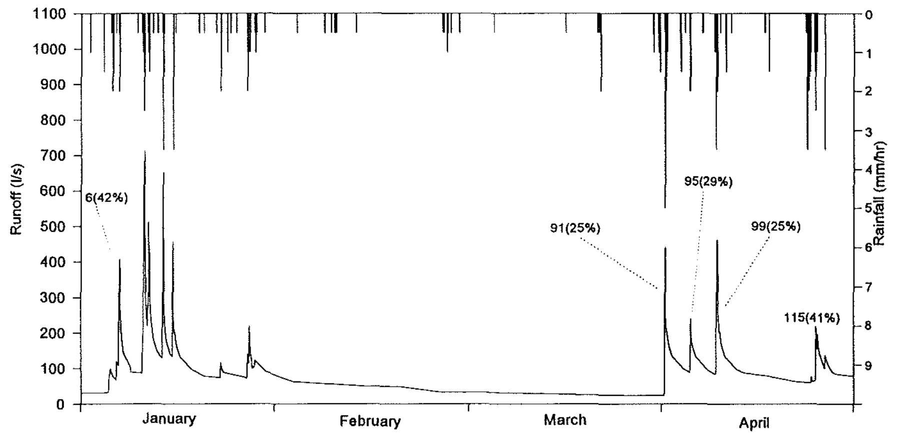


Figure 6-16 Rainfall and runoff for the agricultural sub-catchment between January and April 1993 showing storm events monitored at Site A

6.3.1 Results from the storm event on 6/1/93 (Julian day 6)

6.3.1.1 Chlorotoluron and isoproturon

Figure 6-17 shows the chlorotoluron concentration and flux during a storm event that occurred on 6/1/93 (JD 6) which took place 436 days after the chlorotoluron application. This event occurred after 7.5mm of rainfall, with a peak intensity of 2 $mmhr^{-1}$, had fallen onto the agricultural sub-catchment producing a maximum flow rate of $355ls^{-1}$.

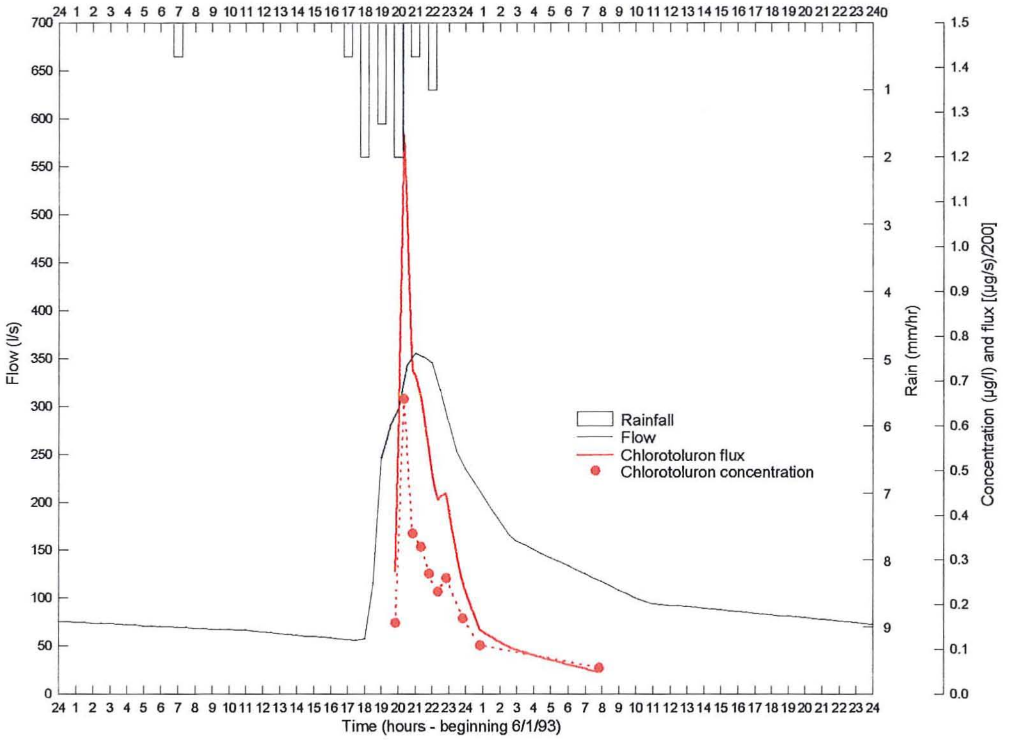


Figure 6-17 Chlorotoluron concentrations and fluxes at site A during the storm event occurring on 6/1/93 (JD 6) (Rainfall intensities (bar chart) and storm runoff also shown)

Twenty samples were collected during the event but chlorotoluron was only detected in the first ten samples to be analysed; there was no detection of isoproturon in any of the samples. The chlorotoluron flux curve peaked at 249µg/s which occurred 60 minutes before the hydrograph peak. The integration of the hydrograph and chlorotoluron-flux curves showed that during the sampling period of the event, 2.07g of chlorotoluron was transported in $9.2x10^{6}$ litres of event runoff. This corresponds to an application loss of $2.6x10^{-3}$%. The event mean concentration, based on direct runoff only, was calculated at $0.65µgl^{-1}$. The first sample had a concentration of $0.16µgl^{-1}$ whereas the second sample, occurring one hour before the hydrograph peak, contained the maximum chlorotoluron concentration of $0.66µgl^{-1}$. In the following four hours the chlorotoluron concentration rapidly fell to a value equivalent to that of sample one. The next sampled storm event (on 1/4/93) occurred after the isoproturon application in early February.

Prior to this April event and after the isoproturon applications, manual samples were taken at site A. The results are shown in Table 6-7. Surprisingly the sample taken on 12/2/93 did not contain any detectable isoproturon but in the 26/2/93 sample a concentration of 0.14μgl^{-1} was detected. This may be explained by the below average rainfall during February 1993 which may have delayed the leaching of the isoproturon into the field drainage water. Considering the low volume of rainfall and the relatively quick appearance of the isoproturon at site A, it was probable that the isoproturon travelled rapidly from the soil surface to the flow channel via by-pass channels in the soil column.

Table 6-7 Results of 1993 manual sampling

Date	Location	Flow (l/s)	Pesticide concentration (µg/l) Simazine	Atrazine	Chlorotoluron	Isoproturon
12/2/93	Site A	46.1	nd	nd	0.04	nd
26/2/93	Site A	30.7	nd	nd	nd	0.14
24/3/92	Site A	19.2	0.04	nd	0.06	0.09

Site A: Outlet of agricultural sub-catchment. nd - not detected

6.3.2 Results from the storm event of 1/4/93 (Julian day 91)

6.3.2.1 Chlorotoluron and isoproturon

A total weight of 39.692kg of isoproturon was applied to fields known as Little Park Hall, Hither Lawns, and Middle Lawns on 3/2/92 (Table 6-1). The first four storm events that occurred after the application (all during April 1993) were comprehensively sampled. This allowed the importance of the first event after application to be assessed and also allowed an accurate determination of the main seasonal losses of isoproturon. Because of the below average rainfall during February and March 1993, the first storm event did not occur until 57 days, after the isoproturon application, on 1/4/93 (Figure 6-18). The event occurred after 17.5mm of rainfall, with a peak intensity of 5$mmhr^{-1}$, had fallen onto the agricultural sub-catchment producing a maximum flow rate of 440ls^{-1}. Nineteen samples were taken during the event with isoproturon being detected in every one although chlorotoluron was only detected in the first four samples. The peak of the isoproturon concentration coincided with the hydrograph peak and the chlorotoluron concentration peaked approximately one hour before the hydrograph peak. The chlorotoluron and isoproturon flux curves peaked at 95.4μg/s and 4337μg/s respectively, both coinciding with the peak flow rate. The integration of the hydrograph and isoproturon and chlorotoluron-flux curves showed that during the sampling period of the event, 64.83g of isoproturon and 0.41g of chlorotoluron were removed from the catchment in 12.56×10^{6} litres of event runoff. The removed herbicide corresponded to application losses of 0.13% and 5.2×10^{-4}% respectively. The event mean concentrations, based on direct runoff only, were 0.33μgl^{-1} for chlorotoluron and 10.35μgl^{-1} for isoproturon.

The first and second samples had an isoproturon concentration of 0.11μgl^{-1}; the concentration then rapidly rose to a maximum concentration of approximately 10μgl^{-1} in sample three. The concentration of the following two samples remained close to this value and then the subsequent samples showed a gradual exponential decay over the following twenty-two hours to a value of 0.57μgl^{-1}. The pattern of the isoproturon concentration decay curve was similar to that observed during the storm event of 1/5/92. During both storm events, the rapid appearance and increase of isoproturon concentration detected in the runoff suggested that the herbicide was being rapidly transported via a network of macro-pore by-pass channels passing through the soil column and that its removal was not limited by the hydraulic conductivity of the soil matrix.

The chlorotoluron concentration rose from 0.1μgl^{-1} in sample one, to a peak value of 0.26μgl^{-1} in sample two. The following two samples showed a rapid decrease in concentration to a point of no detection which occurred within three hours of the first sample. The relatively short detection time of chlorotoluron compared to isoproturon can be explained by the comparatively minor quantities of chlorotoluron left remaining in the soil after the degradation and runoff losses that had occurred since its application 521 days previously. The peak of the chlorotoluron concentration occurred approximately one hour before the peak of the isoproturon concentration (Figure 6-18). This suggests that the two herbicides were extracted from different locations within the soil profile. Possibly, the bulk of the remaining chlorotoluron was present at some depth below the soil surface due to prolonged leaching whereas due to its recent application, the isoproturon would be mainly present at the soil surface. With the onset of rainfall, it is likely that the infiltrating rainfall would have displaced the existing soil water from the soil column and that the surface soil water containing isoproturon would eventually drain from the soil column some time after the deeper soil water. Therefore, if the bulk of the remaining chlorotoluron resided at some depth below the soil surface, the fraction present within the soil water would have entered the main flow channel in advance of the soil water containing isoproturon. This suggestion may explain the earlier concentration peak of chlorotoluron compared to isoproturon. It was unlikely that overland surface runoff was not generated during this event, since the preceding two months of below average rainfall (Table 5-1) would have resulted in the soil profile drying out, producing soil cracks and a soil moisture deficit. In such a condition it is probable that the majority of rainfall travelled through the soil profile via soil cracks (preferential flow paths) and sub-surface matrix interflow.

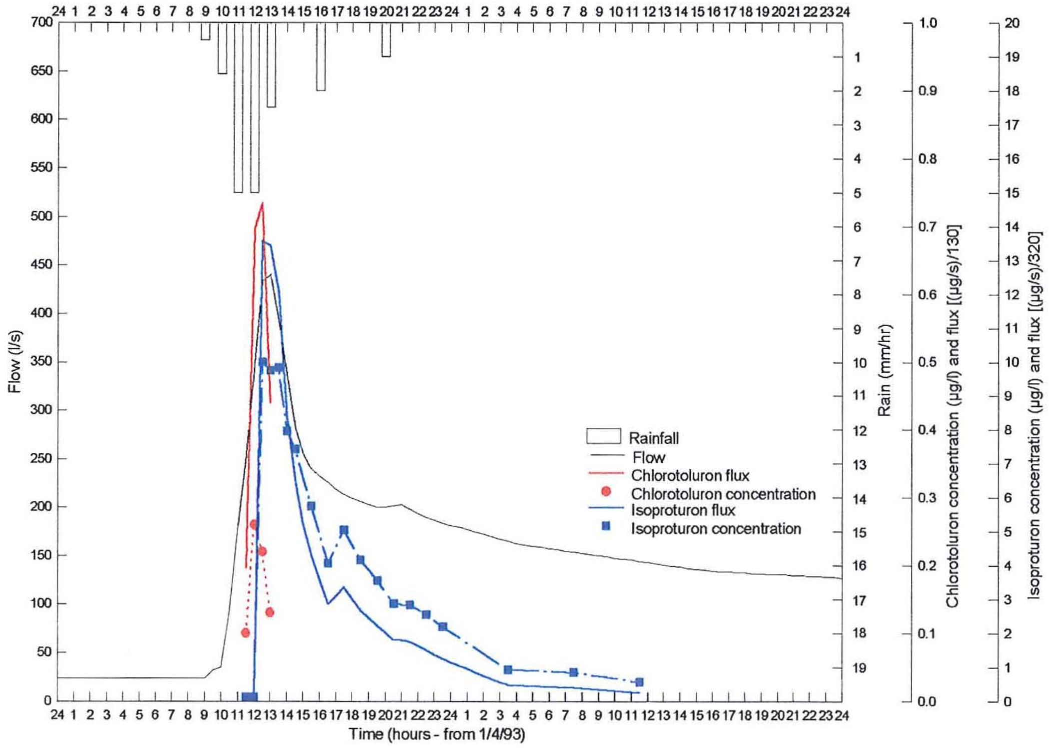


Figure 6-18 Chlorotoluron and isoproturon concentrations and fluxes at site A during the storm event occurring on 1/4/93 (JD 91) (Rainfall intensities (bar chart) and storm runoff also shown)

6.3.3 Results from the storm event of 5/4/93 (Julian day 95)

6.3.3.1 Chlorotoluron and isoproturon

This event followed only four days after the storm event described in Section 6.3.2. It was triggered by 8mm of rainfall, with a peak intensity of $2mmhr^{-1}$, falling on to the agricultural sub-catchment to produce a maximum flow rate of $240ls^{-1}$ (Figure 6-19). Nineteen samples were collected and isoproturon was detected in all but the first two samples and chlorotoluron was detected in samples 3 to 10. The peak of the isoproturon concentration occurred approximately half an hour before the hydrograph peak and the chlorotoluron concentration peaked approximately one and a half hours before the hydrograph peak. The chlorotoluron and isoproturon flux curves peaked at 40.1µg/s and 2109.3µg/s respectively and both coincided with the timing of the flow peak. The integration of the hydrograph together with isoproturon and chlorotoluron flux curves showed that during the sampling period of the event, 34.08g of isoproturon and 0.55g of chlorotoluron were removed from the catchment in $7.76x10^{6}$ litres of event runoff. The application losses for isoproturon and chlorotoluron were $6.8x10^{-2}\%$ and $7.0x10^{-4}\%$ respectively. The event mean concentrations, based on direct runoff only, were $0.36\mu gl^{-1}$ for chlorotoluron and $16.69\mu gl^{-1}$ for isoproturon.

Following initial non-detectable levels, the concentration of isoproturon rose rapidly to approximately $8.5\mu gl^{-1}$ where it remained constant for one-and-a-half hours. The concentrations of the following fourteen samples showed a gradual exponential decay over a period of sixteen hours to $0.49\mu gl^{-1}$. Again, the pattern of the isoproturon concentration curve was similar to that observed during the storm events of 1/4/93 and 1/5/92, and was probably the result of the isoproturon being rapidly transported via preferential flow paths through the soil profile.

Chlorotoluron, like isoproturon, was not detected in the first two samples and the maximum concentration of $0.24\mu gl^{-1}$ was achieved by sample five. The following six samples showed the chlorotoluron concentration slowly decrease to a point of no detection, nine hours after the first sample was taken. Again, the chlorotoluron concentration peaked before that of isoproturon, which as discussed for the previous event (1/4/93), was probably caused by the two herbicides being leached from differing locations within the soil column. The absence of any detectable herbicide levels in the first two samples may be explained by the relatively high baseflow, which was supplemented by spring water supplied from outside the agricultural sub-catchment (see Section 5.2.3). The dilution by the spring water, which was assumed to be free of pesticide residues, would have had the effect of reducing the concentration of any isoproturon and chlorotoluron residues to below the detection limit of the analytical method (0.05μgl^{-1}).

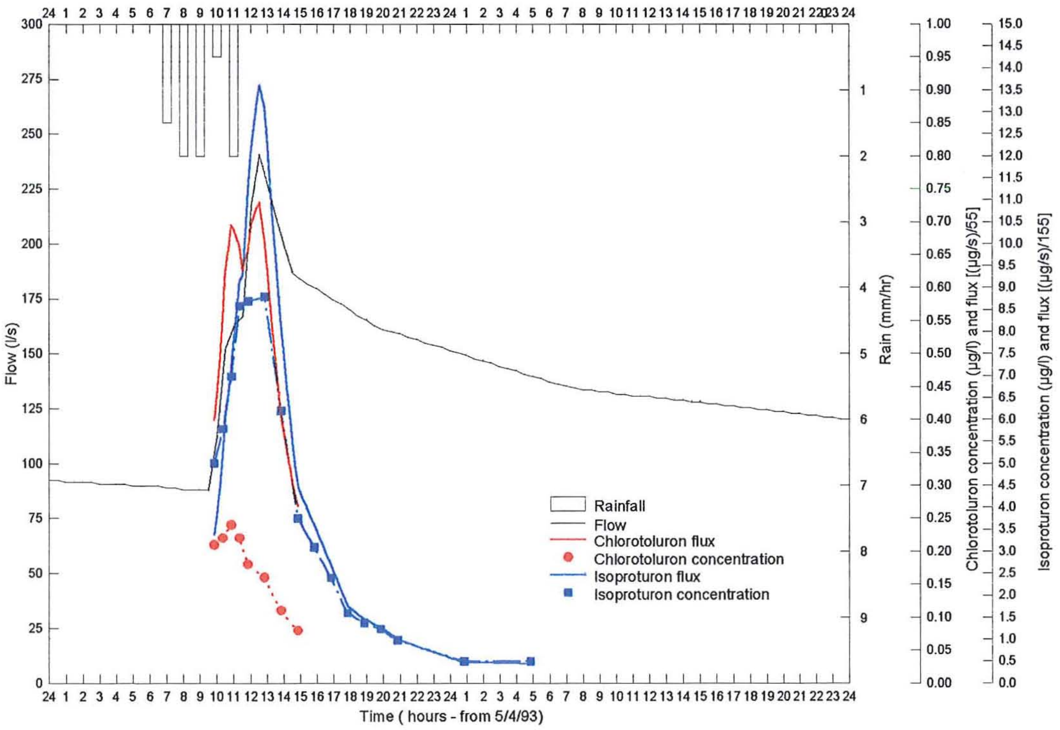


Figure 6-19 Chlorotoluron and isoproturon concentrations and fluxes at site A during a storm event occurring on 5/4/93 (JD 95) (Rainfall intensities (bar chart) and storm runoff also shown)

6.3.4 Results from the storm event of 9/4/93 (Julian day 99)

6.3.4.1 Chlorotoluron and isoproturon

The event of 5/4/93 was followed four days later by the third event to occur after the isoproturon application, 65 days previously. Details of the event which occurred after 15.5mm of rainfall, with a peak intensity of 3.5mmhr^{-1}, had fallen onto the agricultural sub-catchment are shown in Figure 6-20. Two flow peaks (471ls^{-1} and 457ls^{-1}) were produced. The split hydrograph may have been caused by a portion of the agricultural sub-catchment behaving as a minor sub-catchment and possessing slightly different response characteristics. Examination of Figure 6-1 would suggest that the wooded area of Mount Wood and Birching Coppice may have acted as a minor sub-catchment, however inspection of Figure 6-20 shows that in general, the two hydrograph peaks are mirrored by peaks in the concentrations of isoproturon and chlorotoluron. Since there was no record of either herbicide being applied to the wooded area it was unlikely that the second peak may be explained using the minor sub-catchment argument. Therefore, it was more probably an effect caused by a variation in the event rainfall distribution. Ward (1975) suggests that a catchment can either produce a single hydrograph in response to rainfall or a multiple hydrograph depending on whether the rain storm moves down the catchment or up the catchment, i.e. opposite to the direction of the catchment runoff. The topography and main drainage channel of the agricultural sub-catchment falls in a north easterly direction which is aligned with the general direction of the frontal rain systems moving across the British Isles. Therefore, it was probable that the split hydrograph of the event of 9/4/93 was the result of a less common rain system moving in a south easterly direction since the majority of the event hydrographs recorded contained a single flow peak.

Isoproturon was detected in each of the collected eighteen samples whereas chlorotoluron was detected only in samples 2 to 6 and 8 to 16. Three flux peaks were observed for isoproturon at values of 1311μg/s, 3998μg/s and 3570μg/s; the second and third peaks coincided with the two peaks of the hydrograph whilst the first occurred 90 minutes before the first hydrograph peak. For chlorotoluron, two flux peaks of 91μg/s and 109μg/s were recorded, the first peak occurred 60 minutes before the first peak of the hydrograph and the second peak occurred 30 minutes before the second peak of the hydrograph. The integration of the hydrograph together with the isoproturon and chlorotoluron-flux curves showed that during the sampling period of the event, 81.01g of isoproturon and 1.90g of chlorotoluron were transported in 22.85×10^{6} litres of event runoff. These removed weights corresponded to application losses of 0.16% and 2.4×10^{-3}% respectively. The event mean concentrations, based on direct runoff only, were 0.18μgl^{-1} for chlorotoluron and 7.24μgl^{-1} for isoproturon.

Following an initial isoproturon concentration of 0.08µgl^{-1} the isoproturon concentration showed three distinct peaks, with the second and third peaks occurring approximately one hour before the two hydrograph peaks. The values of the three peak concentrations were 5.66µgl^{-1}, 8.67µgl^{-1}, and 7.97µgl^{-1} respectively. In the fourteen hours following the last peak, the isoproturon concentration decayed in an exponential manner to a value of 0.81µgl^{-1}. The shape of isoproturon concentration curve may be explained using the same argument as that used previously to explain the split hydrograph. During the storm event, if the rainfall front had moved up the catchment in a south-easterly direction it would have encountered the fields that had received the isoproturon application at different times. As previously discussed, the fields of the agricultural sub-catchment were under-drained and separated by drainage ditches and to a certain extent could have been considered as hydrologically isolated.

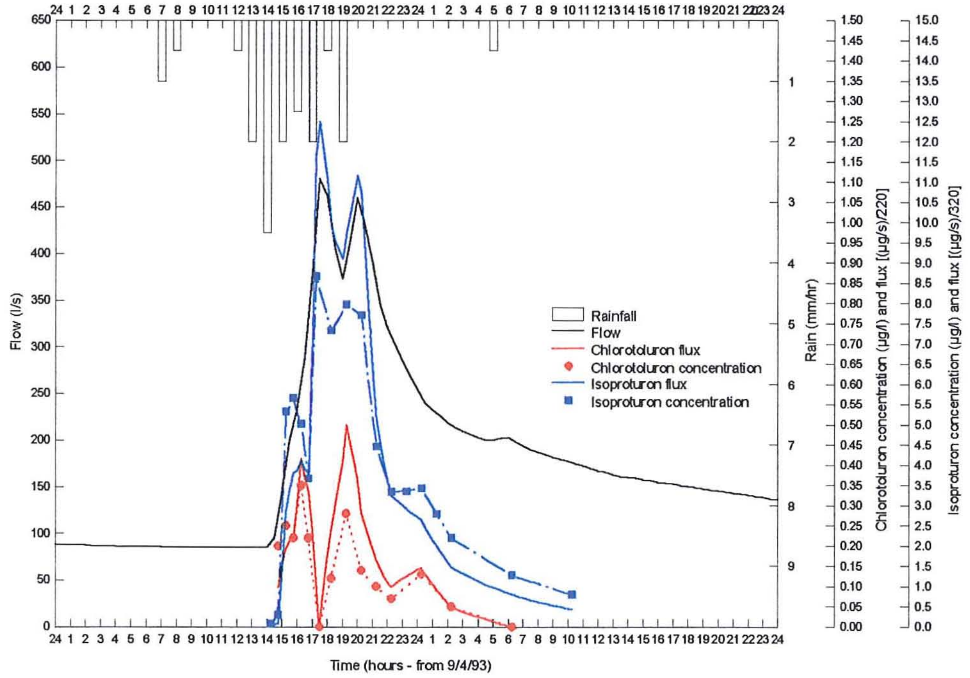


Figure 6-20 Chlorotoluron and isoproturon concentrations and fluxes at site A during the storm event occurring on 9/4/93 (JD 99) (Rainfall intensities (bar chart) and storm runoff also shown)

Therefore, it was possible that the three isoproturon concentration peaks may have represented three separate geographic contributions, that were also separated by time, from the treated fields (Middle Lawns, Hither Lawns, and Little Park Hall; Figure 6-1). To substantiate this argument, it would have been necessary to monitor the rainfall distribution and to locate, monitor, and sample the main drainage channels of the three fields in addition to the operation of the monitoring station at site A.

Chlorotoluron was first detected in the second sample at a concentration of 0.20μgl^{-1} and then increased to its first concentration peak at 0.35μgl^{-1} which occurred approximately half an hour after the first isoproturon peak and one and a half hours before the first hydrograph peak (Figure 6-20). The following samples showed the chlorotoluron concentration decreasing to a point of no detection that coincided exactly with the first hydrograph peak. The next two samples showed the chlorotoluron concentration increase again to a second peak at a concentration of 0.28μgl^{-1} which occurred approximately 30 minutes before the second hydrograph peak. Over the next eleven hours, the chlorotoluron concentration decayed in an exponential manner to a point of no detection. The presence of the two chlorotoluron peaks may also have been the result of the storm rainfall distribution which in this case leached chlorotoluron from two geographically different sources from within the agricultural sub-catchment.

6.3.5 Results from the storm event of 25/4/93 (Julian day 115)

6.3.5.1 Chlorotoluron and isoproturon

This was the fourth monitored storm event in April and occurred 81 days after the isoproturon application. The event occurred after 9.5mm of rainfall, with a peak intensity of 2.5$mmhr^{-1}$, had fallen onto the agricultural sub-catchment producing two flow peaks, at 225ls^{-1} and 202ls^{-1} (Figure 6-21). The pattern of split hydrograph and multi-peak isoproturon and chlorotoluron concentration curves makes this event very similar to that of 9/4/92 and therefore was probably the result of a similar rainfall distribution where the rainfall front moved up the agricultural sub-catchment, towards the south-west.

Isoproturon and chlorotoluron were detected in all eighteen samples obtained during the event. During the event chlorotoluron and isoproturon each produced three flux curve peaks. For chlorotoluron, values of 69μg/s, 23μg/s and 26μg/s were observed; the first peak coinciding with the first peak of the hydrograph, the second occurring 120 minutes later, and the third flux peak coinciding with the second peak of the hydrograph. For isoproturon, values of 586μg/s, 390μg/s and 301μg/s were obtained. The first and second flux peaks occurred 30 and 120 minutes after the first peak of the hydrograph whilst the third flux peak coincided with the second peak of the hydrograph. The integration of the hydrograph together with the isoproturon and chlorotoluron-flux curves showed that during the sampling period of the event, 9.41g of isoproturon and 0.76g of chlorotoluron were removed from the catchment in 7.15×10^6 litres of event runoff. The application losses were $2.3 \times 10^{-2}\%$ and $9.7 \times 10^{-4}\%$ and the event mean concentrations, based on direct runoff only, were $0.30\mu gl^{-1}$ for chlorotoluron and $3.68\mu gl^{-1}$ for isoproturon.

The isoproturon-concentration curve demonstrated three distinct peaks, with the first and second concentration peaks occurring approximately at 30 minutes and two hours after the first hydrograph peak and the third concentration peak occurring one hour after the second hydrograph peak. The values of the three peak concentrations were $2.69\mu gl^{-1}$, $2.17\mu gl^{-1}$, and $1.59\mu gl^{-1}$ respectively. Unlike the exponential decay observed in the three previous storm events, in the two hours following the last concentration peak, the isoproturon concentration decreased rapidly to a value of no detection. This rapid decrease in concentration may suggest that the isoproturon source represented by the peak may have been reaching a point of exhaustion.

Chlorotoluron was detected in the first sample at $0.20\mu gl^{-1}$ and then increased to its maximum concentration of $0.31\mu gl^{-1}$ which coincided with the first hydrograph peak. Subsequent samples showed the chlorotoluron concentration gradually decreasing in an exponential manner to a point of no detection, nine hours after the concentration peak.

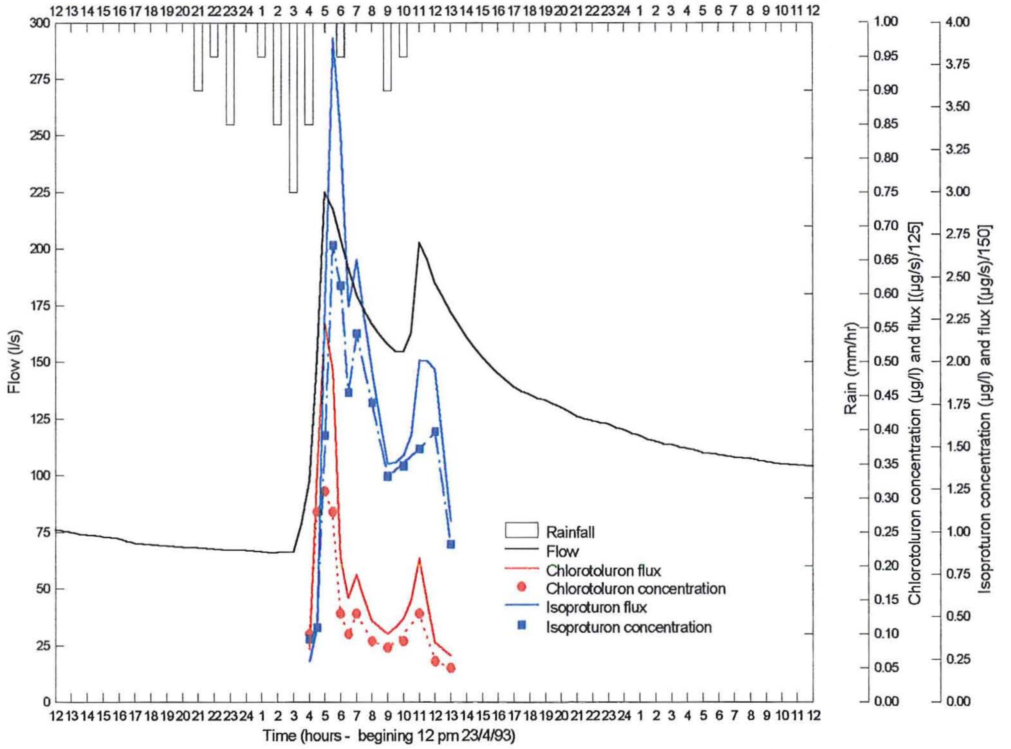


Figure 6-21 Chlorotoluron and isoproturon concentrations and fluxes at site A during the storm event occurring on 25/4/93 (JD 115) (Rainfall intensities (bar chart) and storm runoff also shown)

6.4 Discussion and interpretation of storm event runoff data from the agricultural sub-catchment

The storm event herbicide data described in Sections 6.2 and 6.3 are summarised in Tables 6-8, 6-9 and 6-10. Table 6-8 shows the maximum concentration of each pesticide detected during the sampled storm events and also, where known, the period of time elapsed between herbicide application and the occurrence of a storm event. The dates on which the storm events occurred are also represented using the Julian day convention. Table 6-9 shows the actual mass of each herbicide transported during the sampled storm events and also the percentage loss with respect to application mass. The storm event mean concentrations for each herbicide detected during the eleven storm events are shown in Table 6-10. For each event two values are given; the first value relates to the total herbicide mass transported during the storm event sampling period by the total runoff volume during the same period and the second value relates only to the herbicide mass transported during the period when direct runoff occurred.

Table 6-8 Summary of storm event maximum pesticide concentrations and elapsed time between pesticide application and storm event

Event	Date	Maximum storm event concentration (µg/l)				Time from application (days)			
(JD)		Simazine	Atrazine	Chlorotoluron	Isoproturon	Simazine	Atrazine	Chlorotoluron	Isoproturon
122	1/5/92	0.29	0.21	0.79	1.00	155	na	186	177[1]
226	13/08/92	0.6	0.16	1.47	0.29	259	na	290	271[1]
276	02/10/92	0.33	0.09	1.62	0.27	309	na	340	321[1]
294	20/10/92	0.11	0.11	0.73	nd	327	na	358	339[1]
314	09/11/92	0.13	0.03	2.23	0.08	347	na	378	359[1]
320	15/11/92	nd	nd	1.00	nd	353	na	384	365[1]
6	06/01/93	nd	nd	0.66	nd	404	na	436	417[1]
91	01/04/93	nd	nd	0.26	10	489	na	521	57
95	05/04/92	nd	nd	0.24	8.79	493	na	525	61
99	09/04/92	nd	nd	0.35	8.67	497	na	529	65
115	25/04/93	nd	nd	0.31	2.69	510	na	545	81

[1] The isoproturon time from application was taken as a weighted average between 167 and 186 days

As discussed in Section 5.2.3, it was considered that during the 1992/93 winter period, the baseflow component of the total runoff was augmented with spring water that was supplied from a source from outside the agricultural sub-catchment.

Table 6-9 Summary of storm event herbicide loadings and percentage losses in runoff

Event	Date	Event pesticide load [Total runoff] (µg)				Event pesticide load [% loss)			
(JD)		Simazine	Atrazine	Chlorotoluron	Isoproturon	Simazine	Atrazine	Chlorotoluron	Isoproturon
122	1/05/92	265419	133444	333026	438275	0.003	na	0.0004	0.001
226	13/8/92	845952	317258	2673538	595296	0.009	na	0.0034	0.001
276	02/10/92	3261841	362140	15650163	3361696	0.036	na	0.0200	0.006
294	20/10/92	2861553	1625589	16850312	nd	0.032	na	0.0215	nd
314	09/11/92	478862	40139	3630597	nd	0.005	na	0.0046	nd
320	15/11/92	nd	nd	835072	nd	nd	na	0.0011	nd
6	06/01/93	nd	nd	2069868	nd	nd	na	0.0026	nd
91	01/04/93	nd	nd	409285	64829043	nd	na	0.0005	0.163
95	05/04/93	nd	nd	551716	34084875	nd	na	0.0007	0.086
99	09/04/93	nd	nd	1899732	81013132	nd	na	0.0024	0.204
115	25/04/93	nd	nd	767101	9409006	nd	na	0.0010	0.024
Total load		7713629	2478570	45670411	4395268 [1] 189336055 [2]	0.085		0.058	0.008 [1] 0.477 [2]

nd: no detection, na: no application data available, [1]total mass lost for first application, [2]total mass lost for second application

Since the volume of spring flow was unknown, it was impossible to take into account the effect it had on the dilution of the herbicide concentration in the total runoff. Therefore, the storm-event mean concentration based on direct runoff only was considered to be a more accurate value and particularly important for comparison purposes. The storm event mean concentrations, based on direct runoff volume, for each herbicide during each of the sampled storm events are represented diagrammatically in Figure 6-22. The herbicide data summarised in Tables 6-8, 6-9 and 6-10 and shown in Figure 6-22 are considered and fully discussed.

Table 6-10 Summary of storm-event mean concentrations of herbicide in both total runoff and direct runoff

Event	Date	Total runoff EMC (µg/l)				Direct runoff only EMC (µg/l)			
(JD)		Simazine	Atrazine	Chlorotoluron	Isoproturon	Simazine	Atrazine	Chlorotoluron	Isoproturon
122	1/05/92	0.21	0.1	0.25	0.34	0.28	0.15	0.37	0.49
226	13/08/92	0.33	0.12	1.03	0.23	0.34	0.13	1.09	0.24
276	02/10/92	0.2	0.06	0.98	0.21	0.26	0.07	1.28	0.28
294	20/10/92	0.1	0.07	0.59	nd	0.1	0.08	0.63	0.08
314	09/11/92	0.07	0.03	0.57	nd	0.12	0.04	1.15	nd
320	15/11/92	nd	nd	0.45	nd	nd	nd	0.79	nd
6	06/01/93	nd	nd	0.23	nd	nd	nd	0.65	nd
91	01/04/93	nd	nd	0.2	3.64	nd	nd	0.33	10.35
95	05/04/92	nd	nd	0.16	3.37	nd	nd	0.36	16.69
99	09/04/92	nd	nd	0.11	4.25	nd	nd	0.18	7.24
115	25/04/93	nd	nd	0.13	1.63	nd	nd	0.3	3.68

6.4.1 Simazine and atrazine

An application of simazine (9.027kg) was made to the agricultural sub-catchment on 28/11/91 (JD 332) but due to the below average rainfall during the 1991/92 winter, the first significant detected storm event did not occur until 155 days after the application on 1/5/92 (JD122). Simazine was detected in four further storm events, the last one occurring on 9/11/92 (JD314) which was 347 days after application. The data in Table 6-8 show that simazine was detected during storm event conditions at a concentration above the limit of the EC Drinking Water Directive (0.1μgl^{-1}) 347 days after application. The maximum concentration detected (0.6μgl^{-1}), occurred 259 days after application during the storm event of 13/8/92. The direct runoff event mean concentrations for each storm event were 0.28μgl^{-1}, 0.34μgl^{-1}, 0.26μgl^{-1}, 0.1μgl^{-1}, and

$0.12\mu g l^{-1}$. The gradual decrease in event mean concentration to a point of no detection (Figure 6-22), probably represented the degradation of simazine in the soil matrix due to biochemical decay. Simazine and isoproturon were applied at similar times, therefore the disappearance of isoproturon approximately one month before the disappearance of simazine (see Section 6.4.2) confirms the order of half-life values given in Table 6-4. The total loss of simazine in runoff during the five monitored storm events was 0.09% of that applied.

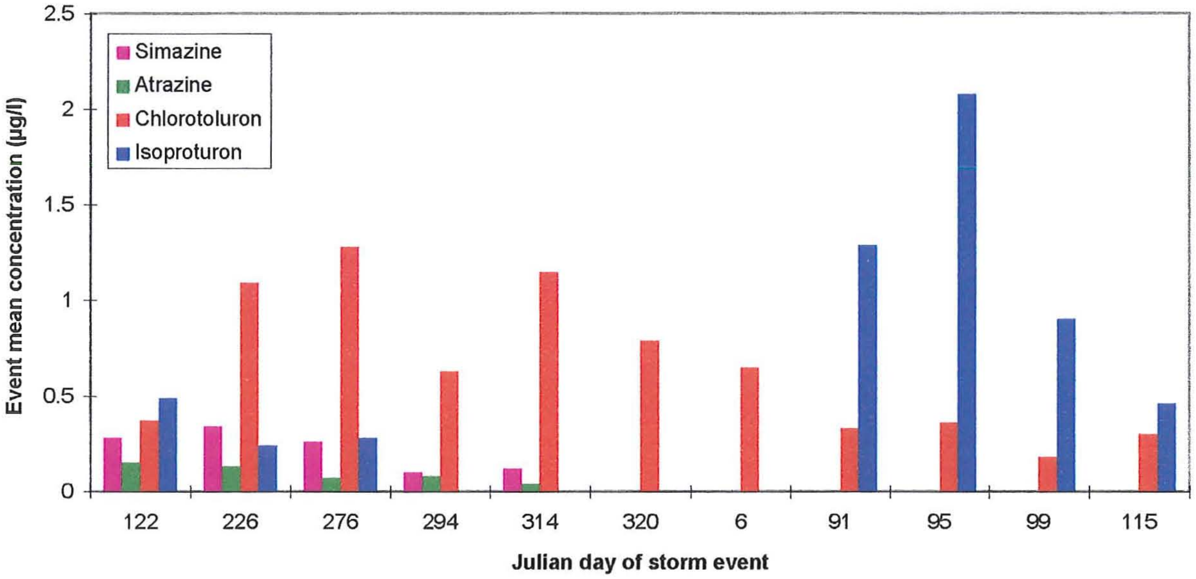


Figure 6-22 Herbicide event mean concentration, based on direct runoff, for each storm event sampled during the course of monitoring programme [For events JD 91 to JD 115 the isoproturon data shown has been divided by a factor of eight]

The maximum concentration of atrazine detected was $0.21\mu g\ l^{-1}$ during the first-monitored storm event of 1/5/92 (Table 6-8). Atrazine was detected in the same events as simazine and a similar gradual decrease in event mean concentrations was observed (Figure 6-22). Although no atrazine application data was available, given the similar patterns of occurrence and similar physico-chemical properties (Table 6-4), it could be proposed that atrazine and simazine were applied in similar quantities and at the same time. Turnbull (1995) found a similar parallel occurrence between simazine and atrazine in storm runoff at Rosemaund, where only an application of simazine was recorded. In this case it was considered that a fraction of the simazine may have transformed into atrazine via isomerisation. However, examination of the five simazine and atrazine pollutographs in Figures 6-6, 6-8, 6-10, 6-12, and 6-14 suggests that the sources of the two herbicides were different. Generally, simazine tended to respond in parallel with the storm hydrograph, suggesting transport in direct runoff, whereas the atrazine concentration remained reasonably constant throughout the hydrograph suggesting transport in the baseflow. Whereas the source of the simazine was the application to Little Park Hall field on 28/11/91, the source of the atrazine was likely to be from a different location. Considering its main use at the time was non-agricultural, it was possible that the source of atrazine was an application to the M11 motorway. If this was the case, it was possible that application residues were transported in storm runoff, through the road drainage system, into the underlying sub-soil layer and groundwater to then emerge in the baseflow at site A.

6.4.2 Chlorotoluron and isoproturon

An application of chlorotoluron (78.330kg) was made to the agricultural sub-catchment on 28/10/91 (JD 301) but, as for simazine, due to the below average rainfall during the 1991/92 winter, the first significant storm event and herbicide detection did not occur until 1/5/92 (JD122), which was 186 days after application. Subsequently, unlike the three other herbicides, chlorotoluron was detected in every storm event sampled including the last storm event occurring 545 days after application on 25/4/93 (JD115) (Table 6-8). The prolonged occurrence of chlorotoluron was probably the result of its persistence in the organic content of the soil matrix as defined by its relatively long half-life ($t_{1/2}$ 140 days) and high soil organic carbon partition coefficient (K_{oc} 190) (Table 6-4). Cable *et al* (1994) report a similar behaviour by chlorotoluron during an experiment at Brimstone Farm, where chlorotoluron was detected in field drainage water approximately eighteen months after its application. In this study, chlorotoluron was detected in storm runoff at concentrations three times above the EC Drinking Water Directive (0.1μgl) 545 days after application. The maximum detected concentration of chlorotoluron was 2.23$\mu g l^{-1}$ during the storm event of 9/11/92 which was 378 days after application.

Due to constant microbial degradation, it was considered that the event mean concentration of chlorotoluron would decay in an exponential manner after the first storm event on 1/5/92. However the chlorotoluron event mean concentrations increased over the next two sampled storm events before beginning to decrease (Figure 6-22). The anomalously low chlorotoluron event mean concentration of the storm event of 20/10/92 (JD294) may possibly be explained by excessive dilution from the largest volume of direct runoff recorded during the monitoring programme. The hydrochemical correlation analysis described in Section 6.4.3 does not suggest that the variation of the chlorotoluron event mean concentrations could be associated with hydrological variables such as rainfall volume and rainfall intensity. However, the variation may be explained through consideration of the temporal soil-sorption behaviour of chlorotoluron, as initially discussed in Section 6.2.3.1. During the generally dry period between the chlorotoluron application and the onset of significant runoff from the agricultural sub-catchment, the soil moisture deficit of the catchment would have been relatively high and may have allowed chlorotoluron molecules to occupy vacant sorption sites on the soil surfaces that were normally occupied by more-polar water molecules. As the wetness of the catchment increased during Autumn 1992 the greater abundance of the water molecules may have displaced the chlorotoluron molecules into soil water, thus increasing the mass of chlorotoluron available for leaching, leading to higher chlorotoluron event mean concentration values. With time this effect would have diminished and have been superseded by the effect of microbial degradation, reducing the mass of chlorotoluron available for leaching and producing lower chlorotoluron event mean concentration values. The concept of this argument has been more widely discussed by Koskinen and Harper (1990). The total loss of chlorotoluron in runoff during the eleven monitored storm events was 0.058% of that initially applied.

Two applications of isoproturon were made to the agricultural sub-catchment. The first was between 28/10/91(JD 301) and 16/11/91 (JD 310) and the second was on 3/2/93 (JD 34). After the first application (60.780kg), isoproturon was detected in four storm events beginning with the storm event of 1/5/92 (JD122) which was 186 days after application (Table 6-7). The last detection of isoproturon occurred 359 days after the first application, during the storm event of 9/11/92 (JD314), where it was only detected once at a concentration of $0.08\mu gl^{-1}$. The isoproturon event mean concentration values for each storm event were $0.49\mu gl^{-1}$, $0.24\mu gl^{-1}$, $0.28\mu gl^{-1}$, and $0.08\mu gl^{-1}$. The gradual decrease in the event mean concentration values to a final point of no detection (Figure 6-22), probably represented the degradation of isoproturon in the soil matrix due to biochemical decay. The data in Table 6-8 showed that during storm event conditions isoproturon was detected at a concentration approximately three times higher than the limit of the EC Drinking Water Directive (0.1μgl^{-1}) 321 days after application. The maximum concentration detected was 1.00μgl^{-1} which was during the storm event of 1/5/92, 177 days after last 1991 application. Chlorotoluron and isoproturon were applied at similar times and therefore the relatively rapid disappearance of isoproturon compared to chlorotoluron confirms the order of the half-life values given in Table 6-4, i.e. 55 days for isoproturon and 140 days for chlorotoluron. In the first storm event of 1/5/92, the higher isoproturon event mean concentration probably reflects its greater mobility compared to chlorotoluron, which is due to its lower tendency to partition with soil organic matter (as defined by its lower K_{oc} value of 107 compared to that of chlorotoluron (K_{oc}; 190)). In the subsequent storm events where isoproturon and chlorotoluron were detected, the order of the event mean concentration values were reversed, which probably reflected the more rapid degradation of isoproturon due to its shorter half-life.

The second application of isoproturon (39.692kg) was made to the agricultural sub-catchment on 3/2/93 (JD34) during a particularly dry period. After 57 days without any significant rain the first storm runoff event occurred on 1/4/93 (JD91) and this was shortly followed by three further storm events on 5/4/93 (JD95), 9/4/93 (JD99), and 25/4/93(JD115). For presentation purposes the isoproturon event mean concentration values shown in Figure 6-22 have been divided by a factor of eight. The isoproturon event mean concentration for the first event was 10.35μgl^{-1}, and the values for the second, third, and fourth events were 16.69μgl^{-1}, 7.24μgl^{-1}, and 3.68μgl^{-1} respectively. Apart from the second event mean concentration value, the observed decrease in isoproturon event mean concentration values decrease exponentially. The high second value was not associated with hydrological variables and may possibly be explained using the same soil-sorption argument as applied to chlorotoluron, considering that the period during and after the isoproturon application was unusually dry. The data in Table 6-8 shows that isoproturon was detected, during storm event conditions, at a concentration approximately twenty-seven times higher than the limit of the EC Drinking Water Directive (0.1μgl^{-1}) 81 days after application. The maximum concentration detected was 8.79μgl^{-1}, 61 days after application during the storm event of 5/4/93. The total loss of isoproturon during the four monitored storm events following the second application was 0.477% of that applied (Table 6-9). This value agrees with similar work on isoproturon carried out on small catchment and field plot sites where runoff has occurred during similar time scales (Brown *et al*, 1995; Williams *et al* 1995; Harris *et al*, 1994).

The runoff data from the two consecutive isoproturon applications clearly show the importance to seasonal isoproturon loss of the storm event timing in relation to application. To illustrate this more clearly, the runoff data for the first sampled storm events after each application are shown in Table 6-11, along with the total monitored loss of isoproturon. Although other factors will have had some influence on the fate of isoproturon during the two monitoring periods, such as half-life variations due to differences in soil temperature and soil moisture content, as other research has found (Williams *et al*, 1995), the period between the pesticide application and the first storm event had a significant effect on the amount of pesticide lost. The data in Table 6-11 compare the isoproturon data for the first storm event to be sampled after the autumn 1991 isoproturon application, with the data for the first storm event to be sampled after the early spring 1993 application. Clearly, the isoproturon removed from the catchment for the storm event that occurred 57 days after application was much higher than that which occurred 177 days after application. The isoproturon direct runoff event mean concentration was 21 times higher; the percentage loss was 310 times higher; and the cumulative loss from all the storm events sampled after the application was 119 times higher.

Table 6-11 Comparison of isoproturon runoff data for the first sampled storm event after application and total monitoring loss for the 1991/92 and 1992/93 crop seasons

Crop season	Mass applied (kg)	Time from application (days)	Maximum concentration (μg/l)	Event mean concentration (μg/l)	Percentage loss over first post application event	Total % loss over monitoring period
1991/92	60.780	177	1.00	0.49	0.0001	0.008
1992/93	39.692	57	10.00	10.35	0.163	0.477

The timing of the 1993 application and monitoring of isoproturon at North Weald coincided remarkably well with a similar experiment based at Wytham Farm, Oxfordshire (Johnson *et al*, 1994). This experiment involved the monitoring of a 0.18 ha field plot in which instruments had been installed to measure and sample the overland runoff and the soil drainage from an isolated field drain. Isoproturon was applied at a rate of 2.45kgha^{-1} to the plot on 10/2/93. Fifty days later, on 1/4/93, a storm event occurred during which the resultant runoff was sampled from the two sites by an autosampler. The results for the two storm events are shown in Table 6-12 along with the results from the North Weald storm event on 1/4/93.

Table 6-12 Comparison of simultaneous isoproturon runoff event data on 1/4/93 at North Weald and Wytham Farm Oxfordshire (Johnson *et al*, 1994)

Site	Type	Total area (ha)	Application area (ha)	Rate (kg/ha)	Mass applied(kg)	Date of application	Date of first storm event	Time from application (days)	% loss	emc. (μg/l)
NW	Catchment	160	23.61	1.68	39.692	3/2/93	1/4/93	57	0.1	10.35
WF	Field plot	0.18	0.18	2.45	0.441	10/2/93	1/4/93	50	0.5	357

NW: North Weald, WF: Wytham Farm; emc: event mean concentration

On comparing catchments, the Wytham Farm field plot was 0.11% of the area of the North Weald agricultural sub-catchment; with respect to application areas the Wytham Farm plot was 0.76% of the area that received isoproturon at North Weald; further the two sites both had very similar heavy clay soils. No rainfall data was available from Wytham Farm (Johnson *et al*, 1994), but it was probable that the rainfall at both sites was from the same frontal system and may have had similar duration and intensity. When the differences in scale between the two sites are taken into account, the agreement between the percentage loss of isoproturon at the two sites was very good. The agreement may have been even closer if the period between application and rainfall had been the same. Although only comparing one storm event, the result adds weight to the argument of a number of researchers that the use of field plots is representative of larger systems and in many ways more useful since they can be more intensively controlled and monitored (Ronnefahrt *et al*, 1997; Wauchope *et al*, 1993).

6.4.3 Correlation analysis of hydrological and hydrochemical storm event data

In order to identify the significance of hydrological variables, the herbicide storm runoff data shown in Tables 6-8, 6-9 and 6-10 have been correlated with the related storm event hydrology data derived from the hydrological analysis of selected storm events (see Chapter 5). The combined hydrological–hydrochemical dataset is shown in Tables 6-13 and 6-14 and the resultant correlation matrix is shown in Table 6-15.

The data in Table 6-13 show the hydrological parameters associated with the ten storm events sampled at site A during the monitoring period. The hydrochemical herbicide data shown in Tables 6-8, 6-9 and 6-10 are summarised in Table 6-14. The hydrological and hydrochemical data in Table 6-13 and Table 6-14 were linearly regressed (using Microsoft Excel©–Version 5.0) against each other and the results shown as a correlation matrix in Table 6-15. The procedure was carried out in order to identify hydrological variables that may significantly affect the transport of the four monitored herbicides in storm event runoff.

Table 6-13 Hydrological data from the ten storm events sampled at site A during the course of the monitoring programme.

JD	RI	RV	LAG	PF	TR	BFV	DRV	%BFV	%DRV	WB	ED	C	ADP
122	3.5	9.5	260	35.5	0.76	0.25	0.51	33	67	5.45	18	0.023	60.5
226	6.5	23.5	480	97.7	2.81	0.49	2.32	17.5	82.5	9.9	33	0.034	19.7
276	4	17.5	200	434	6.87	1.86	5.01	27	73	29	14	0.244	50.2
294	9.5	49.5	231	1148	27.73	4.63	23.1	17	83	47	38.5	0.272	214.4
314	3	12	145	350	4.43	1.71	2.71	38.8	61.2	22.6	14	0.262	164.2
320	5	7.5	77	326	2.66	1.31	1.34	49.4	50.6	18	7	0.147	80.8
6	2	7.5	142	355	5.75	3.62	3.16	53	46	42	13	0.458	18.5
91	5	17.5	103	440	7.85	3.38	4.5	43	57	25.7	17	0.198	15.8
95	2	8	260	240	4.84	2.55	2.28	53	47	29	18.5	0.27	31.5
99	3.5	30.5	354	525	14.28	6.63	7.64	46	54	25	28	0.289	90.2
115	2.5	9.5	220	225	4.468	na	na	na	na	47	na	0.2023	na

JD: Julian day on which event occurred
RI: Peak rainfall intensity during event (mmhr^{-1})
RV: Volume of rainfall during duration of event (mm)
LAG: Period between rainfall centroid and peak hydrograph flow (min)
PF: Peak hydrograph flow (l/s)
TR: Total volume of runoff during of event (mm)
BFV; Volume of baseflow during event (mm)
DRV: Volume of direct runoff during event (mm)
%BFV: Percentage baseflow wrt total volume of runoff
%DRV: Percentage direct runoff wrt total volume of runoff
WB: Event water balance (%)
ED: Event duration (hrs)
C: Runoff coefficient
ADP: Antecedent dry period (hrs)
na: no data available

The correlation matrix (Table 6-15) shows the correlation coefficients for the linear regressions between the hydrological and the hydrochemical herbicide data. Linear regression analysis of a larger dataset of hydrological-only variables, taken from the rainfall-runoff record for the agricultural sub-catchment, was examined and has been discussed in Chapter 5. The correlation coefficients significant at a 95% confidence level are shown in bold type and underlined. Since it was known that all herbicides, once applied, degraded following an exponential relationship (Bollag and Liu, 1990; Wolfe *et al*, 1990; Helweg, 1993; Nicholls *et al*, 1993); those regressions involving 'time from application' data were exponential rather linear. The results of the regression analyses for each herbicide are discussed in the following sections.

Table 6-14 Hydrochemical data from the ten storm events sampled at Site A during the course of the monitoring programme.

JD	Semc	Aemc	Cemc	Iemc	Spk	Apk	Cpk	Ipk	Closs	Iloss	Sloss	Stfa	Ctfa	Itfa
122	0.28	0.15	0.37	0.49	0.29	0.21	0.79	1.00	4E-04	1E-03	0.003	158	186	177
226	0.34	0.13	1.09	0.24	0.6	0.16	1.47	0.29	0.003	1E-03	0.009	262	290	271
276	0.26	0.07	1.28	0.28	0.33	0.09	1.62	0.27	0.02	0.006	0.036	312	340	321
294	0.10	0.08	0.63	na	0.11	0.11	0.73	na	0.022	na	0.032	330	358	339
314	0.12	0.04	1.15	0.08	0.13	0.03	2.23	0.08	0.005	na	0.005	350	378	359
320	na	na	0.79	na	na	na	1.00	na	0.001	na	na	356	384	365
6	na	na	0.65	na	na	na	0.66	na	0.003	na	na	408	436	417
91	na	na	0.33	10.35	na	na	0.26	10	5E-04	0.163	na	492	521	57
95	na	na	0.36	16.69	na	na	0.24	8.79	7E-04	0.086	na	497	525	61
99	na	na	0.18	7.24	na	na	0.35	8.67	0.002	0.204	na	501	529	65
115	na	na	0.3	3.68	na	na	0.31	2.69	1E-03	0.0243	na	517	545	81

Semc: Simazine emc (μgl^{-1})[DRV]* Aemc: Atrazine emc(μgl^{-1})[DRV]
Cemc: chlorotoluron emc (μgl^{-1})[DRV] Iemc: Isoproturon emc (μgl^{-1})[DRV]
* emc calcuated with respect to direct runoff volume
Spk: Peak simazine concentration(μgl^{-1}) Apk: Peak atrazine concentration (μgl^{-1})
Cpk: Peak chlorotoluron concentration (μgl^{-1}) Ipk: Peak isoproturon concentration (μgl^{-1})
Closs: % chlorotoluron loss Iloss: % isoproturon loss
Sloss: % simazine loss na: no data available
emc: event mean concentration
JD: Julian day of storm event
Stfa: Period between simazine application and storm event (days)
Ctfa: Period between chlorotoluron application and storm event (days)
Itfa: Period between isoproturon application and storm event (days)

6.4.3.1 Simazine

Data from the correlation matrix (Table 6-15) show that a significant linear correlation existed between the maximum simazine concentration and both the rainfall-runoff lag time and the antecedent dry period for a given storm event. However, careful examination of the relationships which are also shown in Figure 6-23, suggests that the underlying factor that related the two variables for each relationship shown was the time between the simazine application and the occurrence of a given storm event. By cross-referencing the data labels of the charts in Figure 6-23 with the data in Table 6-13 and Table 6-14, the 'time from application' values were obtained.

For example, for the chart relating rainfall-runoff lag time to maximum event concentration, the data point labelled with a lag time of 480 minutes refers to an event that occurred 262 days after the simazine application and had a maximum event concentration of 0.6μg/l whereas the data point labelled with a lag time of 145 minutes refers to an event that occurred 350 days after the simazine application and had a maximum event concentration of 0.13μg/l—as the period between simazine application increased so the maximum event concentration decreased.

Table 6-15 Correlation matrix of hydrological-hydrochemical data from the ten storm events sampled at Site A during the course of the monitoring programme.

	RI	RV	LAG	PF	TRF	BFV	DRV	PBFV	PDRV	WB	ED	C	ADP	Stfa	Ctfa	Itfa
Semc	0.065	0.204	0.523	0.578	0.457	0.036	0.422	0.036	0.036	0.568	0.007	0.671	**0.957**	0.444	na	na
Aemc	0.006	0.017	0.476	0.243	0.107	0.085	0.081	0.085	0.085	0.412	0.074	**0.868**	0.358	na	na	na
Cemc	0.020	0.005	0.000	0.000	0.045	0.211	0.03	0.211	0.208	0.000	0.022	0.008	0.018	na	**0.819**	na
Iemc(I)	0.077	0.077	0.012	0.510	0.310	0.442	0.223	0.020	0.020	0.340	0.000	0.465	0.346	na	na	0.734
Iemc(ii)	0.026	0.09	0.000	0.024	0.947	0.740	0.391	0.657	0.657	0.336	0.441	0.188	0.367	na	na	0.761
Spk	0.010	0.058	**0.777**	0.392	0.287	0.161	0.260	0.161	0.161	0.383	0.023	0.520	**0.774**	0.101	na	na
Apk	0.014	0.004	0.363	0.161	0.054	0.093	0.036	0.093	0.093	0.301	0.077	0.754	0.285	na	na	na
Cpk	0.002	0.001	0.000	0.001	0.072	0.271	0.020	0.192	0.181	0.060	0.023	0.035	0.092	na	**0.806**	na
Ipk(I)	0.019	0.230	0.021	0.510	0.545	0.543	0.493	0.005	0.005	0.511	0.000	0.497	0.133	na	na	**0.902**
Ipk(ii)	0.261	0.167	0.007	0.367	0.000	0.167	0.001	0.453	0.453	0.957	0.446	0.140	0.966	na	na	**0.950**
Closs	0.289	0.431	0000	0.507	0.428	0.032	0.534	0.423	0.419	0.294	0.145	0.039	0.284	na	0.032	na
Iloss(i)	0.096	0.017	0.395	0.991	0.919	0.991	0.873	0.006	0.006	0.983	0.391	**1.000**	0.052	na	na	0.633
Iloss(ii)	0.457	0.779	0.033	**0.932**	0.845	0.714	0.914	0.657	0.660	0.974	0.437	0.000	0.363	na	na	0.465
Sloss	0.223	0.356	0.056	0.503	0.434	0.427	0.418	0.247	0.247	0.630	0.046	0.388	0.048	0.268	na	na

Iemc(i): Data relating to first isoproturon application; Iemc(ii); Data relating to second isoproturon application
Note, for key to other abbreviations see Table 6-14
Correlation coefficients significant at a 95% confidence level are shown in bold type and underlined.
The value at which correlation coefficients are significant varies with the size for the specific dataset.
Regressions involving Stfa, Ctfa, and Itfa are exponential

For the charts shown in Figure 6-23, the higher concentrations were associated with shorter 'time from application' values that appeared to coincidentally occur with longer rainfall-runoff lag time and shorter antecedent dry period times. As discussed above in Section 6.4.1, the simazine storm event mean concentrations and peak concentrations were observed to decrease as the period between the simazine application and the occurrence of a storm event increased. Therefore, it was probable that it was the 'time from application' effect rather than the variation in lag time and ADP that was the underlying factor that produced the simazine behaviour shown in Figure 6-23; to substantiate this suggestion further data would be required.

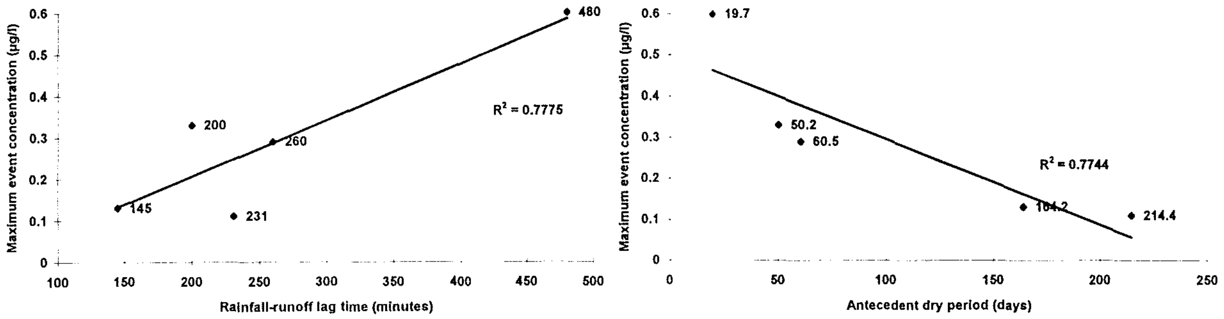


Figure 6-23 Relationship between peak simazine concentration and both rainfall-runoff lag time and antecedent dry period (data label refer to rainfall-runoff lag time {chart LHS} and antecedent dry period {chart RHS}

6.4.3.2 Atrazine

Examination of the correlation matrix shown in Table 6-15 shows that only one significant correlation was identified between the hydrological and hydrochemical variables. The highest value shown in the correlation matrix, relates to the relationship between the atrazine event mean concentration and the runoff coefficient, where a value of 0.868 was obtained. The runoff coefficient which relates rainfall intensity to peak runoff flow is considered to dependent on the imperviousness of the catchment surface (Shaw, 1991). From the description of the storm events that occurred during the monitoring programme, the transport of atrazine appeared to be connected with the baseflow component of event runoff which would have been somewhat independent from the event hydrology relating to the soil surface characterised by the runoff coefficient. Therefore it is considered that the relationship between atrazine event mean concentration and runoff coefficient is probably not real and may, similarly to simazine (6.4.3.1), be a function of the period between storm event occurrence and herbicide application timing. However, without atrazine application data this suggestion is impossible to verify.

6.4.3.3 Chlorotoluron

The regression coefficients generated by the regression analysis with respect to chlorotoluron were the most statistically robust of the four herbicides investigated, as they were derived from the dataset of eleven storm events which occurred throughout the period of the monitoring programme. Table 6-15 shows that there were no correlations between the chlorotoluron runoff data and the related hydrological data. However, significant correlation was observed between both the storm event mean concentration and the maximum event concentration with the time at which a given storm event occurred after the chlorotoluron application (Figure 6-24). The dataset used for the exponential regression omitted the data for the event of 1/5/92, since this produced an outlier which skewed the regression. It was considered that the outlier was the result of the anomalous soil-sorption phenomenon previously discussed in Section 6.4.2, which appeared to have retarded the mobility of chlorotoluron molecules during this period.

The data in Figure 6-24 shows that the chlorotoluron event mean concentration and the maximum event concentration follow an exponential decay with time. The behaviour shows very close similarity with the exponential decay associated with the degradation of herbicides in soils (Bollag and Liu, 1990). The half-life value derived for the event mean concentration was 108 days which was slightly below the half-life value due to soil microbial degradation of 135-143 days given in Table 6-4. The half-life value for the maximum event concentration was calculated at 87 days.

It is proposed that the decay behaviour of the chlorotoluron storm event mean concentration curve and the associated half-life value, demonstrate the underlying dependence of chlorotoluron on the soil-based degradation and also the dynamics of the chlorotoluron partitioning between soil particles and soil water. The manner in which the decay behaviour of the event mean concentration value mirrors the microbial decay of the herbicide in the soil may be possibly explained as follows. After application to the soil, the herbicide partitions itself between the soil water and soil particles, depending on the soil partition coefficient (K_d) for the particular pesticide-soil combination (Koskinen and Harper, 1990). The bio-available herbicide, dissolved in the soil water, begins to be broken down, principally by microbial degradation, and follows a exponential decay curve determined by the herbicide's chemical structure (Bollag and Liu, 1990). With the onset of a storm event, the rainfall rapidly displaces the original soil water which is of high pesticide concentration, and forces it through the soil column via the soil matrix or more rapidly through soil cracks if present, into the drainage system. As discussed in Section 3.1.3.2., the re-equilibration of the pesticide between the soil particles and soil water is unlikely to be instantaneous. Therefore, the pesticide concentration in the drainage water rapidly decreases as the mass of pesticide originally present in the soil water becomes exhausted. With the cessation of the storm event, the less dynamic movement of water through the soil matrix allows the equilibrium of the pesticide between the soil water and soil particles to be re-established, and the pesticide dissolved in the soil water again begins to undergo microbial degradation. With the onset of the next storm event the process is repeated. However, on this occasion the mass of the pesticide available in the soil water for displacement will be lower because of the pesticide degradation that has occurred since the previous storm event, but also because of the reduced pesticide mass available for degradation. Therefore, in a theoretical field system, if all other conditions remained constant and the volume of periodic storm event rainfall remained constant, the event mean concentration decay curve would almost mirror the soil degradation decay curve of an identical undisturbed field system. However, due to the pesticide mass displaced from the field system on receipt of periodic rainfall, the overall rate of decay of the event mean concentration curve would always be greater than that of the soil degradation decay curve. This mechanism may explain why the chlorotoluron event mean concentration half-life value of 108 days was lower than the accepted literature half-life value of 140 days due to soil degradation. The same argument could equally be applied to explain the relationship between the decay curve of the maximum event concentration and the decay curve for degradation in the soil. The lower half-life value for maximum event concentration decay curve compared to the event mean concentration decay curve may be explained by the source of the pesticide bearing soil water becoming physically less readily available with time.

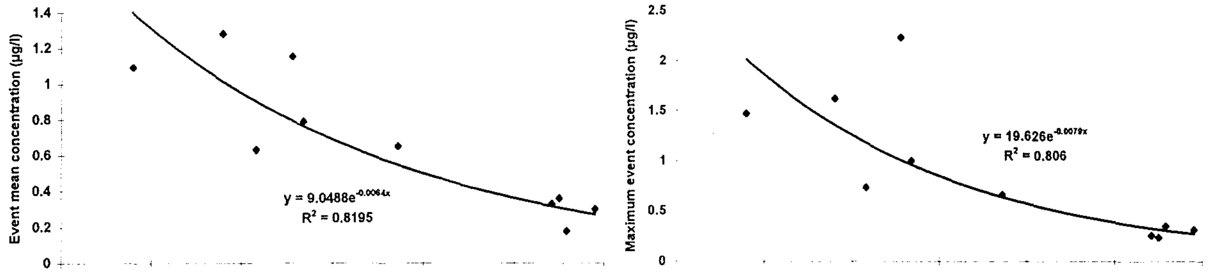


Figure 6-24 Relationship between chlorotoluron storm event mean concentration (shown on left) and maximum chlorotoluron concentration (shown on right), with the time from application of a given storm event

6.4.3.4 *Isoproturon*

Table 6-15 shows that there was no correlation between the two sets of isoproturon runoff data and the related hydrological data, apart from that between peak flow (PF) and isoproturon loss (Iloss (ii)) for the Spring 1993 application (Figure 6-25). This relationship may be explained through the association of peak flow rate with rainfall intensity as described by the rational formula (Section 5.2.2.1), in conjunction with the reported relationship between rainfall intensity and pesticide loss (Leonard, 1990; Johnson, 1995) Therefore, in this situation, peak flow and isoproturon loss would have probably increased with increasing rainfall intensity. The fact that peak flow rate and not rainfall intensity is related to isoproturon loss (Table 6-15) may be attributed to the much greater accuracy of the flow rate measurement. At Site A, the flow rate of the runoff from the entire catchment was sampled whereas rainfall was sampled over an area of approximately 314cm^2 and data assumed to be representative for the whole catchment (Shaw, 1991).

Although not statistically significant, a relatively high correlation coefficient between the isoproturon event mean concentrations and the timing of a storm event after the application was observed for both isoproturon applications. In view of the similar chlorotoluron behaviour discussed above, it was considered that the isoproturon correlations justified further investigation.

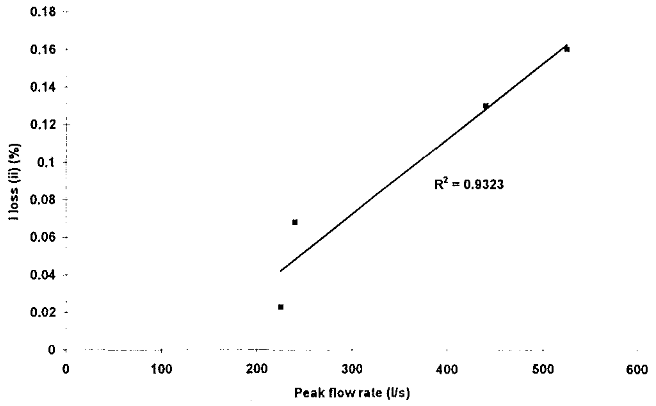


Figure 6-25 Relationship between peak flow rate and isoproturon loss for the Spring 1993 application

Figure 6-26 shows the event mean concentration decay curves for the autumn 1991 isoproturon application and the early spring 1993 application. As stated previously, it is known that all herbicides, once applied to soil, degrade following an exponential relationship, therefore the regression plots in Figures 6-26 and 6-27 are exponential rather than linear. The event mean concentration half-life values for the two applications were 83 days and 13 days respectively, compared to the soil degradation half-life value of 6 to 55 days (Table 6-4). The variation between the two event mean concentration half-life values can be explained by the difference in the age of the two datasets from which they were derived with respect to the time of the two isoproturon applications. The first half-life value represented a dataset that was sampled between 177 and 339 days after application, while the second half-life value represented a dataset sampled between 57 and 81 days after application. Beck *et al* (1995) showed that the isoproturon soil-partition coefficient (K_d) increased with the age of the sample; Wauchope and Myers (1985) reported similar behaviour for atrazine and linuron (Section 3.1.3.2). Therefore, as the soil partition coefficient increased with time the mass fraction of bio-available isoproturon available for degradation in soil solution would have decreased, in effect leading to greater persistence of isoproturon within the soil. Consequently, as the isoproturon soil persistence increased with time it was reasonable to expect that the isoproturon event mean concentration half-life value would also increase with time.

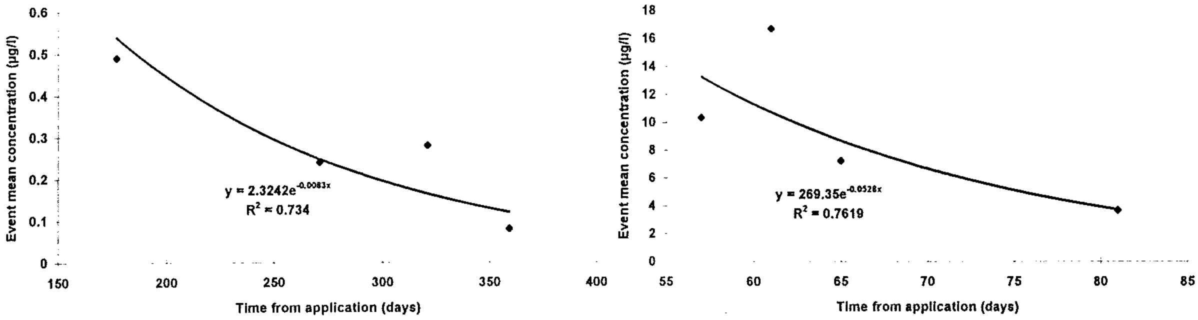


Figure 6-26 Relationship between isoproturon storm event mean concentration with the timing of a given storm event after application, for autumn 1991 application (shown on left) and the early spring 1993 application (shown on right)

This argument may explain the observed difference between the two event mean concentration half-life values. The half-life value of 13 days relating to the dataset generated from the early spring 1993 isoproturon application probably represented the situation where the association of isoproturon molecules with restricted sorption sites was relatively minor. Conversely, the half-life value of 83 days relating to the dataset generated from the autumn 1991 isoproturon application, probably reflected the situation where the soil-partition coefficient had increased and the association of isoproturon molecules with restricted sorption sites was relatively significant, with the effect of increasing the isoproturon soil persistence and the event mean concentration half-life.

Significant correlation was observed between the maximum event concentration and the timing of a given storm event after the isoproturon application. The two decay curves (Figure 6-27) represent the gradual decrease of the maximum event concentration with the time elapsed after the two isoproturon application. The half-life value for the maximum event concentration decay curve for the first isoproturon application was 58 days, and the value for the second application was 12 days. The difference between the two values was probably a combination of the soil-partition coefficient increasing with time and the source of the isoproturon-bearing soil water becoming physically less readily accessible with time

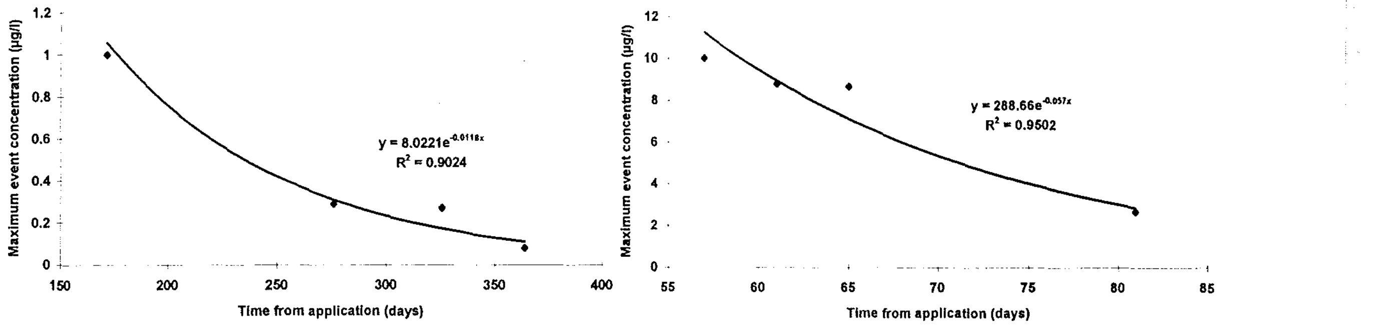


Figure 6-27 Relationship between isoproturon maximum event concentration with the timing of a given storm event after application, for autumn 1991 application (shown on left) and the early spring 1993 application (shown on right)

CHAPTER SEVEN

7. Pesticide runoff in the urbanised catchment

This chapter provides details of the pesticide applications made to the urbanised catchment together with descriptions of the storm events monitored at Site D during the monitoring period. For each storm event the pesticide concentration and flux data is described in relation to the storm event hydrograph recorded at Site D.

7.1 Pesticide applications within the urbanised catchment

Figure 7-1 shows a schematic map of the North Weald catchment which highlights the locations of the agricultural sub-catchment and the urbanised catchment. In contrast to the agricultural sub-catchment, the urbanised catchment was characterised by more diverse land usage, ranging from grassed and arable land to urban hard surfaces. These areas included agricultural land, areas of residential housing, grassed amenity areas, a railway line and an array of roads. Accordingly the nature of the land use dictated the type and quantity of pesticide used in each case. In order to construct a database of the pesticide inputs into the urbanised catchment during the period of the monitoring programme, the major pesticide users were identified and questioned regarding their pesticide application policy. The results are described in Sections 7.1.1, 7.1.2, 7.1.3, and 7.1.4 and are summarised in Table 7-1 which also includes pesticide applications made in the agricultural sub-catchment. As well as applications from major pesticide users, it was considered likely that a certain amount of pesticidal products may have been used during the period of the monitoring programme by private gardeners. However, it was decided that a survey of all the private addresses within the urbanised catchment would have been impractical. Instead, it was decided that during the interpretation of the monitoring data, an awareness that pesticide residues determined in storm event runoff samples may not be solely attributable to the major inputs should be maintained. In addition, they may have arisen as a result of minor domestic use or even misuse such as emptying or rinsing a garden sprayer down a sewer drain. Also shown in Figure 7-1 are agricultural fields which belonged to Cold Hall Farm, labelled 'Park', 'Big House Rick', 'Nineteen Acres' and an area of land owned by British Telecom labelled as 'BT Land' which was rented to a local arable-crop farmer.

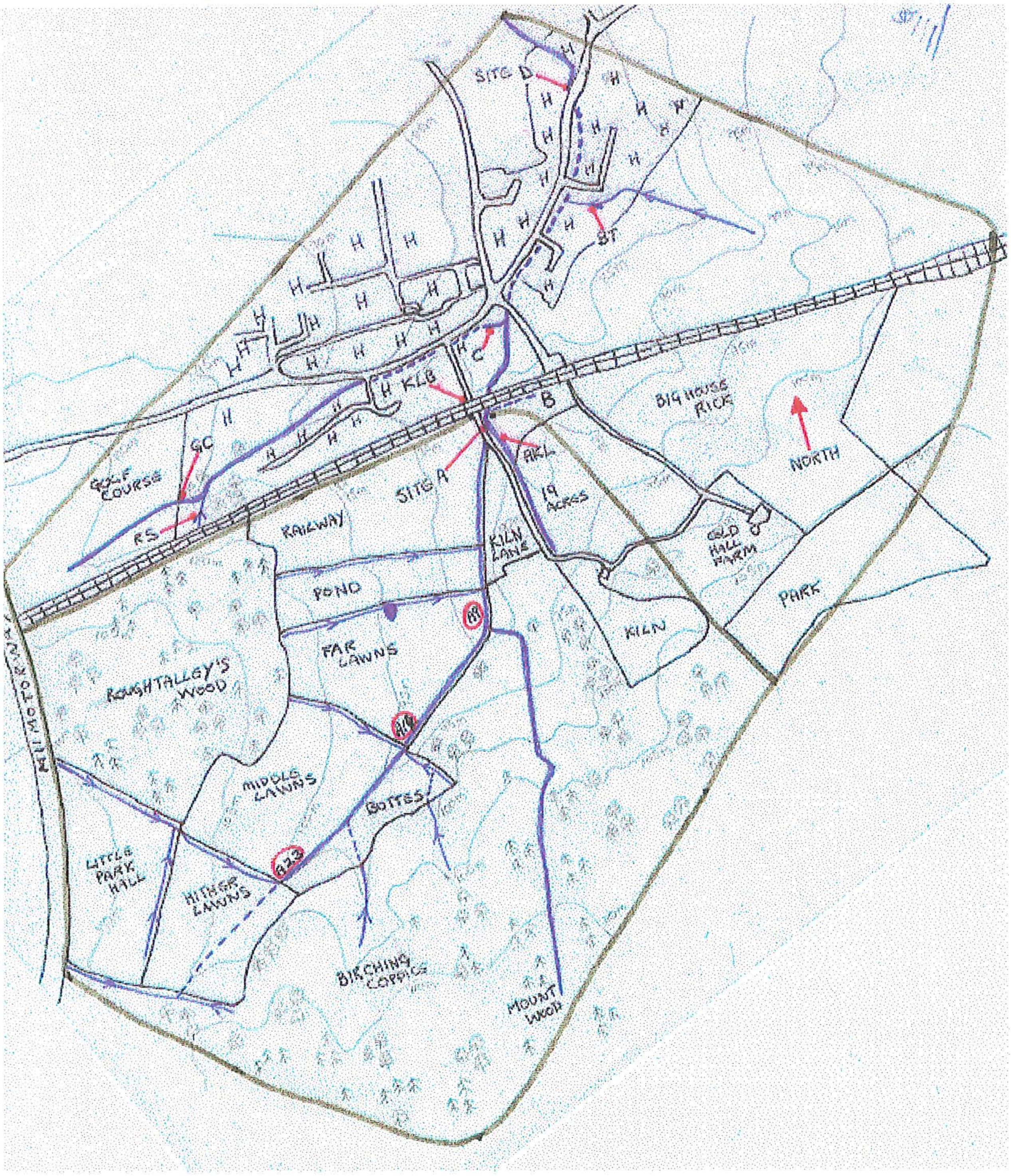


Figure 7-1 Schematic plan of the North Weald catchment showing the location and varying land use of the urbanised catchment

B- Manual sampling site, KLB - Kiln Lane Bridge manual sampling site, RS-Railway stream manual sampling site, GC-Golf course manual sampling site, C-manual sampling site, BT-British Telecom land manual sampling site

Table 7-1 Pesticide applications within the urbanised catchment: 1990-1993 (also showing applications made to agricultural sub-catchment)

Applicator	Application date	Amount of pesticide applied (Kg)					
		Simazine	Atrazine	Mecoprop	Isoproturon	Chlorotoluron	Diuron
1990							
LUL	11/3/90	0.346	na	na	na	na	na
PRD	January	na	0.065	na	na	na	0.083
RHD	May	na	na	na	na	na	0.800
ASC	*4/9/90*	*na*	*na*	*na*	*59.025*	*na*	*na*
ASC	*11/11/90*	*na*	*na*	*na*	*21.38*	*71.801*	*na*
CHF		na	na	na	na	na	na
BTL		na	na	na	na	na	na
Total ASC		*0*	*0*	*0*	*80.405*	*71.801*	*0*
Total UC		**0.346**	**0.208**	**0**	**0**	**0**	**0.883**
1991							
LUL	10/9/91	0.346	na	na	na	na	na
PRD	w/e 25/1/91	na	0.208	na	na	na	0.083
RHD	May	na	na	na	na	na	0.800
CHF		na	na	na	na	na	na
ASC	*28/10/91*	*na*	*na*	*na*	*13.055*	*78.330*	*na*
BTL	18/11/91	na	na	na	na	70.000	na
ACS	*6/11/91*	*na*	*na*	*na*	*25.25*	*na*	*na*
ACS	*16/11/91*	*na*	*na*	*5.394*	*22.475*	*na*	*na*
ACS	*28/11/91*	*9.027*	*na*	*na*	*na*	*na*	*na*
Total ASC		*9.027*	*0*	*5.394*	*60.780*	*78.330*	*0*
Total UC		**0.346**	**0.208**	**0**	**0**	**70.000**	**0.883**
1992							
LUL	29/10/92	na	na	na	na	na	0.461
PRD	w/e 8/2/92	na	0.208	na	na	na	0.083
RHD	5/5/92	na	na	na	na	na	0.867
CHF	14/4/92	na	na	18.99	na	na	na
ACS	*14/4/92*	*na*	*na*	*4.71*	*na*	*na*	*na*
BTL	15/11/92	na	na	na	na	na	na
Total ACS		*0*	*0*	*4.71*	*0*	*0*	*0*
Total UC		**0.0**	**0.208**	**18.99**	**0**	**0**	**1.411**
1993							
ASC	*3/2/93*	*na*	*na*	*na*	*39.692*	*na*	na
LUL	14/9/93	na	na	na	na	na	0.461
PRD	February	na	na	na	na	na	0.083
RHD	14/5/93	na	na	na	na	na	0.867
CHF		na	na	na	na	na	na
BTL		na	na	na	na	na	na
Total ASC		*0*	*0*	*0*	*39.692*	*0*	
Total UC		**0**	**0**	**0**	**0**	**0**	**1.328**

LUL-London Underground Limited, PRD-Epping Forest District Council, Parks & Recreation Department, RHD-Epping Forest District Council, Roads & Highways Department, CHF-Three fields of Cold Hall Farm (see Table 7-2 for details), BTL-British Telecom Land (see Table 7-2 for details), na-no application, #-Propyzamide reportedly used instead of atrazine but runoff data suggests not (see Section 7.4.3) ASC-Agricultural sub-catchment, UC-Urbanised catchment, Applications made to the agricultural sub-catchment are shown in italics

7.1.1 Pesticide applications to Cold Hall Farm and British Telecom land

Table 7-2 gives details of the pesticide applications made to the arable farmed land within the urbanised catchment before and during the monitoring period. For Cold Hall Farm, three fields named Big House Rick, Park and Nineteen acres were either wholly or partly located within the boundary of the urbanised catchment, and had a combined area of 31.65 hectares. During the first year of the monitoring programme (1991/92), the fields were sown with linseed which received an application of mecoprop (0.6Kg a.i./ha) on 14/4/92; during the second year of the monitoring programme (1992/93) the fields were sown with barley which received pesticide applications that were not included in the monitoring suite.

Table 7-2 Pesticide applications within the urbanised catchment to Cold Hall Farm and British Telecom land

Date	Herbicide	Location & total area (ha)	a.i. (g/l)	Rate (l/ha)	Amount (Kg)	Crop
14/4/92	Mecoprop	BHR, PF, NA (31.65)	600	1	18.99	Linseed
18/11/91	Chlorotoluron	BTL (28)	500	5	70	Winter barley

BHR: Big House Rick Field PF: Park Field NA: Nineteen acres field BTL: British Telecom Land

During the first year of the monitoring programme, the 28 hectares of land belonging to British Telecom, that was rented to an arable crop farmer, were sown with winter barley which received an application of chlorotoluron (2.5Kg a.i./ha) on 18/11/91. During the second year of the monitoring programme, the land was sown with linseed which received an application of a pesticide not included in the analysis suite. The field management and pesticide application data were obtained by liaison with the farm manager of Cold Hall Farm and the farmer renting the British Telecom land.

7.1.2 Pesticide applications by London Underground Limited to the Central Line at North Weald

On an annual basis, London Underground Limited sprayed their entire track network with herbicide in order to control vegetation for the following two safety reasons:

- Overgrown vegetation could cause a safety hazard to track maintenance workers.
- In summer months, dried weeds could easily catch fire and damage the electrical control cables that were located at the side of the railway track.

Herbicide applications were made using modified rolling stock referred to as the 'weed killing train' (see Plate 3-1). During any year, the time of an application to a particular section of the track network was determined by the requirement to conduct the spraying operation during passenger service hours, rather than during the optimum herbicide efficacy conditions. The length of track passing through the urbanised catchment was 2.08km, which was sprayed to a width of 4.44m, giving a total application area of 0.0923ha. Prior to 1992, London Underground Limited spraying operations were carried out using simazine which was applied using *controlled droplet application* (CDA) technology as described by De'Arth and Collins (1991). The herbicide was applied as a component of a product known as Simflow which was composed of amitrole (100g/l) and simazine (300g/l); the product was diluted by 50% and applied at a rate of approximately 25l/ha. In May 1992, the MAFF registration for the industrial use of triazine herbicides was withdrawn. Therefore subsequent herbicide applications were made using a mixture of diuron (500g/l) and glyphosate, with the diuron being applied at a rate of 10l/ha. Details of the London Underground Limited herbicide loads applied by spraying during the period of the monitoring programme are given in Table 7-1.

7.1.3 Pesticide applications made by the Parks and Recreation Department of Epping Forest District Council

Minor quantities of herbicides were used by the Parks and Recreation Department as an additional tool for the management of grassed public-amenity areas. The herbicides were employed to back up mechanical grass cutting operations where access for mowers was restricted. Applications were made using a CDA knapsack sprayer. From 1990 to 1992, the herbicide marketed as *Rassapron CDA* was used (amitrole, atrazine, diuron; 61, 139, 177 g/l a.i.). In 1993, due to MAFF restrictions, the use of atrazine was replaced by propyzamide. Applications were made by trained staff during the January to March period before the weeds had become well established. Details of herbicide applications that were made before and during the monitoring period are shown in Table 7-1.

7.1.4 Pesticide applications made by the Roads and Highway department of Epping Forest District Council

Herbicides were used by the Roads and Highways Department for the total control of vegetation on public roads for reasons of safety and aesthetics. Applications were made once a year, usually during

May, to road kerbstones and backwalls[1] which were sprayed to a width of 0.45 metres. During the monitoring period, the road spraying operations in North Weald were contracted out by Epping Forest District Council to Weedfree Limited (Goole, Humberside) who were contacted for application data. The application data obtained indicated the use of the product type: MSS Diuron 80 WP (80% diuron), at an application rate of 2.5kg/ha such that the amount of 2.0kg was applied in North Weald. Considering that approximately only 40% of the village was located within the boundary of the urbanised catchment, it was assumed that approximately 0.800kg a.i. was applied within the urbanised catchment. The kerbstones and backwalls were sprayed using a knapsack sprayer fitted with a conventional nozzle. Details of herbicide applications that were made before and during the monitoring period are shown in Table 7-1.

7.2 Results of runoff monitoring for 1992

The results discussed in this section cover the manual and automatic samples taken between March and November 1992 for the urbanised catchment. Unlike the seasonally based applications made to the agricultural sub-catchment, the pesticide applications made to the urbanised catchment reflected seasonal agricultural use as well as industrial and amenity use which occurred regularly throughout the year. As described in Section 5.3, because of the intermittent failure of the instrument monitoring stream-flow leaving the urbanised catchment at Site D, it was not possible to present a complete hydrograph showing both the rainfall and runoff that occurred during the monitoring period. Observations made during numerous site visits showed that unlike the agricultural sub-catchment, the urbanised catchment supported a baseflow throughout the monitoring period. This contrasts with the baseflow supported by the agricultural sub-catchment that was generally absent during the spring and summer seasons. This may have been caused by the Site A stream-bed being approximately four metres above the stream-bed at Site D and therefore unable to intersect with the depressed water table during the spring and summer seasons. Of the total area of the urbanised catchment (150ha), 20 ha was composed of hard impervious services such as roads and roofs where

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[1] A backwall defines the boundary of a pavement and, for example a garden, as opposed to a kerb stone which defines the boundary of a pavement and a road

runoff was rapidly drained to the water-course as it passed through the village. During the driest seasons such as Spring 1992, when the soil moisture deficit was high and vegetation interception was significant, runoff was generated at Site D during rainfall events whereas the stream bed at Site A remained almost dry. A typical rainfall event that illustrated this behaviour is described in Section 7.4.4 in which 25.5 mm of rainfall generated significant runoff at Site D but negligible flow resulted at Site A.

During the course of the monitoring programme the operation of the pesticide sampler trigger at Site D was problematic. Compared to Site A, the stream at Site D was generally polluted with dumped materials such as floating aluminium drink cans, and on a number of occasions the pesticide sampler was prematurely triggered by floating debris. During the spring and summer periods of the monitoring programme, the trigger switch was often smothered with clumps of algae and aquatic weeds which had been carried down the stream. This had the effect of disabling the trigger switch during storm events and preventing any samples from being taken.

During the monitoring period, manual samples were taken during non-storm conditions to supplement the samples taken automatically during storm events. During the non-storm condition, the flow leaving the urbanised catchment would have been entirely composed of baseflow runoff and therefore the manual sampling data represented the baseflow pesticide concentrations and also provided a reference point from which to assess the elevated pesticide concentrations during storm events. On the relatively infrequent occasions when a storm event coincided with a site visit, manual samples were taken at various points around the urbanised catchment outlet in an attempt to identify the exact source of a pesticide detected at Site D.

7.2.1 Results for 1992 and 1993 manual sampling

Details of the manual samples collected between March 1992 to March 1993 are given in the following sections for different groupings of herbicides.

7.2.1.1 Chlorotoluron, isoproturon and diuron

The analytical data for the manual samples collected from the urbanised catchment during the monitoring period are shown in Table 7-3; for comparison, the corresponding data for the manual samples taken within the agricultural sub-catchment are shown in Table 7-4. The first manual samples were taken on 6/3/92 (Julian Day 66) during non-storm conditions at Site D and at location C when the stream flow at Site D was less than 5l/s. The concentrations of chlorotoluron, isoproturon and diuron were 0.28µg/l, 0.26µg/l and (nd)µg/l respectively for Site D and (nd)µg/l for all three compounds at location C.

Table 7-3 Results for 1992 and 1993 manual sampling within the urbanised catchment

Date	Location	Flow	Pesticide concentration (µg/l)				
		(l/s)	Simazine	Atrazine	Chlorotoluron	Isoproturon	Diuron
6/3/92	Site D	< 5	0.45	0.69	0.28	0.26	nd
	C	< 5	0.21	0.24	nd	nd	nd
8/4/92	Site D	< 5	0.15	0.12	0.08	nd	0.14
	GC	< 5	nd	nd	nd	nd	nd
29/5/92	B	< 5	2.11	0.48	0.08	0.09	nd
	BT	~ 7	0.31	0.30	0.23	34.56	nd
	KLB	< 0.2	9.2	2.68	0.09	nd	nd
	GC	< 5	nd	nd	nd	nd	nd
6/11/92	Site D	< 50	0.18	0.07	0.11	nd	nd
	RS	na	1.26	0.36	nd	nd	nd
	GC	na	0.08	0.14	0.06	nd	nd
12/2/93	Site D	< 50	0.08	0.14	0.06	nd	nd
26/2/93	Site D	< 50	0.1	0.3	0.11	nd	0.34
	GC	na	nd	nd	nd	nd	nd
22/3/93	Site D	< 50	nd	0.09	0.06	0.09	0.32
1/4/93	BT	na	nd	nd	0.08	nd	nd
	KLB	< 1	0.67	nd	nd	nd	nd
	RS	na	0.40	0.27	nd	nd	0.24
	GC	na	nd	nd	nd	nd	nd

(see Figure 7-1 for location references)

B: Culverted drain outlet, draining land south of the railway line and made up of a portion of Nineteen Acre Field and Big House Rick Field; the culvert joins the stream approximately 1 metre down-stream of Site A weir; **GC**: Outlet from golf course; **BT**: Square sectioned open culvert channelling drainage water into main water course from BT land area; **KLB**: The output from a vertical drain carrying drainage from the underside of the railway bridge, over Kiln Lane, into a roadside gullypot; **RS**: Ephemeral stream flowing north-east from railway line opposite Roughtalley's Wood. **na**: not available, **nd**: not detected.

The manual sample taken at location C is believed to contain water that had drained from the western area of the urbanised catchment and therefore did not receive any runoff from the agricultural sub-catchment. The absence of chlorotoluron and isoproturon at location C is consistent with this as these two compounds were only present in products designed for agricultural use. According to the records of pesticide applications made to the North Weald catchment (see Table 7-1), the applications of isoproturon and chlorotoluron made to the agricultural sub-catchment and to the BT area of the urbanised catchment prior to the manual sampling date, would explain their detection at Site D. The isoproturon and chlorotoluron application to the agricultural sub-catchment were made 111-121 days and 130 days respectively before the sampling date; for the urbanised catchment the chlorotoluron application was made 109 days before the sampling date. Comparison with the sample taken at Site A on the same date (see Table 7-4), shows that the chlorotoluron concentration was higher at Site D with a reverse situation for the isoproturon concentrations.

Table 7-4 Results of the 1992 manual sampling within the agricultural sub-catchment

Date	Location	Flow (l/s)	Pesticide concentration (μg/l)			
			Simazine	Atrazine	Chlorotoluron	Isoproturon
6/3/92	Site A	0.5	0.30	0.39	0.19	0.31
	A9	<0.1	0.30	0.16	0.26	0.46
	A14	<0.1	0.31	0.18	nd	1.44
	A23	<0.1	0.13	0.13	0.41	0.48
24/3/92	Site A	1.9	0.23	0.19	0.17	0.19
8/4/92	Site A	1.5	0.12	0.07	0.06	0.14
29/5/92	Site A	2.8	0.53	0.54	0.16	0.13

Key;(see Figure 5-1 for location references)
Site A: Outlet of agricultural sub-catchment.
A14: Main drainage ditch, 1 metre down stream of junction of Far Lawns and Middle Lawns
A9: Main drainage ditch, 5 metres upstream of junction of Pond and Far Lawns.
A23 Outlet of main drain from Hither Lawns.

This suggests that the chlorotoluron leaching from the agricultural sub-catchment was augmented by the chlorotoluron application made to the BT area of the urbanised catchment. Analysis of railway line ballast samples indicates that this source could also have contributed a minor amount of chlorotoluron (see Section 7.3). The absence of diuron detection in the manual sample may have reflected the relatively minor amount of diuron (0.083kg) which had been previously applied during the week ending 8/2/92 by the Park and Recreation department of Epping Forest District Council, as well as its absence in the baseflow at Site D.

The second set of manual samples from the urbanised catchment was taken on 8/4/92 (Julian Day 99) from Site D and location GC, the outlet to the stream from the golf course (Figure 7-1). The concentrations of isoproturon, chlorotoluron and diuron at Site D were (nd)µg/l, 0.08µg/l and 0.14µg/l respectively, and none of the three pesticides were detected at location GC (see Table 7-3). On the same occasion, manual samples were also taken from Site A where the concentrations were 0.14µg/l, 0.06µg/l and (nd)µg/l respectively (see Table 7-4). As in the case of the manual sample taken on 6/3/92, the sources of the isoproturon and chlorotoluron were most probably applications made to the agricultural sub-catchment as well as contributions form the chlorotoluron application made to the BT land and, possibly, minor amounts of chlorotoluron from the railway line. For the agricultural sub-catchment, the isoproturon application was made 144-154 days before the sampling date and for chlorotoluron, the application was made 163 days before the sampling date. In the urbanised catchment, the chlorotoluron was applied to the BT area 142 days prior to the sampling date. A similar pattern to that for the manual samples taken on 6/3/92 was observed in that the concentration of isoproturon was less at Site D compared to Site A and likewise the concentration of chlorotoluron was higher at Site D than it was at Site A. These results again show that chlorotoluron carried down from the agricultural sub-catchment was augmented with chlorotoluron from within the urbanised catchment. The diuron detection was most probably the result of the application made by the Epping Forest District Council Parks and Recreation Department approximately 60 days earlier during the week ending 8/2/92. The fact that it was detected on this occasion and not the previous manual sample may be explained by intervening rainfall which had transported the diuron into a more favourable environment from where it was able to leach into the baseflow of the watercourse.

The absence of any pesticide detection in the sample taken from the stream as it left the golf course suggested that the pesticides that were used as part of the management of the golf-greens were not part of the analysis suite. A number of attempts were made to identify the pesticide products used on the golf course but on every occasion the owner refused to release any information.

A third set of manual samples was taken during a storm event on 29/5/92 (Julian Day 150), which is fully described below in Section 7.4.4. During this storm, 25.5mm of rainfall produced a significant runoff response from the urbanised catchment resulting in a peak flow rate of 330 l/s at Site D at 10:00 am. The response from the agricultural sub-catchment was relatively insignificant with a peak flow rate of 2.6l/s being recorded at Site A at 12:00 am. The runoff response from the urbanised catchment triggered the automatic sampler at Site D and nine samples were taken over the duration of the storm event. In addition, during this event and between 14:30 and 15:00, manual samples were taken at Site A, location B, location BT, location KLB and location GC. The concentrations of chlorotoluron were 0.16µg/l, 0.08µg/l, 0.23µg/l 0.09µg/l and (nd)µg/l respectively; the concentrations for isoproturon were 0.13µg/l, 0.09µg/l, 34.56µg/l, (nd)µg/l and (nd)µg/l respectively; the concentrations of diuron were (nd)µg/l at all manual sampling sites (see Table 7-3 and Table 7-4).

The detection of chlorotoluron and isoproturon at Site A was probably the result of previous applications made to the agricultural sub-catchment where 60.780kg of isoproturon was applied 195-205 days prior to the sampling and 78.330kg of chlorotoluron was applied 214 days prior to the sampling. The absence of diuron at Site A probably reflected the fact that it was only registered for non-agricultural applications. At location KLB, the absence of isoproturon and diuron detection was expected considering that the flow at this location was entirely made up of drainage water from the section of railway track above the bridge over Kiln Lane. The track would not have received isoproturon because its use was only licensed for agriculture, and according to data from London Underground diuron had never been applied to the railway line prior to the sampling date. However, the detection of chlorotoluron (0.09µg/l) was unexpected since it was only licensed for agricultural use. It's presence in runoff from the railway line was confirmed in the results from the artificial rainfall-runoff tests conducted on samples of track ballast taken from the railway line (see Section 7.3). The origin of the chlorotoluron was unclear. It seemed extremely unlikely that London Underground would knowingly apply an unlicensed pesticide, and it was more probable that the presence of chlorotoluron was the result of a contaminated application of simazine or atrazine or alternatively was the result of spray drift from a nearby agricultural application.

At location B, the detection of chlorotoluron and isoproturon was unexpected because according to the agrochemical records for Cold Hall Farm (see Tables 6.1, 6.2 and 7.1), the land draining to location B had never received applications of either herbicide. However, it was likely that nearby areas of the southern embankment of the railway line, where chlorotoluron residues have been shown to be present, would have drained to location B. The detection of isoproturon was unexplainable. The absence of diuron in the sample at location B was expected since records showed that prior to the sampling date, no applications of this herbicide were made to the railway line or the nearby area belonging to Cold Hall Farm.

At location BT, the detection of chlorotoluron (0.23μg/l) was probably the result of the chlorotoluron application (70kg) made to the BT land area 193 days prior to the sampling date. The relatively high concentration of isoproturon (34.56μg/l) cannot be associated with a known application. According to the agrochemical records obtained from the farmer responsible for the land, the area had not received an application of isoproturon for at least two years prior to the sampling date (see Table 7-1). Therefore, the detection may have been the result of badly kept application records or the presence of an unidentified source. Possibly an isoproturon application was made to land adjoining the BT land area and then the sprayer was moved onto the BT land area where it was rinsed. The absence of diuron in the BT sample was expected because it was unlicensed for agricultural land. At location GC, the stream outlet of the golf course, no detections were made for chlorotoluron, isoproturon and diuron. As previously mentioned, information on the applications made to the golf course during the monitoring period was unavailable, however, it did appear that the pesticides that were used in the agronomical management of the golf greens did not include any of the pesticides analysed in the samples taken.

At Site D, the automatic sample that coincided with the approximate sampling time of the manual samples contained chlorotoluron (1.10μg/l), isoproturon (2.64μg/l) and diuron (40.98μg/l). The chlorotoluron concentration was approximately five times higher than that determined at Site A and therefore it appears that the amount of chlorotoluron transported into the urbanised catchment was significantly augmented by chlorotoluron applications made to the BT area and possibly also the railway line. The detections in the manual samples taken from locations KLB, B and BT most probably only accounted for a fraction of the concentration of chlorotoluron at Site D and , it was likely that the remaining amount of chlorotoluron was supplied from a continuum of unidentified minor flow routes leading from the railway line and the BT area to the main water course. The source that produced the increased detection of isoproturon was mainly the unidentified application to the BT area as well as a minor input from the agricultural sub-catchment. The high concentration of diuron detected at Site D was directly attributable to an application made on behalf of the Roads and Highways Department of Epping Forest District Council on 5/5/92, 24 days prior to the application. This is further discussed in Section 7.4.4.2.

A fourth set of manual samples was taken during non-storm conditions on 6/11/92 at locations GC, RS (the ephemeral stream originating from the northern embankment of the railway line east of the golf course; see Figure 7-1) and Site D. At the three manual sampling sites the concentrations of chlorotoluron were 0.06µg/l, (nd)µg/l and 0.11µg/l respectively and the concentrations of isoproturon and diuron were consistently below the detection limit (see Table 7-3). During the period since the previous manual samples were taken (29/5/92), the North Weald catchment had become considerably wetter, to such an extent that the base flow at the time of the manual sampling was approaching 50l/s at Site D. The sample taken at location GC was the first to show any evidence of the presence of chlorotoluron. The detection of this herbicide may have been the result of contaminated groundwater seeping into the stream as it passed through the golf course. The wetness of the catchment may have elevated the water table to a point where it interacted directly with the stream. Aldous and Turrell (1994) and Gomme *et al* (1992) have described how simazine and atrazine, applied to a railway line, could rapidly drain through the clinker foundations into the groundwater, by-passing the upper soil layers that would have normally attenuated the downward leaching process. Previous manual samples (e.g. sample KLB 29/5/92) have shown that the railway line appeared to be a source of chlorotoluron and this could have been available for leaching downwards into the groundwater. However, the absence of chlorotoluron in the sample taken at location RS, the stream originating from the railway line, appeared to contradict this. However, this may be explained by the chlorotoluron originally present in the railway line material in the vicinity of the stream, having been leached out of the local ballast material to a point where the level in the baseflow was below the detection limit. The source of the chlorotoluron detected at Site D was probably a combination of contaminated runoff from the BT area and minor amounts from the railway line together with chlorotoluron residues transported into the urbanised catchment from the application (70kg) made to the agricultural sub-catchment on 28/10/91 (Table 7-1).

The fifth manual sample was collected from Site D during non-storm conditions on 12/2/93 (Julian day 43). The only phenylurea detected, was chlorotoluron at a concentration of 0.06µg/l. As in the case of the previous detection at Site D, the source of the chlorotoluron was probably a combination of runoff from the BT area where a chlorotoluron application was made 452 days earlier and chlorotoluron transported into the urbanised catchment from an agricultural sub-catchment application, 431 days earlier on 28/10/91(Table 6-2).

The sixth set of manual samples was taken during non-storm conditions fourteen days later on 26/2/93 (Julian day 57) at Site D and location GC. No phenylureas were detected at location GC. At Site D, chlorotoluron was detected at a concentration of 0.11µg/l and diuron was detected at a concentration of 0.34µg/l. Again, the sources of the chlorotoluron were probably identical to those previously described (Table 6-2). The source of diuron was probably the London Underground application (0.461kg) made to the railway line on 29/10/92, 106 days prior to the sampling date.

The seventh manual sample was taken during non-storm conditions on 22/3/93 at Site D. Chlorotoluron, isoproturon and diuron were detected at concentrations of 0.06µg/l, 0.09µg/l and 0.32µg/l respectively. Again, the low level of the chlorotoluron was probably due to the contributions identified for the fifth and sixth manual samples at Site D (Table 6-2). As for the previous manual sample taken at Site D, the source of the diuron detection was probably the London Underground application (0.461kg) made to the railway line on 29/10/92, 144 days prior to the sampling date. The detection of isoproturon at Site D was the first since the event on 29/5/92, 297 days previously and was most probably the result of the isoproturon application (39.692kg) made to the agricultural sub-catchment, 47 days previously on 3/2/93.

The eighth and final set of manual samples was taken during storm conditions on 1/4/93 (Julian day 91) at locations BT, KLB, RS and GC. The only phenylurea to be detected at location BT was chlorotoluron at a concentration of 0.08µg/l and the only application that it could be associated with was that made to the BT land area (70kg) on 18/11/91, 500 days earlier. Similar lengthy periods between application and detection of chlorotoluron were found during the description of the hydrochemical data for the agricultural sub-catchment (Section 6.4.2.). No phenylurea detections were observed at locations KLB or GC. At location RS, the only phenylurea to be detected was diuron at a concentration of 0.24µg/l. The source of this was probably the London Underground application (0.461kg) made to the railway line on 29/10/92.

7.2.1.2 Simazine and atrazine

On the 6/3/92 (Julian day 66), manual samples were taken from Site D and location C (Figure 7-1). The concentrations for simazine and atrazine at Site D were 0.45µg/l and 0.69µg/l respectively and for location C, the concentrations were 0.21µg/l and 0.24µg/l respectively (see Table 7-3). Also on the 6/3/92, a manual sample was taken at Site A and found to have simazine and atrazine concentrations of 0.30µg/l and 0.39µg/l respectively (Table 7-4). From the survey of pesticide applications made to the North Weald catchment, it seems probable that the main sources of the simazine detected at all three sampling sites was the application (9.027kg) to the agricultural sub-catchment on 28/11/91. This was 99 days before the sampling date. There was also a simazine application (0.346kg) to the railway line by London Underground on 10/9/91 (178 days before sampling). The fact that the simazine concentration was higher in the sample taken at Site D compared to that taken at Site A suggests that the amount of simazine available for transport increased within the urbanised catchment. This situation would have been opposed by the increased flow rate of the main water course as it approached the outlet of the catchment and therefore produced a dilution effect on the concentration of simazine. The source of the simazine within the urbanised catchment was most probably the leaching from the application made to the railway line as well as any applications that were made by private domestic users. The detection of atrazine at location C and Site D was probably the result of the atrazine application (0.208kg) made by Epping Forest District Council Parks and Recreation Department during the week ending 8/2/92, approximately 27 days before the sampling date. Also, atrazine data from manual samples taken further into the monitoring programme, at various locations around the urbanised catchment (see Table 7-3) suggest that the railway line and the BT area, as well as private domestic use may have contributed to the atrazine detected at Site D as well as that imported from the agricultural sub-catchment.

The second set of manual samples from the urbanised catchment was taken on 8/4/92 (Julian day 99) from Site D and location GC and also from Site A (Tables 7-3 and 7-4). The simazine concentrations at Site A, location GC and Site D were 0.12µg/l, (nd)µg/l and 0.15µg/l respectively. Likewise, the atrazine concentrations were 0.07µg/l, (nd)µg/l and 0.12µg/l respectively. Similar to the previous samples taken on 6/3/92, the source of the simazine detection at Site D was most probably the result of residues carried down from the application made to the agricultural sub-catchment on 28/11/91, 132 days prior to the sampling date, combined with residues leaching from the application made to the railway line on 10/9/91 (211 days previously). Additionally, it was possible that the simazine application to the railway line may have been augmented by residues of previous applications. Artificial rainfall-runoff tests on samples of ballast from the railway line (Section 7-3) showed that significant concentrations of atrazine and simazine were detected in the artificial runoff at periods of 7 years and 1.5 years respectively, after they were applied to the railway line for total vegetation control. A further source of atrazine in the sample taken at Site D may have been an application made by the Parks and Recreation Department. The non-agricultural use of simazine and atrazine was invoked in 1992 and therefore atrazine was reported as being replaced by propyzamide. However, from the storm event data described in Sections 7.5.2 and 7.5.3 it appeared that atrazine may have continued to have been used. The absence of simazine and atrazine from the sample taken at the outlet of the golf course suggests that the two products were not common to the pesticide products used as part of the management of the golf-greens.

A third set of manual samples was taken during a storm event on 29/5/92 (Julian Day 150). The runoff response from the urbanised catchment triggered the automatic sampler at Site D and nine samples were taken over the duration of the storm event. In addition, during the storm event between 14:30 and 15:00, manual samples were taken at Site A, location B, location BT, location KLB and location GC (Tables 7-3 and 7-4). The concentrations of simazine were 0.53µg/l, 2.11µg/l, 0.31µg/l, 9.20µg/l and (nd)µg/l respectively. The automatic sample taken at Site D at approximately the same time as the manual sampling, had a concentration of 1.08µg/l. The concentrations of atrazine were 0.54μg/l, 0.48μg/l, 0.30μg/l, 2.68μg/l and (nd)μg/l respectively. The automatic sample taken at Site D which coincided with the timing of the manual sampling had a concentration of 1.18μg/l. The detection of simazine and atrazine at location B was most probably associated with runoff from the southern embankment of the nearby railway line (Figure 7-1). The source of the simazine and atrazine was likely to have been the applications made by London Underground to control vegetation on the railway line. The simazine was known to have been applied (0.346kg) on 10/9/91 (262 days prior to the sampling date) and the atrazine was applied approximately seven years earlier.

The detection of simazine and atrazine at location KLB can be explained in the same manner as that for their detection at location B i.e. as a consequence of residues leaching from applications made by London Underground to the railway line. The fact that the concentrations of simazine and atrazine were higher in the KLB sample compared to the B sample can be explained by the KLB sample being entirely composed of runoff from the railway line whereas the B sample was diluted by runoff from the nearby area of Cold Hall Farm. The detection of simazine and atrazine in the sample taken at location BT was not directly associated with known applications of the two herbicides. Their detection may be attributed to a number of possible sources, including undisclosed application by Epping Forest District Council or possible leaching from re-used railway line clinker used to construct a nearby trackway (see Section 7.3). Harris *et al* (1992) have shown that simazine and atrazine can leach from railway clinker for a number of years after application. The leaching process may occur in the original setting or when the clinker has been removed and used for a secondary purpose such as permeable fill for minor road construction.

Again, the absence of simazine and atrazine detection at location GC showed that the products were not used for the routine upkeep of grassed areas within the golf course. The fact that the simazine and atrazine levels detected in the automatic sample taken at Site D were approximately double those detected in the manual sample from Site A shows that the Site D sample was augmented by what was probably a continuum of sources of simazine and atrazine from within the urbanised catchment. The data from the KLB sample showed that the railway line may well have been a significant source of simazine but not so much for atrazine. Prior to the sampling date, the most recent simazine application to the railway line was on 10/9/91 (approximately 262 days previously). Possible known sources of atrazine may have included applications made by the Parks and Recreation Department as part of their horticultural management programme. The most recent application with respect to the sampling date was during the week ending 8/2/92 (approximately 111 days prior to the sampling date).

A fourth set of manual samples was taken during non-storm conditions on 6/11/92. Samples were taken at Site D, location GC and location RS (Figure 7-1). At the three manual sampling sites the concentrations of simazine were 0.18µg/l, 1.26µg/l and 0.08µg/l respectively and the concentrations of atrazine were 0.07µg/l, 0.36µg/l and 0.14µg/l respectively (Table 7-3). The sample taken at location GC was the first from this location to show the presence of simazine and atrazine. This may have been due to shallow groundwater, contaminated with simazine and atrazine from the railway line, seeping into the stream as it passed through the golf course. The wetness of the catchment may have elevated the water table to a point where it interacted with the stream at this point.

The detection of simazine and atrazine in the manual sample taken from location RS, the stream originating from the north side of the railway line immediately east of the golf course (Figure 7-1), was probably the result of herbicide residues leaching into the stream from applications made to the railway line ballast. The detection of simazine was probably associated with the application (0.346kg) made on 10/9/91 by London Underground (423 days before the sampling date). Similarly, the detection of atrazine was probably associated with applications of atrazine made to the railway line by London Underground approximately 7 years previous to the sampling date (Coleman, *pers comms*). The detection of simazine and atrazine at Site D was due to the combined contributions of the applications to both the agricultural sub-catchment and the urbanised catchment. The relevant applications were 9.027kg to the agricultural sub-catchment on 28/11/91 (345 days prior to the sampling date), 0.346kg of simazine to the railway line on 10/9/91 (423 days prior to the sampling date) and 0.208 kg of atrazine by the Parks and Recreation Department during the week ending 8/2/92 (272 days prior to the sampling date).

The fifth manual sample was taken during non-storm conditions on 12/2/93 (Julian day 43) at Site D. The concentrations of simazine and atrazine were 0.08µg/l and 0.14µg/l respectively and were derived from the three applications described above. The sixth set of manual samples was taken during non-storm conditions on 26/2/93 (Julian day 57) at Site D and location GC. Simazine and atrazine were absent from the sample collected at location GC. At Site D, the concentrations of simazine and atrazine were 0.1µg/l and 0.30µg/l respectively and their sources were the same as the applications identified for the fifth manual sample at this site.

The seventh manual sample was taken during non-storm conditions on 22/3/93 (Julian day 81) at Site D. The concentration of atrazine was 0.09µg/l and there was no detection of simazine. Again, the detection of atrazine was probably associated with the 0.208 kg of atrazine applied by the Parks and Recreation Department during the week ending 8/2/92.

The eighth and final set of manual samples was taken during storm conditions on 1/4/93 (Julian day 19) at locations BT, KLB, RS and GC. Simazine and atrazine were not detected at locations BT and GC. At location KLB, simazine only was detected at a concentration of 0.67µg/l. The detection of simazine was probably associated with the application (0.346kg) made to the railway line on 10/9/91 by London Underground. At location RS, simazine was detected at a concentration of 0.40µg/l and atrazine at a concentration of 0.27µg/l. As for the KLB sample, the simazine was probably associated with the application made to the railway line by London Underground. This may also be the explanation for the atrazine detection in the absence of any record of a relatively recent application. Atrazine has been shown to be still present within railway track ballast approximately seven years after application.

Figure 7-2 shows a graphical summary of the concentrations of simazine, atrazine, chlorotoluron, isoproturon and diuron detected in the manual samples taken at Site D during non-storm conditions from March 1992 to March 1993. Detection during non-storm conditions was generally attributed to a pesticide being present within the baseflow of the catchment discharge. The presence of a pesticide in the baseflow was associated with its total or partial leaching from the area of application to a location that was in the proximity of the sub-surface baseflow.

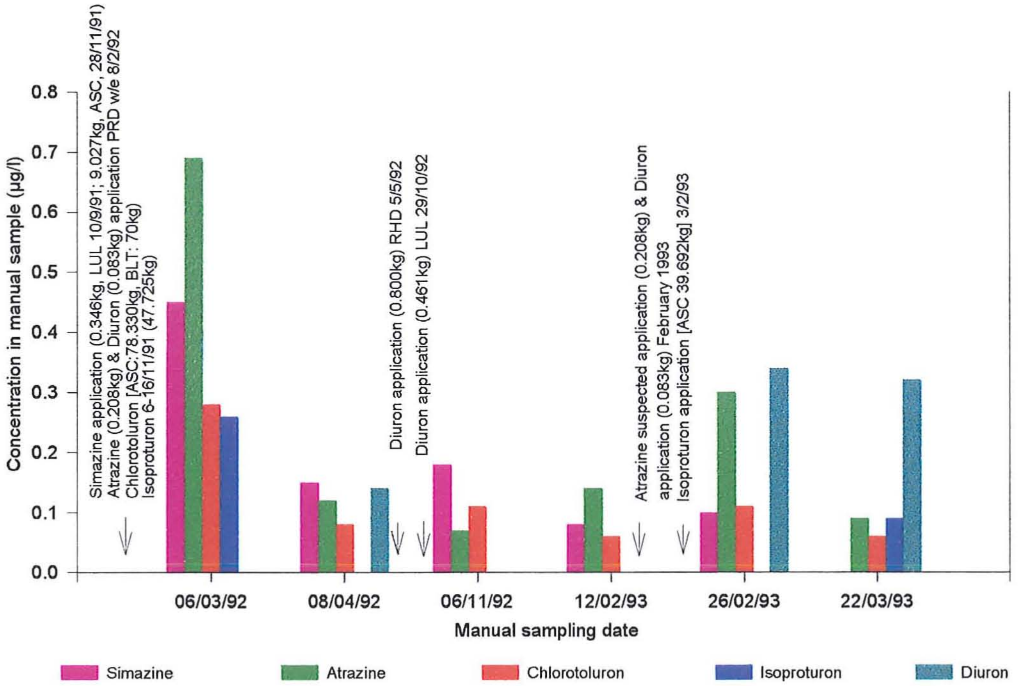

Figure 7-2 Concentrations of atrazine, simazine, chlorotoluron, isoproturon and diuron in manual samples taken at Site D, during non-storm conditions, throughout the duration of the monitoring programme. The dates of significant pesticide applications are shown

Examination of Figure 7-2 and the tabulated data in Table 7-3 indicates that the occurrence of a pesticide in the baseflow was generally related to the timing of its application. The main simazine application was made to the agricultural sub-catchment and railway line before the monitoring programme began in the Spring of 1992. The data in Figure 7-2 shows the gradual decline in baseflow simazine concentration brought about by in-situ degradation and off-site transport. Similar behaviour was observed for chlorotoluron for which the major application also took place before the monitoring programme began. Isoproturon was applied on two occasions to the agricultural sub-catchment; initially between the 6-16/11/91 and secondly on 3/2/93. Isoproturon appeared to be present in the baseflow for up to only four months after the first application (Figure 7-2) and consequently its persistence in the baseflow at Site D was significantly shorter than that of simazine and chlorotoluron. Compared to chlorotoluron, the shorter persistence of isoproturon was probably a combination of its shorter half life (see Table 6-4) and the fact that approximately half the amount was applied (see Table 7-1).

Atrazine was applied (0.208kg) to grassed amenity areas by the Parks and Recreation Department during the week ending 8/2/92 and it was suspected that it was also applied (0.208kg) during February 1993 although the Department reported the use of propyzamide on this occasion. The atrazine concentration data in Figure 7-2 show that the concentration gradually declined after the first application and then increased in the manual sample taken on 26/2/93 which was immediately after the second suspected application.

Between the beginning of 1992 and March 1993, diuron was applied on four occasions, twice by the Parks and Recreation Department, once by the Roads and Highways Department and once by London Underground. After the first application of 0.083kg by the Parks and Recreation Department during the week ending on 8/2/92, diuron was not detected in the baseflow until two months later in the manual sample taken on 8/4/92. The next application of 0.800kg was made by Roads and Highways Department on 5/5/92, followed by an application of 0.461kg to the railway line by London Underground on 29/10/92. The absence of diuron in the manual sample taken on 6/11/92 may be explained by the fact that it had little opportunity to infiltrate into the sub-soil and sub-surface interflow given that it was applied to the road verges where infiltration would have been impeded by the structure of the road. The probability is that the diuron travelled directly to a nearby roadside gully-pot and was transported directly to the main water course, avoiding any interaction with the subsoil and sub-surface interflow. Diuron was next detected in the manual samples taken at Site D on both 26/2/93 and 22/3/93, probably due to the February PRD application and the earlier railway line application.

7.3 Results of artificial rainfall-runoff experiment and immersion test on railway line ballast

As fully described in Section 4.4.7, laboratory leaching tests were carried out on samples of railway track ballast taken from the London Underground Central Line at North Weald. Two different tests were carried out, the first involved a simulated ballast rainfall-runoff test where the runoff was analysed, then the ballast sample (1kg) was dried for twenty four hours at 30°C and extracted with dichloromethane which was also analysed for herbicide residues. The second test involved the constant immersion of a separate sample (1kg) of limestone ballast for twenty four hours in double distilled double deionised water that was subsequently analysed. The results of the rainfall-runoff experiment and the constant immersion experiment are shown in Table 7-5 and Figure 7-3.

Table 7-5 Results of the artificial runoff test separate constant immersion experiment

Artificial runoff test followed by dichloromethane extraction

Runoff Sample	Time (minutes)	Concentration (µg/l)			
		Simazine	Atrazine	Chlorotoluron	Diuron
1	27	0.56	0.12	0.34	2.57
2	55	0.29	nd	0.14	0.78
3	80	0.27	nd	0.12	0.53
4	103	0.21	nd	0.05	0.32
5	125	0.38	nd	0.05	0.48
Total concentration in runoff (µg)		1.71	0.12	0.70	4.69
Mass of herbicide removed from ballast by DCM extraction following runoff experiment (µg)		7.93	2.2	0.71	11.23

Constant immersion test

Total mass leached during immersion test (µg/kg)	24 hours	3.63	nd	1.15	14.85

DCM: dichloromethane nd: below detection limit

The rainfall-runoff experiment shows that simazine, atrazine, chlorotoluron, and diuron were detected in the artificial runoff, and the same herbicides were detected in the dichloromethane extraction of the ballast following the rainfall-runoff experiment (Table 7-5). Simazine, chlorotoluron and diuron but not atrazine were detected in the leachate from the constant immersion test. For the rainfall-runoff experiment, the highest initial artificial runoff concentration detected was for diuron (2.57µg/l), which then decreased in an exponential manner during the test to a concentration of 0.48µg/l (Figure 7-3). The next highest initial concentration was that of simazine at 0.56µg/l followed by chlorotoluron at 0.34µg/l and atrazine at 0.12µg/l. The total mass of diuron, simazine, chlorotoluron and atrazine leached per kilogram of limestone ballast sample during the rainfall-runoff experiment was 4.69µg, 1.71µg, 0.70µg and 0.12µg. Apart from chlorotoluron, the magnitude of losses probably reflected the timings of the previous applications made to the railway line at North Weald. Information provided by London Underground (Coleman *pers comms,* 1993) indicated that the limestone ballast samples used in the experiment were sampled approximately five months after the last diuron application, approximately five months after the last diuron application, approximately eighteen months after the last simazine application and approximately seven years after the last atrazine application.

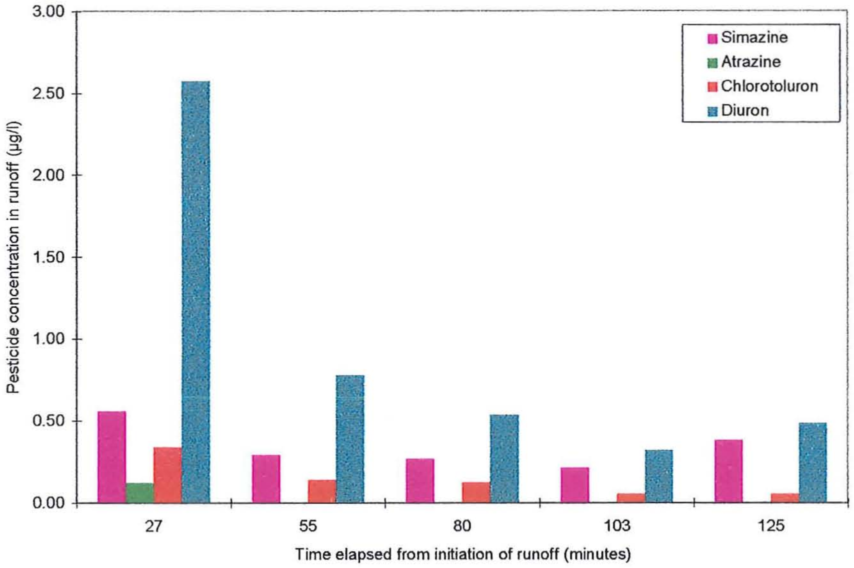

Figure 7-3 Pesticide concentrations of simulated runoff from 1kg of limestone railway line ballast

It was more probable that the artificial runoff concentration order was a function of application timing rather than aqueous solubility because, given the individual amounts of pesticide involved, it is unlikely that the amounts leached would have been limited by aqueous solubility which was greater than 5mg/l for each pesticide (Tomlin, 1997). The detection of chlorotoluron in the runoff from the rainfall-runoff experiment was unexpected since it was only registered by the Ministry of Agriculture, Fisheries and Food for agricultural use.

Table 7-5 shows that the dichloromethane extraction carried out after the rainfall-runoff experiment, yielded 11.23µg/kg of diuron, 7.93µg/kg of simazine, 2.2µg/kg of atrazine and 0.71µg/kg of chlorotoluron. This data is also shown in Figure 7-4, which compares the amount of pesticide leached during the rainfall-runoff experiment with that removed during the dichoromethane extraction of the ballast. The Figure shows that 18.3 times more atrazine was extracted by the dichloromethane than was leached during the rainfall-runoff test. Similarly, 4.6 times more simazine and 2.4 times more diuron were extracted by the dichloromethane whereas an equivalent amount of chlorotoluron was extracted by the dichloromethane and leached during the rainfall-runoff experiment. Excluding chlorotoluron, this order was the reverse of that for the total amount of pesticide lost during the rainfall-runoff experiment and the immersion test. Further, this reversed order cannot be assigned to solubility in dichloromethane since the solubility for every pesticide detected was greater than 20g/l (Tomlin, 1997) and each amount of pesticide was approximately six orders of magnitude below this figure.

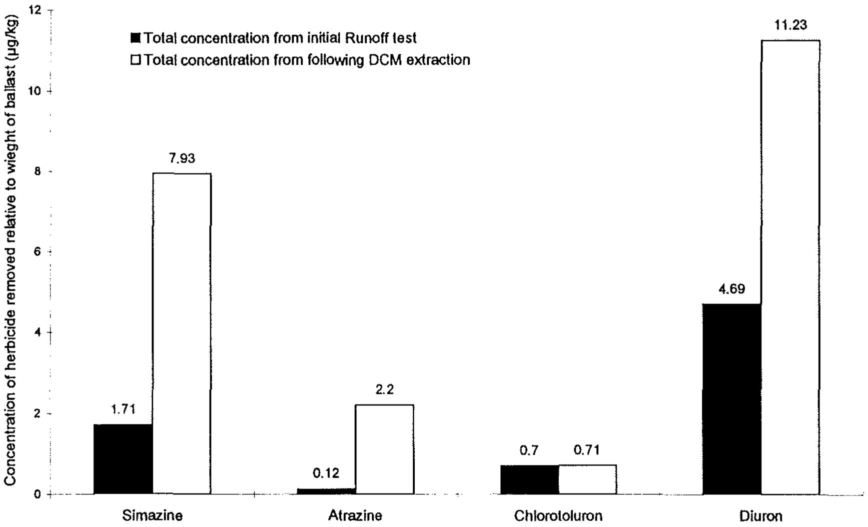

Figure 7-4 Loss of pesticide in simulated runoff from railway line ballast compared to that removed by dichloromethane extraction on the same ballast sample. [Values on bars refer to concentration µg/kg]

However, the order of extraction ratios does agree with the order of application timing for each of the three herbicides (Figure 7-5) in that the herbicide that was most recently applied (i.e. diuron) showed the lowest ratio of dichloromethane extraction to runoff extraction (2.4). Whereas atrazine which was applied seven years previously, showed the highest ratio of 18.3. It is suggested that this relationship may be explained by consideration of the physical location of each pesticide within the ballast material relative to the respective extraction potentials of the artificial rainfall and dichloromethane. Given the widely differing viscosities of water and dichloromethane and the fine porosity of limestone, it is likely that during the duration of the rainfall-runoff experiment the artificial rainfall may have only penetrated and extracted pesticide residues form a location relatively close to the surface of the ballast material, whereas in the following extraction, the dichloromethane would have probably penetrated relatively deep into the ballast material. Therefore, from the order of the dichloromethane extraction/runoff extraction ratios it appears that the majority of the atrazine was located deep within the material and the majority of the diuron was located on or near to the surface of the material, with the simazine residing at an intermediary position.

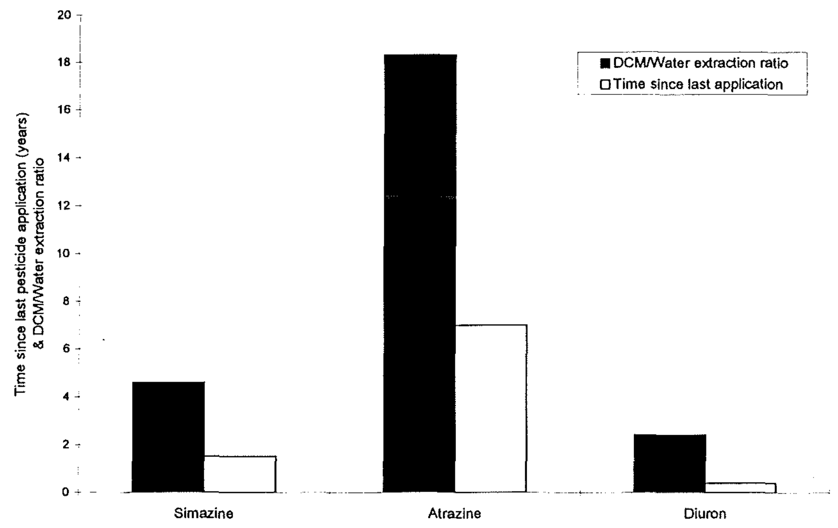

Figure 7-5 **Period since last application of simazine, atrazine and diuron to railway line ballast and ratio of amount of pesticide removed during dichloromethane extraction to amount removed during rainfall-runoff experiment**

The ordered location of atrazine, simazine and diuron within the ballast material may be explained by consideration of the distribution of a pesticide within the ballast material after application and the manner in which it has degraded thereafter. Torstensson (1994) showed that diuron was approximately seventy times more mobile in railway ballast material than in a clay-loam soil and estimated that it had a half-life of two years compared to ninety days for soil. In the same environment it is probable that the half-lives of atrazine and simazine would have been similarly extended. Therefore, once applied to the surface of the ballast material, the pesticide residue would have eventually equilibrated throughout the bulk of the material as it became saturated with water. Once annual or biannual application ceased the pesticide residue closest to the surface would have degraded more rapidly than that located deeper in the ballast material. This assumes that the surface of the ballast material would have been richer in organic matter than the centre of the ballast material. Therefore, during the rainfall-runoff experiment, the simulated rainfall may have only penetrated the outer layers of the limestone ballast, leaching an already depleted residue of atrazine. However, the dichloromethane extraction would have probably extracted atrazine from deep within the material. In the case of diuron, the surface of the ballast material would have been relatively undepleted compared to the deeper layers and therefore the difference between the amounts of diuron removed during the rainfall-runoff experiment and the dichloromethane extraction would not have been as extreme as in the case of atrazine.

A comparison of the amount of each pesticide lost in the rainfall-runoff experiment compared to that lost in the constant immersion test is shown in Figure 7-6. For simazine and chlorotoluron, it can be seen that approximately double the amount of material was removed from the ballast sample during the immersion test compared to the rainfall-runoff experiment. Three times the amount of diuron was lost in the immersion test. However, atrazine was not detected in the leachate of the constant immersion test which may be the result of slightly varying amounts of individual pesticides present in the two different sub-samples of the limestone ballast material that were used in the two experiments. The greater amounts of pesticide that were produced during the immersion test were probably the result of its longer duration. This would have enabled the water to penetrate deeper into the ballast material and subsequently extract more pesticide than during the duration of the relatively short rainfall-runoff test.

It was very unlikely that the chlorotoluron detected during the rainfall-runoff experiment and the constant immersion was the result of an illegal application by London Underground given their position as a respected public body and the strong likelihood that they would closely follow product label guidelines as stipulated by MAFF. It was more probable that the detection was the result of aerial drift deposition deriving from an agricultural application site close to the railway line. Given that comparable amounts of chlorotoluron were detected during the rainfall-runoff test and the following dichloromethane extraction it appeared likely that the chlorotoluron was located at the surface of the ballast material. This may suggest that the detection was the result of a recent application since the chlorotoluron had not had sufficient opportunity to penetrate into the deeper layers of the material.

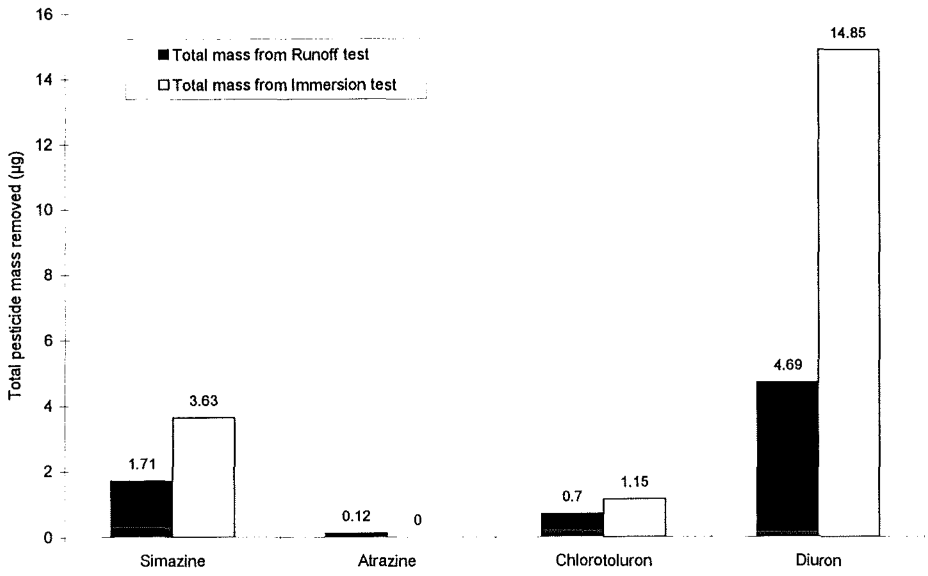

Figure 7-6 Loss of pesticide in simulated runoff from railway line ballast compared to the loss of pesticide during an immersion test on a similar ballast sample. [Numbers on bars represent loss (µg)]

In conclusion, the results of the work on the samples of railway line ballast taken form North Weald can be summarised as follows:

- Simazine, atrazine, chlorotoluron and diuron were all detected in the artificial runoff and the dichloromethane extraction but atrazine was not detected in the immersion leachate from ballast samples. All detected herbicides were consistent with source applications to the railway line by London Underground except for chlorotoluron which was possibly the result of deposition of aerial drift from an agricultural application.

- The results of the dichloromethane extraction suggested that individual pesticides were present at different depths within the ballast material and that the depth appeared to be dependent on the period which had expired since the last application.

- The half-life of the pesticide when applied to ballast material appeared to be considerably longer than when applied to soil. For example, the soil based half-life of atrazine was 60 days, however, atrazine was detected at significant concentration seven years after application to ballast material. This suggested that the half-life of atrazine when applied to railway ballast material was considerable longer and this is supported by the work of Torstensson (1994) who found that the half-life of diuron in ballast material was approximately two years compared to ninety days for soil environments.

7.4 Results of storm event monitoring for 1992

The following sub-sections describe the storm events automatically sampled at Site D during the 1992-1993 monitoring period. In some instances the storm runoff automatically sampled at Site D did not contain any contribution from the agricultural sub-catchment because of the requirement to satisfy high soil moisture deficit and vegetation interception losses, which consumed all incident rainfall before significant runoff was generated. In other instances the agricultural sub-catchment produced significant runoff and this was sampled at Site A and concurrently sampled at Site D. On these occasions, the flow and pesticide flux contribution from the agricultural sub-catchment could be subtracted from that measured at Site D to produce data that were specific to the urbanised catchment. However, due to operation of the by-pass channel only one of the recorded storm events was suitable for this treatment and therefore to maintain uniformity across all storm events this treatment was not carried out. When a storm event was of sufficient magnitude, the by-pass channel came into operation and though the flow rate was monitored the flow was not sampled. In these situations it was possible that a fraction of the pesticide load determined at Site D had been split between the main watercourse flowing through Site D and the by-pass channel. During the following descriptions of the monitored storm events, where appropriate, the likely by-pass load losses have been indicated.

7.4.1 Results for the storm event of 15/4/92 (JD 106)

The first storm event to be automatically sampled at Site D occurred on 15/4/92 (JD 106). The hydrological parameters including the storm event rainfall and the consequent runoff from the urbanised catchment are shown in Figures 7-7 and 7-8. Following an initial flow rate of approximately 1l/s, the event hydrograph peaked at 55.5l/s after 9.5mm of rain fell on the catchment at a maximum intensity of 2mm/hr. The low runoff response suggested that, in general, only the hard-surfaced areas of the urbanised catchment generated runoff. It was probable that the grassed areas of the urbanised catchment did not generate significant runoff due to the requirement to satisfy soil moisture deficit and losses to interception (see Section 5.3.2). No runoff was generated from the agricultural sub-catchment and the event was of insufficient magnitude to bring the by-pass channel into operation, therefore the runoff represented only the storm runoff from the urbanised catchment. Figures 7-7 and 7-8 also show the concentration (μg/l) curves for simazine, atrazine, chlorotoluron, isoproturon and diuron that were determined from the nine samples that were automatically taken over the duration of the storm event. For each pesticide, a flux (μg/s) curve is shown which is the product of the concurrent concentration and flow rate values.

7.4.1.1 Chlorotoluron, isoproturon and diuron

The storm event occurred 149 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and approximately 67 days after the diuron application (0.083kg) by the Parks and Recreation Department to grassed amenity areas within the urbanised catchment, during the week ending 8/2/92. From the agrochemical records compiled for the urbanised catchment, there does not appear to be any record of an application of isoproturon prior to the storm event (see Table 7-1). Over the course of the storm event, nine automatic samples were collected and the different trends in the concentrations of the three herbicides are shown in Figure 7-7. The diuron concentration was initially high and then decreased throughout the duration of the storm event. The chlorotoluron concentration remained approximately constant and the isoproturon concentration decreased as the storm event flow rate increased and then recovered as the flow rate subsided. The first automatic sample was taken three hours before the peak flow rate, when runoff had only just begun to enter the watercourse and the flow rate was approximately 3.5l/s. In this sample, the concentrations of chlorotoluron and isoproturon were 0.22μg/l and that for diuron was 1.06μg/l. Compared to the manual sample taken at Site D on 8/4/92 (JD 99), the chlorotoluron concentration was 2.6 times higher and the diuron concentration was 7.6 times higher. In the manual sample there was no isoproturon detection.

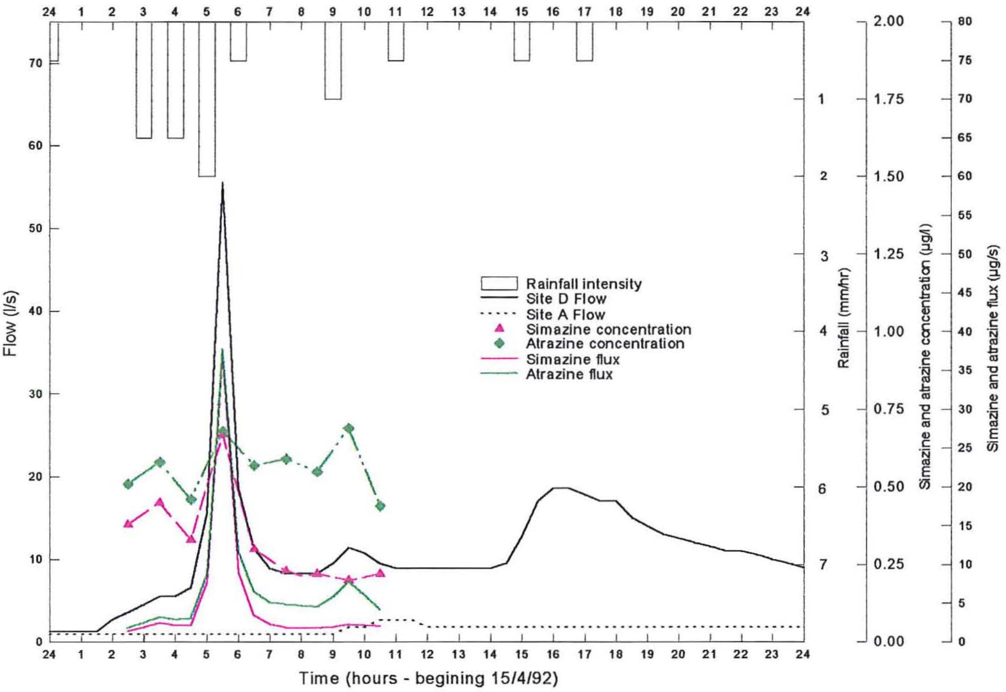

Figure 7-7 Chlorotoluron, isoproturon and diuron concentrations (µg/l) and flux (µg/s) at Site D during the storm event occurring on 15/4/92 (JD 106) [Rainfall intensities (bar chart) and storm runoff are also shown]

During the course of the storm event the diuron concentration fell, in an approximately linear manner, from its maximum value of 1.06µg/l in sample one, to a concentration of 0.27µg/l in sample nine, which was taken five hours after the peak flow of the storm. However, during the gradual decrease in concentration the diuron concentration momentarily peaked at the same time as the flow peak before continuing to decrease (Figure 7-7). The pattern of diuron concentrations during the course of the storm event suggests that the diuron was either transported rapidly from hard surfaces or from areas close to the main watercourse or to entries into the storm water drainage system. In practice, it was probable that the diuron was transported from a combination of all three types of area. As the storm proceeded, the remaining hard-surfaced areas of the urbanised catchment responded and the increased runoff volume gradually diluted the diuron concentration as the storm progressed (Figure 7-7).

In summary, even though the diuron application was reported to have been made to grassed amenity areas within the urbanised catchment (see Table 7-1), the variation of the diuron concentration over the storm event suggested that the diuron was probably also applied, in part, to hard surfaced amenity areas. Figure 7-7 also shows the variation of the diuron flux (μg/s) during the course of the storm event, which peaked at a value of 46μg/s, coinciding with the peak flow rate. The integration of the diuron flux curve and flow curve show that during the monitored period of the storm event 242.6mg of diuron was transported in the flow at Site D corresponding to an event mean concentration of 0.66μg/l. With respect to the diuron application (0.083kg) made by the Parks and Recreation Department during the week ending 8/2/92, the mass transported during the storm event corresponded to 0.29% of the total mass applied. Compared to percentage loss values for herbicides removed in runoff from agricultural land which are typically 2×10^{-2}% (Williams *et al*, 1995), the value of 0.29% further suggests that the diuron was lost from an area partially composed of hard surfaces where its transport would not have been restricted by a soil matrix.

The chlorotoluron concentrations of samples oscillated between 0.18μg/l and 0.32μg/l with sample nine having a concentration of 0.26μg/l. No major trend in the chlorotoluron concentration was observed, although the concentration curve did show a small peak (0.33μg/l) coincident with the flow rate peak. Figure 7-7 also shows the variation of the chlorotoluron flux (μg/s) during the course of the storm event which peaked at a value of approximately 17μg/s, coinciding with the peak flow rate. The integration of the chlorotoluron flux and flow curves during the monitored period of the storm event showed that 91.3mg of chlorotoluron was transported in the flow at Site D. This corresponds to an event mean concentration of 0.24μg/l. With respect to the chlorotoluron application (70kg), made to the British Telecom land 149 days before the storm event, the mass transported during the storm event corresponded to 1.3×10^{-4}% of the mass applied which is comparable with the level determined for the chlorotoluron application made to the agricultural sub-catchment after a similar period of time following application (see Section 6.4.3). This result is surprising considering the fact that the agricultural sub-catchment, under similar field management, did not produce significant runoff during this event. The assumption that the source of the chlorotoluron was the application made to the British Telecom land may not be strictly correct, as the results of the manual samples discussed in Section 7.2.1 and the results of the artificial rainfall-runoff tests (see Section 7.3) suggest that the railway line was also a source of chlorotoluron. Therefore, it seems probable that the chlorotoluron detected at Site D may have been transported from the railway line as well as the British Telecom land.

For isoproturon, after sample one the concentration decreased from 0.22μg/l to 0.07μg/l for sample two, and to below the detection limit for sample four which was taken one hour before the peak flow rate and remained below the detection until sample six, which was taken three hours after the flow peak. After sample six the concentration increased above the detection limit to 0.06μg/l for sample seven, eventually reaching 0.13μg/l for sample nine (Figure 7-7). The absence of isoproturon detection in the manual sample taken at Site D on 8/4/92 during non-storm conditions seven days before this event, showed that isoproturon was absent from or present at levels below the detection limit in the baseflow. Therefore its detection in the early pre-flow peak samples, of this event, followed by a decrease to levels below the detection limit during the flow peak suggests that the isoproturon may have been present in the early elevated levels of interflow entering the main watercourse which in effect, was then diluted by the main body of direct surface runoff flowing from the hard-surfaced areas of the urbanised catchment. The recovery of the isoproturon concentrations towards the end of the storm event may have reflected a reduction in the interflow dilution as the volume of direct surface runoff subsided. The integration of the isoproturon flux curve, which was at a minimum during the hydrograph peak, and the flow curve showed that during the monitored period of the storm event, 10.05mg of isoproturon was transported in flow at Site D. This corresponded to an event mean concentration of 0.03μg/l. From the manual sample taken during event JD150, it appeared likely that the source of the isoproturon was an unidentified application in the British Telecom land area.

7.4.1.2 Atrazine and simazine

The temporal variation in simazine and atrazine concentrations and fluxes detected during the storm event on 15/4/92 are illustrated in Figure 7-8. The event occurred 218 days after the simazine application (0.346kg) to the railway line and approximately 67 days after the previous atrazine application (0.208kg) to grassed amenity areas by the Parks and Recreation Department. Nine samples were taken during the event and simazine and atrazine were detected in all of the samples. The concentrations of the atrazine were generally higher than those of simazine. Though the preceding simazine application was approximately 66% higher than that of atrazine, the atrazine concentrations may have been higher because of its more recent application combined with the closer proximity of the atrazine application to the sampling site. Both simazine and atrazine exhibited concentration peaks coincident with the hydrograph peak which produced flux curves that peaked with the flow rate. The integration of the flux and hydrograph curves showed that during the sampling period, 213.0mg of atrazine and 147.9mg of simazine were transported in the event runoff. The atrazine weight corresponded to an application loss of 0.1% with respect to the recent application and an event mean concentration of 0.58μg/l. The simazine weight corresponded to an application loss of $4.2x10^{-2}$ % with respect to the railway application and an event mean concentration of 0.40μg/l.

The concentration of atrazine in sample one, taken three hours before the event flow rate peak, was 0.51μg/l which was approximately four times higher than the atrazine concentration determined in the manual sample taken at Site D on 8/4/92. This suggests that three hours before the event peak surface runoff was already contributing to the flow. This was confirmed by the marginally elevated flow rate at that time shown in the hydrograph in Figure 7-8. Throughout the event the trend of the atrazine concentration remained approximately constant with a fluctuation between 0.69μg/l and 0.44μg/l. Sample four corresponded to a minor concentration peak (0.68μg/l) which coincided with the flow peak and added to the magnitude of the flux peak at this time.

The concentration of simazine in sample one, taken three hours before the event flow rate peak, was 0.38μg/l which was approximately double the simazine concentration determined in the manual sample taken at Site D on 8/4/92. This behaviour was similar to atrazine and can be explained in the same way. Samples two and three had simazine concentrations of 0.45μg/l and 0.33μg/l respectively and sample four, occurring at the same time as the flow peak demonstrated the maximum concentration of 0.67μg/l. The subsequent samples showed an exponential decrease in concentration, falling to 0.20μg/l for sample nine.

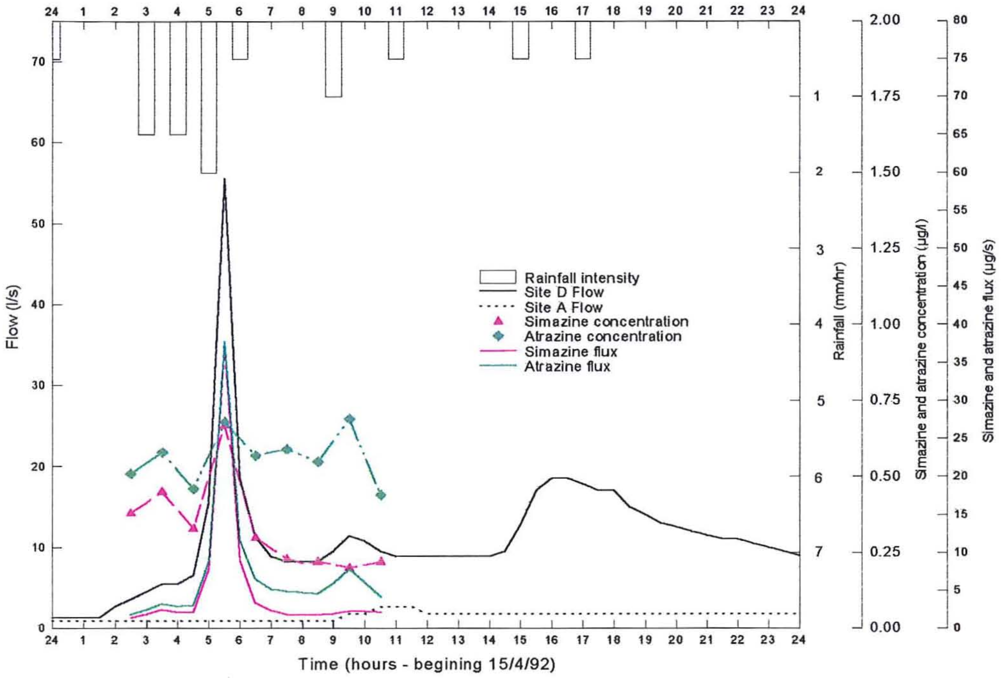

Figure 7-8 Simazine and atrazine concentrations (µg/l) and flux (µg/s) at site D during the storm event occurring on 15/4/92 (JD 106) [Rainfall intensities (bar chart) and storm runoff also shown]

7.4.2 Results for the storm event of 28/4/92 (JD 119)

The second storm event to be automatically sampled at Site D occurred on 28/4/92 (JD 119) and the data collected for this storm are shown in Figures 7-9 and 7-10. The concentration (µg/l) and flux (µg/s) curves are plotted for simazine, atrazine, chlorotoluron, isoproturon and diuron that were determined in the eleven samples automatically collected over the duration of the storm event.

Following an initial flow rate of approximately 13l/s, the event hydrograph peaked at 161l/s after 18.5mm of rain fell on the catchment over a period of nine hours at a maximum intensity of 3mm/hr. Compared to the previous storm event of 15/4/92 (JD106), the hydrograph for this event was much less sharply defined which suggests that the grassed areas of the urbanised catchment generated runoff as well as the hard-surfaced areas. This was further indicated by a comparison of total runoff volume with respect to rainfall volume. For the 15/4/92 event, the catchment received 9.5mm of rain at a peak intensity of 2mm/hr and generated 0.63mm of runoff, whilst this event generated 3.89mm of runoff from 18.5mm of rainfall at an intensity of 3mm/hr (Table 5.5). Therefore, this event received approximately twice the volume of rain but generated approximately five times the volume of runoff even when taking into account the minor contribution from the agricultural sub-catchment. The increased response from the grassed areas of the urbanised catchment was probably the result of the increased overall catchment wetness brought about by the previous event on 15/4/92. The agricultural sub-catchment generated only a minor runoff response with a maximum flow rate of approximately 11l/s, which represents only 6.8% of the maximum Site D flow rate. The minor hydrograph peak at Site A coincides with the second hydrograph peak at Site D which may suggest that the major flow peak for Site D represents runoff from the grassed areas of the urbanised catchment. This assumes that the urban grassed areas have similar response characteristics to the agricultural sub-catchment. If this was the case, it could be that the first two peaks in the Site D hydrograph corresponded to the response of areas possessing hard-surface response characteristics within the urbanised catchment.

7.4.2.1 Chlorotoluron, isoproturon and diuron

The storm event occurred 162 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and approximately 80 days after the diuron application (0.083kg) by the Parks and Recreation Department to grassed amenity areas within the urbanised catchment, during the week ending 8/2/92. From the agrochemical application records compiled for the urbanised catchment, there does not appear to be any record of an application of isoproturon prior to the storm event (see Table 7-1). Since the runoff sampled at Site D also contained a minor contribution from Site A, applications made to the agricultural sub-catchment may also have been significant for the explanation of pesticide concentrations. Relevant applications include chlorotoluron (78.330kg) applied 165 days before the event and isoproturon (13.055kg, 25.250kg and 22.475kg) applied 183, 174 and 164 days before the event (see Table 7-1). Chlorotoluron, isoproturon and diuron were detected in all eleven automatically collected samples. Sample one was taken one hour before the first minor peak of the hydrograph and five and a half hours before the main hydrograph peak. The pattern of the diuron concentration throughout the storm was markedly different from that of chlorotoluron and isoproturon, which behaved similarly (Figure 7-9).

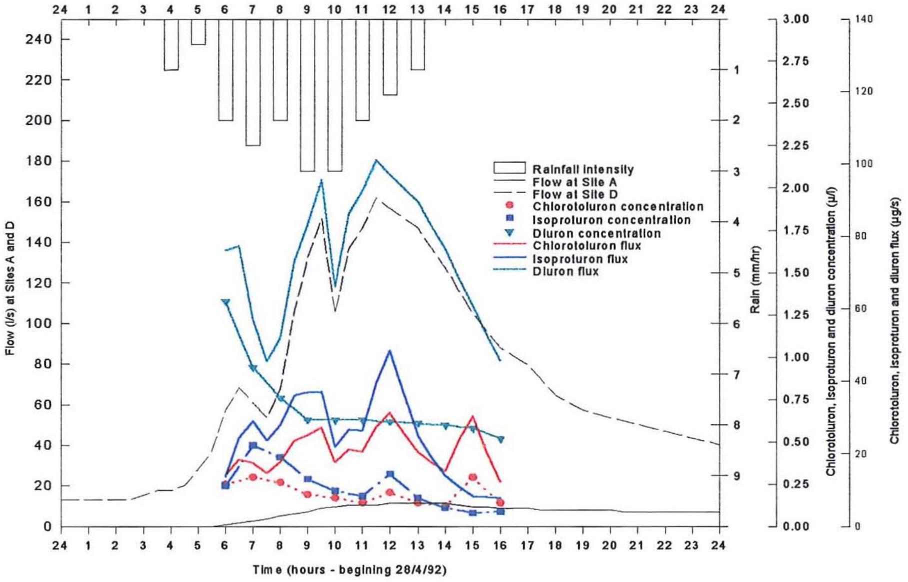

Figure 7-9 Chlorotoluron, isoproturon and diuron concentrations (µg/l) and flux (µg/s) at site D during the storm event occurring on 28/4/92 (JD 119) [Rainfall intensities (bar chart) and storm runoff also shown]

The diuron concentration was initially high and then appeared to fall exponentially to a constant value, whereas the chlorotoluron and isoproturon concentrations appeared to peak slightly in sample two and then very gradually decrease. From the beginning of the sampling period, the diuron concentration decreased from a concentration of 1.33µg/l to a concentration of 0.52µg/l in sample eleven, which was taken four and a half hours after the peak flow of the storm hydrograph. This behaviour was similar to that observed during the event on 15/4/92, with the reduction in concentration during the course of the storm event, suggesting that the diuron was transported from a combination of rapid removal from hard surfaces, from areas close to the main watercourse and from entry points into the storm water drainage system. It was probable that the source of the diuron was the application (0.083kg) made by the Parks and Recreation Department during the week ending 8/2/92. Examination of the diuron flux curve shows the existence of three peaks at 77µg/s, 95µg/s and 101µg/s which coincided with the three peaks of the hydrograph. The integration of the diuron flux curve showed that during the sampling period 2.723g of diuron was transported in the event runoff. This diuron weight corresponded to an application loss of 3.28% with respect to the most recent preceding application by the Parks and Recreation Department. The event mean concentration for diuron was 0.65µg/l. The percentage diuron loss value of 3.28% was exceptionally high compared to the typical value of $2x10^{-2}$ for herbicides removed in runoff from agricultural land (Williams *et al*, 1995). This suggests that the diuron was lost from an area partially composed of hard surfaces where its transport would not have been restricted by a soil matrix. The highest rate of mass transport was 101µg/s which coincided with the maximum flow rate (161l/s) of the event (Figure 7-9).

The maximum isoproturon concentration was detected in sample two (0.48µg/l), which was collected four and a half hours before the maximum flow rate. The isoproturon concentration then gradually decreased to 0.18µg/l in sample six before increasing to 0.31µg/l for sample seven which occurred thirty minutes after the maximum flow rate. The concentration then gradually decreased exponentially to a level of 0.09µgl for sample eleven (Figure 7-9). The trend in chlorotoluron concentrations was very similar to that of isoproturon but at an overall lower level in the early samples. The chlorotoluron concentration of sample one was 0.25µg/l which increased to 0.29µg/l for sample two from where the concentration gradually fell to 0.14µg/l for sample six before showing a minor peak at 0.20µg/l for sample seven. The concentration then continued to fall to 0.12µg/l for sample nine before showing another peak at 0.29µg/l for sample ten. For isoproturon and chlorotoluron the periods of highest mass transport generally coincided with the three peaks in flow rate, producing peaks of 29µg/s, 37µg/s and 48µg/s for isoproturon and 18µg/s, 27µg/s and 31µg/s for chlorotoluron. A fourth flux peak of 30µg/s was observed for chlorotoluron, produced by the concentration of 0.29µg/l in sample ten.

Integration of the flux curves and the hydrograph over the sampling period showed that 922.5mg of isoproturon and 773.6mg of chlorotoluron were transported during the storm event, corresponding to event mean concentrations of 0.22µg/l and 0.18µg/l, respectively. Given the very minor runoff from the agricultural sub-catchment, the majority of the chlorotoluron load was probably transported from the application (70kg) made to the British Telecom land on 18/11/91, possibly combined with minor amounts from the railway line (Table 7-3). With respect to the British Telecom application, the diuron load at Site D corresponded to an application loss of 0.001%. The pesticide application data (Table 7-1) suggests that the sources of the isoproturon were probably the applications made to the agricultural sub-catchment. However, the concentration data from the automatic samples taken over the event on 15/4/92, during which there was no flow or pesticide input from the agricultural sub-catchment, suggested that there was a source of isoproturon from within the urbanised catchment. Therefore, it was probable that the bulk of the isoproturon load determined at site D was transported from an unknown source within the urbanised catchment, most likely located near the British Telecom land area.

7.4.2.2 Atrazine and simazine

The temporal variation in simazine and atrazine concentrations and fluxes detected during the storm event of 28/4/92 are illustrated in Figure 7-10. The event occurred 231 days after the simazine application (0.346kg) to the railway line and 80 days after the atrazine application (0.208kg) to the grassed amenity areas of the urbanised catchment by the Parks and Recreation Department. The runoff sampled at Site D contained minor runoff from the agricultural sub-catchment and therefore the relevant agricultural applications also need to be taken into account. There was only one which involved a simazine application (9.027kg) made on 28/11/91. Simazine and atrazine were detected in all eleven samples and as for the storm event of 15/4/92, the concentration of the atrazine was consistently higher than that of simazine. This may have been because of its more recent application combined with the closer proximity of the atrazine application to the sampling site. The atrazine concentration in sample one, taken five-and-a-half hours before the maximum flow rate (161l/s), was 0.26μg/l following which the concentration increased to the event maximum of 0.68μg/l (sample four) which occurred immediately before the second flow peak of 151l/s (Figure 7-10). The atrazine concentration then gradually fell to a value of 0.41μg/l for sample eleven. The two flow peaks preceding the main flow peak (161l/s) were probably associated with runoff from semi-hard-surfaced areas within the urbanised catchment (see also Section 7.4.2). Further, considering the period of highest atrazine flux (91μg/s) and the peak atrazine concentration (0.68μg/l) coincided with the second highest peak flow rate, it was probable that the atrazine was transported from similar hard-surfaced areas. The simazine concentration gradually increased from an initial value of 0.08μg/l to 0.47μg/l for sample seven which occurred thirty minutes after the main flow peak. There was a subsequent decrease in the simazine concentration to 0.25μg/l for sample eleven.

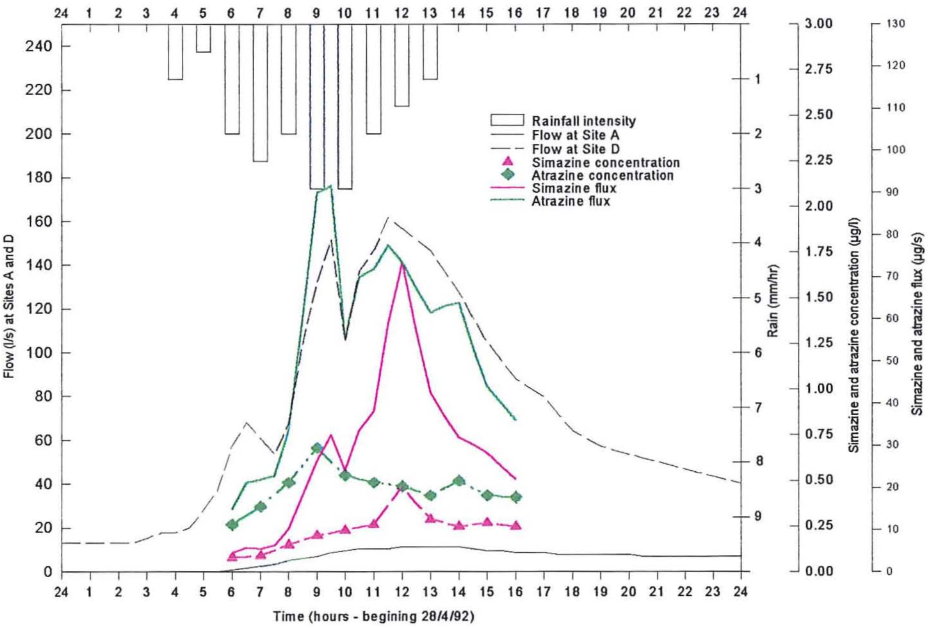

Figure 7-10 Simazine and atrazine concentrations (µg/l) and flux (µg/s) at site D during the storm event occurring on 15/4/92 (JD 119) [Rainfall intensities (bar chart) and storm runoff also shown]

The peak simazine concentration occurred three hours after that of atrazine, and coincided with the main flow peak which was associated with the response from the general grassed areas of the urbanised catchment. This suggests that the sources of the two pesticides were different and it seems probable that the source of the simazine may have been the application (0.346kg) made to the railway line. The timing of the peak simazine concentration compared to that of atrazine indicates a source that was more distant form the monitoring site and less readily leachable. The period of highest simazine flux (73µg/s) coincided with the peak simazine concentration (0.68µg/l) and occurred thirty minutes after the peak flow rate.

The integration of the flux and hydrograph curves for the duration of the sampling period revealed that 1.998g of atrazine and 1.080g of simazine were transported in the event runoff. Given the relative magnitudes of the agricultural sub-catchment runoff volume and that of the urbanised catchment, it was most likely that the bulk of the simazine and atrazine loads determined at Site D were transported from within the urbanised catchment. The weight of atrazine in the runoff corresponded to an application loss of 0.96% with respect to the Parks and Recreation Department application (0.208kg) and an event mean concentration of 0.48μg/l. The event mean concentration of simazine was 0.26μg/l and the monitored runoff load represented an application loss of 0.31% with respect to the railway application (0.346kg).

It is interesting to note that atrazine (0.208kg) and diuron (0.083kg) were applied by the Parks and Recreation Department at the same time during the week ending 8/2/92, as part of the same product known as Rassapron. However, during this storm event (28/4//92) which occurred approximately 80 days after the application, the integration of the flux data showed that 0.96% of the atrazine and 3.28% of the diuron was lost during the storm event and the respective event mean concentrations were 0.48μg/l and 0.65μg/l. This result is not entirely consistent with what might have been predicted from the physico-chemical properties of the two compounds (Table 4.2). Atrazine and diuron have similar solubilities (30mg/l and 42mg/l respectively), similar soil half lives (60 days and 64-90 days respectively) but diuron has a higher organic carbon coefficient (288-480) compared to atrazine (100) suggesting a greater affinity to soil particles. However, the result may be explained if the applicability of the physico-chemical data (Table 4.2) is considered with respect to the nature of the application environment in question. The percentage application loss figures for both atrazine and diuron were extremely high compared to typical loss values for similar compounds applied to the soil environment (Williams *et al*, 1995). It is therefore probable that the two compounds were lost from environments less typical of soils and more representative of the hard surfaces. In such circumstances, the soil half life and soil partition values would not be relevant as they were measured in soil environments characterised by high organic matter contents. Also, when applied to non-soil based surfaces, where the compounds have less opportunity to infiltrate below the surface, their loss by photodegradation would be much more significant. In this case it appears to have led to diuron exhibiting greater persistence and consequently a higher potential to leach during the storm event.

7.4.3 Results for the storm event on 1/5/92 (JD 122)

The third storm event to be automatically sampled at Site D occurred on 1/5/92 (JD 122). The event occurred after 9.5mm of rain fell on the North Weald catchment over a period of four hours at a maximum intensity of 3.5mm/hr. The rainfall generated runoff from both the agricultural sub-catchment and the urbanised catchment. Figure 7-11 shows the storm hydrographs for the urbanised catchment at Site D and the agricultural sub-catchment with associated pollutographs for chlorotoluron, isoproturon and diuron and Figure 7-12 shows the same storm hydrographs and the associated pollutographs for simazine and atrazine. The Site A data are shown for comparison purposes. The increased response from the agricultural sub-catchment was probably the result of the higher overall catchment wetness brought about by the previous storm event three days earlier on 28/4/92.

At site D, following an initial flow rate of approximately 5l/s, the event hydrograph peaked twice at 180l/s. The peaks occurred two and a half hours after the initial rise in flow rate and then one hour later. The concentration (µg/l) curves for chlorotoluron, isoproturon, diuron, simazine and atrazine for the fourteen samples that were automatically collected over the duration of the storm event are shown in Figures 7-11 and 7-12. For each pesticide, a flux (µg/s) curve is shown which is the product of the concurrent concentration and flow rate values.

7.4.3.1 Chlorotoluron, isoproturon and diuron

The storm event occurred 165 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and 83 days after the diuron application (0.083kg) by the Parks and Recreation Department to grassed amenity areas within the urbanised catchment, during the week ending 8/2/92. There was no record of an application of isoproturon prior to the storm event (Table 7-1). Since the runoff sampled at Site D contained a significant contribution from Site A, applications made to the agricultural sub-catchment may exert a significant influence on the measured pesticide concentrations. Relevant applications were chlorotoluron (78.330kg) 168 days before the event and isoproturon (13.055kg, 25.250kg and 22.475kg) 186, 177 and 167 days before the event (Table 7-1).

The first of the fourteen automatic samples was obtained thirty minutes before the major peak of the hydrograph. The temporal pattern of diuron concentrations was markedly different from that of both chlorotoluron and isoproturon which behaved similarly. The diuron concentration was initially relatively high and then appeared to fall, then recover and then fall again, whereas the chlorotoluron and isoproturon concentrations appeared begin low, rise to a peak and then gradually decrease.

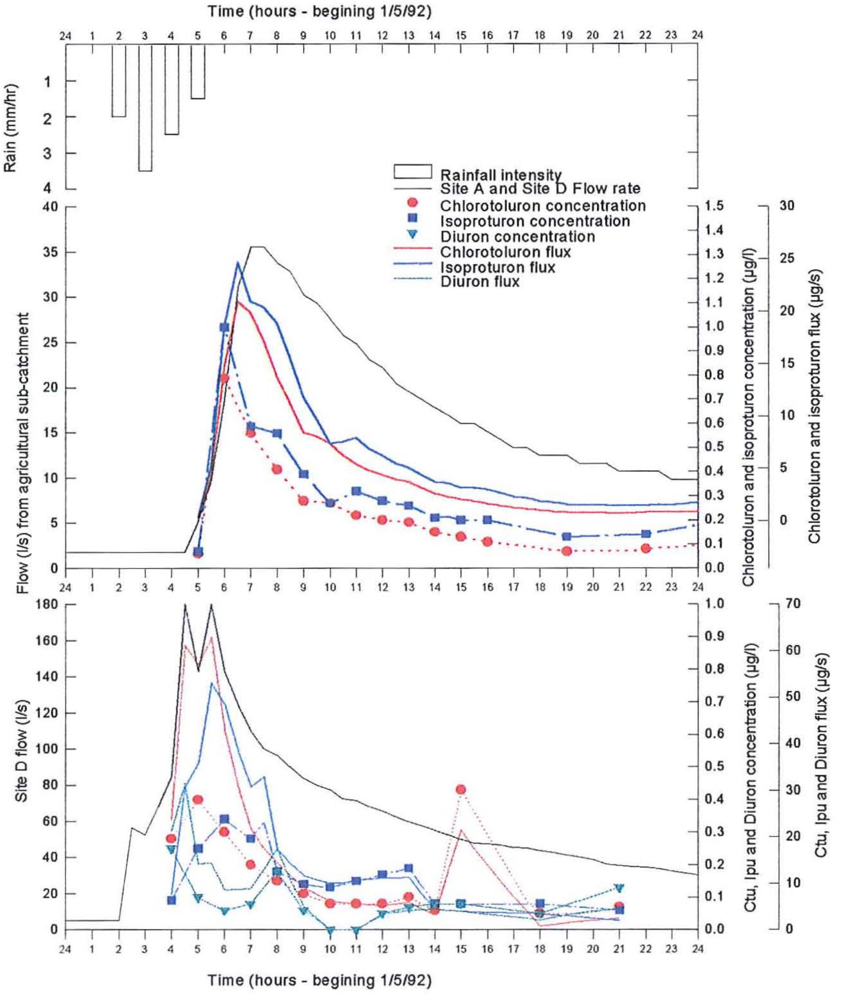

Figure 7-11 Chlorotoluron, isoproturon and diuron concentrations (µg/l), respective fluxes (µg/s) and hydrograph at site D (lower graph) and at site A (middle graph) during the storm event occurring on 1/5/92 (JD 122) [Upper bar chart shows temporal rainfall intensity]

From the beginning of the sampling period, the diuron concentration rapidly decreased from a value of 0.25µg/l in sample one, to a concentration of 0.06µg/l in sample three, which was taken thirty minutes after the last flow peak of the storm hydrograph. The concentration then momentarily recovered, reaching 0.18µg/l in sample five before falling to below the limit of detection in sample seven. Diuron was detected in samples nine to thirteen at concentrations of 0.05µg/l, 0.07µg/l, 0.08μg/l, 0.08μg/l and 0.05μg/l. The concentration then rose unexpectedly to 0.13μg/l in sample fourteen. By adopting a behaviour similar to that observed during the events of 15/4/92 and 28/4/92, the initial high diuron concentration followed by a reduction during the course of the storm event, suggested that the diuron was either transported rapidly from hard surfaces or from areas close to the main watercourse or from entries into the storm water drainage system. As was predicted for the previous events, it was probable that diuron was transported from a combination of all three types of area within the urbanised catchment. The expected source of diuron in the runoff at Site D was the application (0.083kg) made by the Parks and Recreation Department during the week ending 8/2/92. The highest rate of mass transport (31μg/s) coincided with the first flow peak and the peak diuron concentration of 0.25μg/l. The integration of the diuron flux curve and the event hydrograph curve showed that during the sampling period 382mg of diuron was transported in the event runoff. This corresponded to an application loss of 0.46% with respect to the recent application by the Parks and Recreation Department and an event mean concentration of 0.11μg/l.

Sample one exhibited an isoproturon concentration of 0.09μg/l which rose to 0.25μg/l for sample two and 0.34μg/l in sample three which was taken thirty minutes after the second flow peak. The concentration then gradually fell to 0.13μg/l for sample seven before increasing to 0.19μg/l in sample ten after which the concentration decreased to 0.08μg/l and ultimately to 0.6μg/l in sample fourteen. The chlorotoluron concentration in sample one was 0.28μg/l and this increased to 0.40μg/l for sample two, which was taken thirty minutes after the first flow peak. Subsequently the concentration gradually fell to a level of 0.06μg/l which then unexpectedly increased to 0.43μg/l for sample twelve before falling again to 0.07μg/l for sample fourteen.

For chlorotoluron and isoproturon the periods of highest mass transport generally coincided with the three peaks in flow rate, producing flux peaks of 63μg/s and 47μg/s respectively. The integration of the flux curves over the sampling period produced transported chlorotoluron and isoproturon loads of 893mg and 831mg respectively. Comparison with the integrated hydrograph gave event mean concentrations of 0.17μg/l and 0.12μg/l respectively. The source of chlorotoluron was probably a combination of the application made to the BT land on 18/11/91 and leaching from the railway line as well as the application made to the agricultural sub-catchment. Although there was no evidence of isoproturon applications within the urbanised catchment, an analysis of the manual sample taken at location BT on 29/5/92 clearly showed the presence of isoproturon in runoff originating from the BT land area. Therefore, it was probable that the isoproturon detected at Site D on 1/5/92 also originated from runoff generated from this area.

7.4.3.2 Atrazine and simazine

The temporal variation in simazine and atrazine concentrations and fluxes detected during the storm event of 1/5/92 are illustrated in Figure 7-12. The event occurred 234 days after the simazine application (0.346kg) to the railway line and 83 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment by the Parks and Recreation Department. The simazine application (9.027kg) made to the agricultural sub-catchment 155 days previously on 28/11/91 was also relevant. Fourteen samples were taken during the event with simazine being detected in thirteen samples and atrazine being present in all samples.

Following an initial atrazine concentration of 0.21μg/l, the concentrations followed a fairly horizontal linear trend throughout the sampling period with fluctuations between 0.05μg/l and 0.2μg/l (Figure 7-12). The similar trend in simazine concentrations, fluctuating between 0.05μg/l and 0.15μg/l, could have suggested a common source. The point of highest atrazine flux (27μg/s) coincided with the first flow peak (180l/s) whereas the maximum simazine flux (21μg/s) occurred two hours after the second flow peak (180l/s) and coincided with the peak simazine concentration of 0.20μg/l in sample four.

The integration of the flux curves showed that during the sampling period, 632mg of atrazine and 611mg of simazine were transported during the event. The atrazine weight corresponded to an event mean concentration of 0.14μg/l and the simazine weight corresponded to an event mean concentration of 0.11μg/l. Since it was impossible to differentiate between specific applications, the combined application loss for simazine was estimated to be 0.006%; no estimate was available for atrazine due to the absence of application data relating to imports from the agricultural sub-catchment.

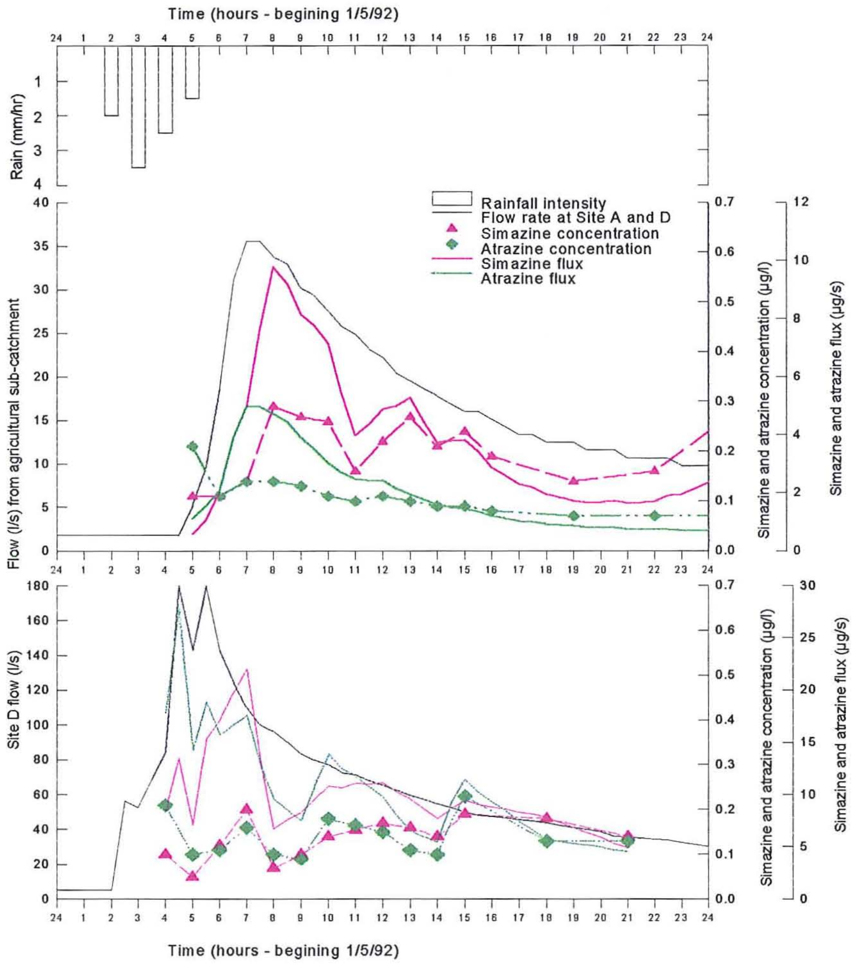

Figure 7-12 Simazine and atrazine concentrations (µg/l), respective fluxes (µg/s) and hydrograph at site D (lower graph) and at site A (middle graph) during the storm event occurring on 1/5/92 (JD 122) [Upper bar chart show temporal rainfall intensity]

7.4.4 Results for the storm event on 29/5/92 (JD 150)

The fourth storm event to be automatically sampled at Site D occurred on 29/5/92 (JD 150) and the collected data are shown in Figures 7-13, 7-14 and 7-15 and fully described below. Significant runoff was only monitored at Site D with no flow being observed in the by-pass channel and only very minor flow recorded at Site A. Therefore the runoff shown in the all the Figures wholly represents the storm runoff from the urbanised catchment. Nine samples were automatically collected over the duration of the storm event.

Following an initial flow rate of approximately 11l/s, the event hydrograph at Site D peaked at 330l/s after 25.5mm of rain fell on the catchment over a period of ten hours at a maximum intensity of 6mm/hr. The negligible flow of approximately 2l/s recorded at Site A is not shown on the Figures. Compared to the previous two storm events on 1/5/92 and 28/4/92, the hydrograph for this event was more sharply defined which suggested rapid runoff from the impervious surface areas within the urbanised catchment. The symmetrical profile of the hydrograph was typical of that of urban runoff from a catchment with a high proportion of hard surface area (Kiely, 1997). The rapid recession after peak flow suggested that negligible rainfall volume was held in temporary storage and that the rain that fell on the urbanised catchment either rapidly generated runoff or fell upon non-hard surfaced areas where it was taken up by the soil to satisfy soil moisture deficit. This explanation of the hydrograph agrees well with the conditions at the time of the event which occurred during a relatively dry period at the beginning of the growing season and the combined effect of these two factors would have generated a significant soil moisture deficit (see Section 5.3.2.2).

7.4.4.1 Chlorotoluron and isoproturon

The storm event occurred 193 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 but there is no record of an application of isoproturon to the urbanised catchment prior to the storm event (Table 7-1). The first sample was taken ninety minutes before the major peak of the hydrograph. The trends in the chlorotoluron and isoproturon concentrations over the sampling period were markedly different suggesting different sources (Figure 7-13).

The chlorotoluron concentration peaked (4.51μg/l) thirty minutes after the flow peak whereas the isoproturon concentration peaked (3.27μg/l) ninety minutes after the flow peak. The chlorotoluron concentration dropped rapidly after sample three, following the hydrograph recession, to a value of 0.82μg/l for sample nine.

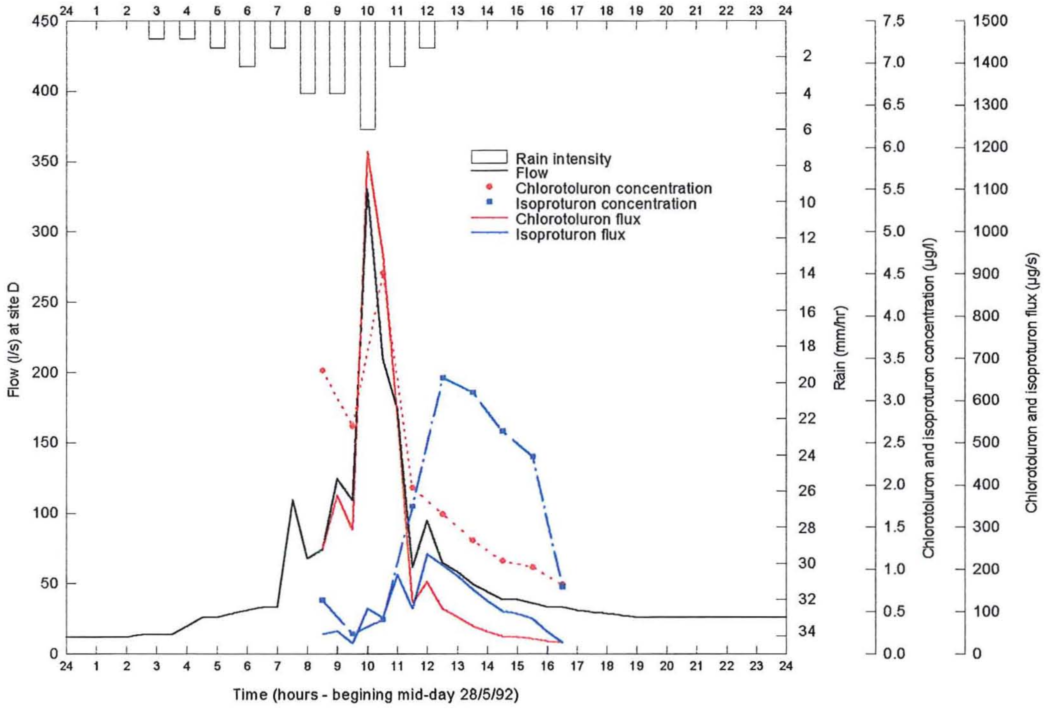

Figure 7-13 Chlorotoluron and isoproturon concentrations (µg/l) and fluxes (µg/s) at site D during the storm event occurring on 29/5/92 (JD 150) [Rainfall intensities (upper bar chart) and storm runoff also shown]

The concentrations of isoproturon in samples one, two and three were 0.64µg/l, 0.24µg/l and 0.41µg/l respectively. After sample three, the concentration increased rapidly to the maximum in sample five, following which there was a decrease to 0.80µg/l in sample nine. The slow response of the isoproturon concentration with respect to the hydrograph peak suggested that the source of the isoproturon was a permeable area that was slow to respond to the rainfall due to the requirement to satisfy soil moisture deficits before runoff was generated. Alternatively, the majority of the isoproturon may have been present in the interflow of the soil profile. As the event proceeded, the emergence of the interflow would have occurred later than the main hard-surface runoff and at a time when the latter was subsiding, thus minimising dilution and giving rise to relatively high isoproturon concentrations. Chlorotoluron was applied to the British Telecom land 193 days prior to the event, but the initially high concentrations, which approximately mirrored the hydrograph, suggested that the chlorotoluron may have been also leached from a purely hard-surfaced area. An explanation for this could be rapid transport from the railway line which was shown to be a chlorotoluron source from manual sampling and ballast analysis (Sections 7.2.1.1 and 7.3).

The integration of the hydrograph and flux curves over the sampling period indicates the masses of chlorotoluron and isoproturon transported during the event were 7,688mg and 3,342mg respectively, which corresponded to event mean concentrations of 2.81μg/l and 1.22μg/l respectively. The source of the chlorotoluron was probably a combination of the application made to the BT land on 18/11/91 and leaching from the railway line. The maximum flux of chlorotoluron (1190μg/s) approximately coincided with the flow peak and the maximum flux of isoproturon (237μg/s) occurred two hours after the flow peak (Figure 7-13).

Although the maximum event concentrations of chlorotoluron and isoproturon were similar (4.51μg/l and 3.27μg/l), the difference in peak flux and total flux values clearly demonstrates the important influence of the relevant timings of peak flow and peak concentration. Compared to the three previously described storm events, the chlorotoluron and isoproturon event mean concentration values obtained for this event, were approximately an order of magnitude greater. The peak flow rates of each event, including this one, were within a factor of two, however the peak rainfall intensity (6mm/hr) was the largest recorded during the monitoring period. Therefore, it appears that the rainfall intensity may have had a significant factor in determining pesticide concentration in the storm event runoff. Similar findings were reported by Johnson (1995), who reported a ten-fold increase in the application loss of isoproturon in response to a fourfold increase in rainfall intensity. This effect was attributed to the nature of the physical process involved.

7.4.4.2 Diuron

The temporal variation in diuron concentration and flux during the storm event of 29/5/92 are shown in Figure 7-14. The concentration and flux were the highest recorded for any pesticide throughout the duration of the monitoring programme. The storm event occurred only 24 days after a diuron application (0.867kg) by the Epping Forest District Council Roads and Highways Department. The application was made to the kerbstones and pavement backwalls within the urbanised catchment to control the ingress of weeds.

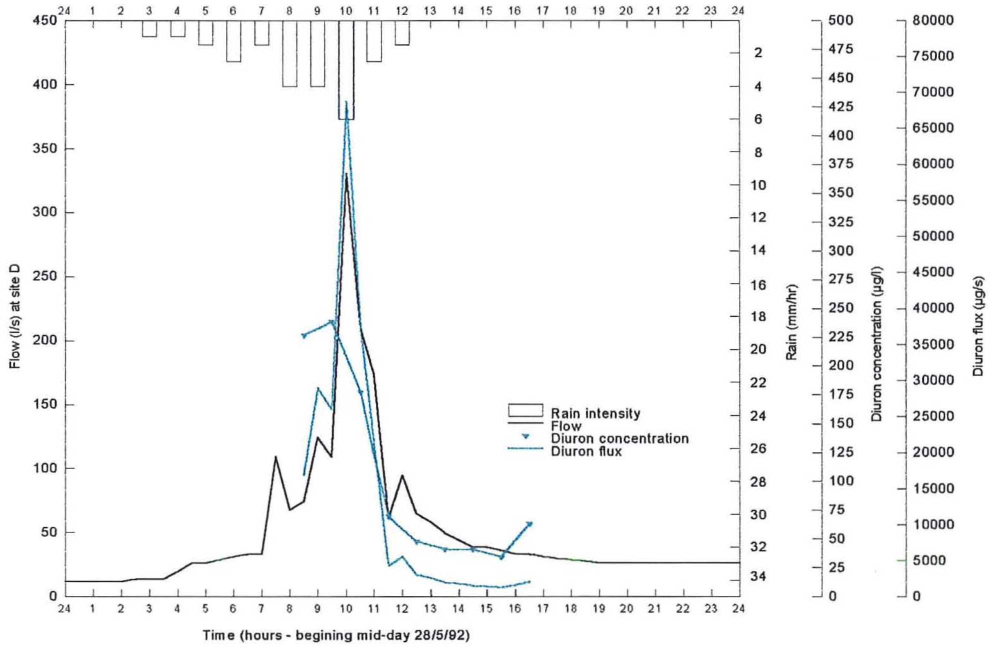

Figure 7-14 Diuron concentrations (µg/l) and fluxes (µg/s) at site D during the storm event occurring on 29/5/92 (JD 150) [Rainfall intensities (upper bar chart) and storm runoff also shown]

The first sample was taken ninety minutes before the main flow peak of 330l/s and had a concentration of 226.75µg/l. The concentration then increased slightly to 238.39µg/l in sample two which was taken thirty minutes before the main flow peak. During the main flow peak the diuron concentration decreased to 177.56µg/l in sample three and then to 69.76µg/l in sample four which coincided with the end of the hydrograph recession limb. The rapid decrease in concentration during the main hydrograph peak was probably a dilution effect due to the increased volume of runoff. The concentrations in samples four to nine showed a much slower rate of decline, decreasing to 34.76µg/l in sample eight but then unexpectedly rising to 68.42µg/l in sample nine.

The variations in the concentrations during the period of the storm event were typical of very rapid runoff from hard surfaces, immediately followed by a dilution effect as the whole catchment began to respond to the rainfall. Similar variations in diuron concentrations were also seen during the events of 15/4/92 and 28/4/92. The application of diuron to the kerbstones and pavement backwalls placed the diuron in an ideal location to ensure rapid transport, during an event, to the nearest roadside storm drain from where the diuron would have been rapidly transported to the main watercourse.

The integration of the diuron flux curve and the event hydrograph curve showed that during the sampling period 390.933g of diuron was transported in the event runoff. The diuron weight corresponded to an application loss of 45.1% with respect to the application by the Roads and Highways Department 24 four days previously, and an event mean concentration of 142µg/l. The highest rate of mass transport was 68mg/s which coincided with the maximum flow rate of the event (Figure 7-14). The application loss of diuron was an order of magnitude higher than the reported loss of any pesticide in agricultural runoff and clearly demonstrates the susceptibility to loss in storm runoff of pesticides applied to a hard surface environment. Further, in this case the period of time between herbicide application and the occurrence of the first storm event was relatively short, thus minimising the amount of herbicide lost prior to the event through degradation and volatilisation and maximising the amount subsequently available to loss in event runoff.

7.4.4.3 Atrazine and simazine

The temporal variation in simazine and atrazine concentrations and fluxes detected during the storm event of 29/5/92 are illustrated in Figure 7-15. The event occurred 262 days after the simazine application (0.346kg) to the railway line and 111 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment made by the Parks and Recreation Department. Simazine and atrazine were detected in all collected samples and the concentration variations for each pesticide show approximately similar trends over the duration of the storm event. Both simazine and atrazine showed relatively high concentrations before the onset of the main hydrograph peak which then decreased during the period of maximum flow and then appeared to recover as the flow rate receded.

The simazine concentration in sample one taken ninety minutes before the flow peak was 2.23µg/l, the concentration then decreased to 1.22µg/l in sample two, taken thirty minutes before the flow peak, and then to 0.85µg/l in sample three, taken thirty minutes after the flow peak. The simazine concentration then remained fairly constant at this level from samples four to six after which the concentration began to gradually increase, reaching 1.64µg/l for sample nine. The atrazine concentration in sample one was 1.14µg/l which fell to 0.38µg/l in sample two. After this point the atrazine concentration gradually rose to 1.28μg/l in sample five and then decreased in an inverse exponential manner to 0.66μg/l in sample nine. The periods of maximum flux for simazine and atrazine both coincided with the main hydrograph peak at values of 341μg/s and 176μg/s respectively (Figure 7-15).

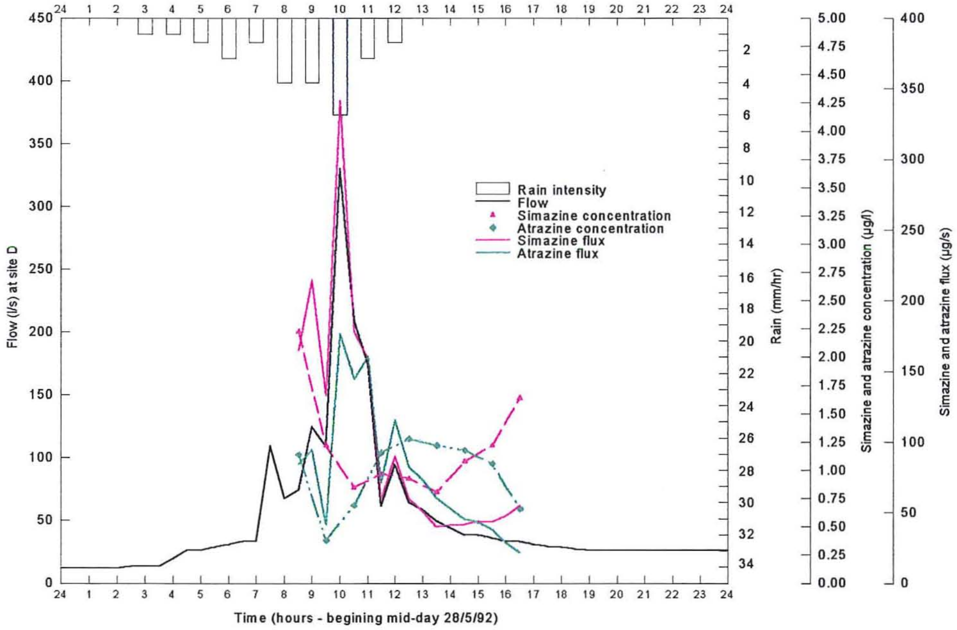

Figure 7-15 Simazine and atrazine concentrations (μg/l) and fluxes (μg/s) at site D during the storm event occurring on 29/5/92 (JD 150) [Rainfall intensities (upper bar chart) and storm runoff also shown]

The integration of the flux curves showed that 2,981mg of simazine and 2,310mg of atrazine were transported in the event runoff during the sampling period. These values corresponded to event mean concentrations of 1.08μg/l and 0.84μg/l respectively. The transported weight of simazine corresponded to an application loss of 0.84% with respect to the railway application (0.346kg). The atrazine storm event load corresponded to an application loss of 1.11% with respect to the Parks and Recreation Department application (0.208kg). The event mean concentrations of simazine and atrazine are similar to those of chlorotoluron and isoproturon for this event in being approximately one order of magnitude higher compared with the three previously described storm events. The influence of rainfall intensity is therefore important in controlling the surface wash-off of simazine and atrazine as was previously explained for chlorotoluron and isoproturon.

7.4.5 Results for the storm event on 2/10/92 (JD 276)

The fifth storm event to be automatically sampled at Site D occurred in the autumn period on 2/10/92 (JD 276) and is represented diagrammatically in Figures 7-16 and 7-17. These Figures show the concentration (µg/l) curves for chlorotoluron, isoproturon, diuron, simazine and atrazine that were determined from the four samples that were analysed to indicate the pesticide concentration behaviour over the duration of the storm event. Based on the concentration trends from previous storm events, the four samples were chosen to represent pre-storm concentration, peak flow concentration and the concentration during the hydrograph recession. For each pesticide, a flux (µg/s) curve is shown which is the product of the concurrent concentration and flow rate values.

During this storm event, significant runoff was generated throughout the entire North Weald catchment and hydrographs were recorded at Sites A, D and at the by-pass channel. The event occurred after 31.5mm of rain fell upon the catchment over a nine hour period at a maximum intensity of 5.5mm/hr. This initial period of rainfall was followed six hours later by another rainfall event which was not sampled at Site D and therefore is not discussed here.

The peak flow rates of the hydrographs recorded at Site D and the by-pass channel were 755l/s and 207l/s respectively. Both these values were augmented by runoff flowing into the urbanised catchment from the agricultural sub-catchment. In this situation, to determine the amount of pesticide that was transported only from the urbanised catchment during the storm event, the amount of pesticide entering the urbanised catchment from the agricultural-sub catchment would need to be accounted for and subtracted from the total combined amount of pesticide monitored at Site D. However, because the by-pass flow was not sampled for pesticide residues, it was impossible to determine a value for the combined amount of pesticide that was exported, and consequently impossible to isolate the amount of pesticide that was transported solely from the urbanised catchment. Therefore, the following sub-sections are limited to a semi-quantitative description of the transport of chlorotoluron, isoproturon, diuron, simazine and atrazine during the storm event.

7.4.5.1 *Chlorotoluron, isoproturon and diuron*

The storm event occurred 319 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and 150 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92.

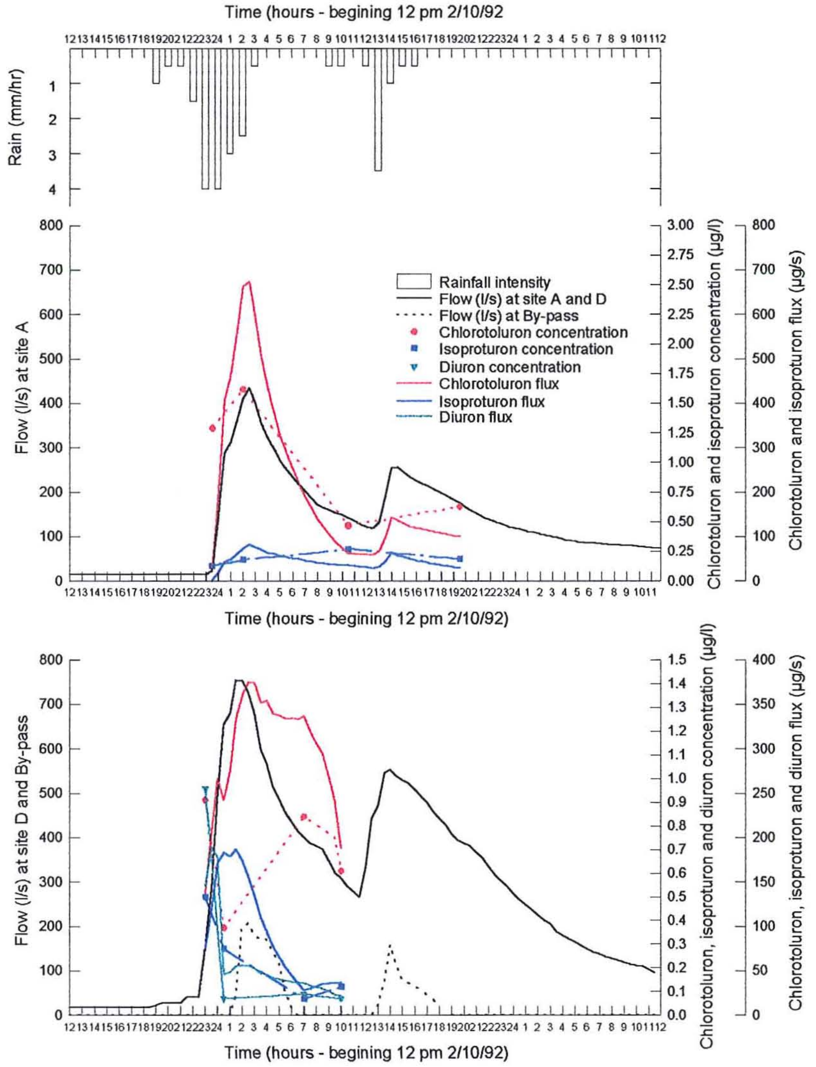

Figure 7-16 Chlorotoluron, isoproturon and diuron concentrations (µg/l) and fluxes (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 2/10/92 (JD 276) [Rainfall intensities (upper bar chart) and storm runoff also shown]

There was no record of any application of isoproturon to the urbanised catchment prior to the storm event (Table 7-1). Since the runoff sampled at Site D contained a major contribution from Site A, applications made to the agricultural sub-catchment could have made significant contributions to the measured pesticide concentrations. Relevant applications included chlorotoluron (78.330kg) 340 days before the event and isoproturon (13.055kg, 25.250kg and 22.475kg) 340, 331 and 321 days before the event respectively (Table 7-1).

The first sample was taken 150 minutes before the major peak of the hydrograph (755l/s) and the second analysed sample was collected 60 minutes before the hydrograph peak. The third and fourth samples which were analysed were taken five-and-a-half and eight-and-a-half hours after the hydrograph peak respectively. Pesticide concentrations between the concentration data points were interpolated and multiplied by relevant values from the flow curve to produce flux curves. Integration of the chlorotoluron, isoproturon and diuron flux curves over the sampling duration, showed that 12,106mg, 3,686mg and 2,226mg respectively of pesticide were transported through Site D during the storm event. These loads correspond to event mean concentrations of 0.62μg/l, 0.19μg/l and 0.11μg/l respectively and a 0.0082% chlorotoluron application loss with respect to the 70kg application to the British Telecom land on 18/11/91 and the 78.330kg application to the agricultural sub-catchment. Due to the absence of details on the isoproturon application to the urbanised catchment, the calculation of a percentage application loss was not impossible. For diuron, the load determined at Site D corresponded to an application loss of 0.25% with respect to the 0.867kg application made by the Roads and Highways Department on 5/5/92.

Due to pesticide inputs from the agricultural sub-catchment, it was impossible to isolate the amounts of pesticide that were transported solely from within the urbanised catchment when applications were made to both catchments, and therefore to provide specific values for application losses with respect to applications made to the urban catchment. Because of the operation of the by-pass channel, it was estimated that the true load leaving the urbanised catchment may have been 10 to 20 % higher. This range is based on the percentage of the total stormflow volume travelling down the by-pass and assuming that the mean concentrations at Site D were applicable to the by-pass flow.

The diuron concentration in sample one, taken 150 minutes before the peak flow, was 0.96µg/l after which the concentration rapidly fell to below 0.1µg/l for the second, third and fourth samples that were analysed. The trend of the diuron concentration during the sampling period of the storm event was very similar to that observed during the storm events previously described. The rapid decrease of diuron concentrations during the hydrograph was an example of 'dilution-exhaustion' typical of many highway discharges as described by Ellis and Revitt (1991).

7.4.5.2 Atrazine and simazine

The temporal variations in simazine and atrazine concentrations and fluxes detected during the storm event of 2/10/92 are illustrated in Figure 7-17. The event occurred 388 days after the simazine application (0.346kg) to the railway line and approximately 237 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment made by the Parks and Recreation Department. Simazine and atrazine were detected in all four analysed samples. The concentrations for each pesticide show opposite trends over the duration of the storm event (Figure 7-17). The simazine concentration in sample one was relatively low and increased during the event, whereas the atrazine concentration demonstrated the reverse trend as the hydrograph flow rate increased.

The simazine concentration progressively increased form 0.09µg/l in sample one to 0.24µg/l in sample two and then 0.43µg/l and 0.53µg/l in samples three and four. Conversely, the atrazine concentrations in sample one to four were 0.84µg/l, 0.37µg/l, 0.07µg/l and 0.05µg/l respectively. The pesticide flux curves were produced by interpolating measured concentrations between the measured data points and multiplying these by the corresponding flow rate values. Integration of the flux curves over the sampling duration, showed that 6694mg and 4625mg of simazine and atrazine respectively were transported through Site D during the storm event. These runoff loads corresponded to event mean concentrations of 0.33µg/l and 0.23µg/l respectively. For simazine the transported load determined at Site D equates to a loss of $7.1\text{x}10^{-4}$ with respect to the previous applications made to the agricultural sub-catchment and the railway line. No value is available for atrazine due to the absence of application records for the agricultural sub-catchment.

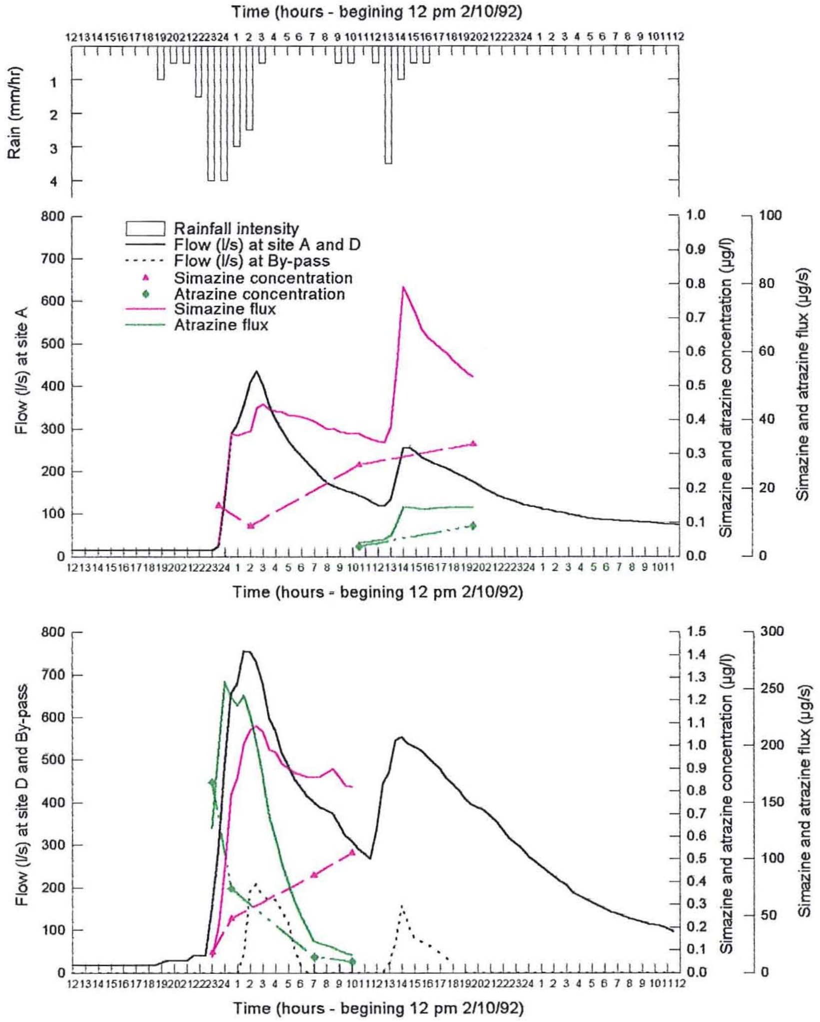

Figure 7-17 Simazine and atrazine concentrations (µg/l) and fluxes (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 2/10/92 (JD 276) [Rainfall intensities (upper bar chart) and storm runoff also shown]

7.4.6 Results for the storm event on 20/10/92 (JD 294)

The sixth storm event to be automatically sampled at Site D occurred on 20/10/92 (JD 294) and the measured hydrographs and pollutographs are shown in Figure 7-18. Chlorotoluron, simazine and atrazine were determined in the three samples that were analysed to represent the pesticide concentration behaviour over the duration of the storm event. No detections were made for diuron and isoproturon because of probable exhaustion of their sources. The three samples were chosen to represent the pre-storm situation, the peak storm situation and the situation during hydrograph recession. For each pesticide, a flux (μg/s) curve was determined using the approach described for the previous event.

Significant runoff was generated throughout the entire North Weald catchment and hydrographs were recorded at Sites A, D and at the by-pass channel. The event occurred after 49.5mm of rain fell upon the catchment over a sixteen-hour period at a maximum intensity of 9.5mm/hr. The peak flow rate of the hydrographs recorded at Site D and the by-pass channel were 1401l/s and 1148l/s respectively. Both these values were augmented by runoff flowing into the urbanised catchment from the agricultural sub-catchment. As was the position with the previously described storm event (2/10/92), the operation of the by-pass channel, which was not sampled, made it impossible to isolate the urbanised catchment from the agricultural sub-catchment, with respect to pesticide input solely from the urbanised catchment. Therefore the following section can only semi-quantitatively describe the pesticide behaviour within the urbanised catchment.

7.4.6.1 Simazine, atrazine and chlorotoluron

The storm event occurred 337 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and 168 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92. The event occurred 406 days after the simazine application (0.346kg) to the railway line and approximately 255 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment by the Parks and Recreation Department. Applications made to the agricultural sub-catchment are also significant to the explanation of pesticide concentrations at Site D. Relevant applications included chlorotoluron (78.330kg) applied 358 days before the event, isoproturon (13.055kg, 25.250kg and 22.475kg) 358, 349 and 339 days before the event and simazine (9.027kg) applied 327 days previously (Table 7-1).

The analysed samples were taken 5 hours before the hydrograph peak, 4 hours before the peak and lastly 5 hours after the hydrograph peak. The adopted sub-sampling approach for analysis was based on the need to maximise the information gained from the full collected sample set and at the same time to conserve laboratory resources and chemicals.

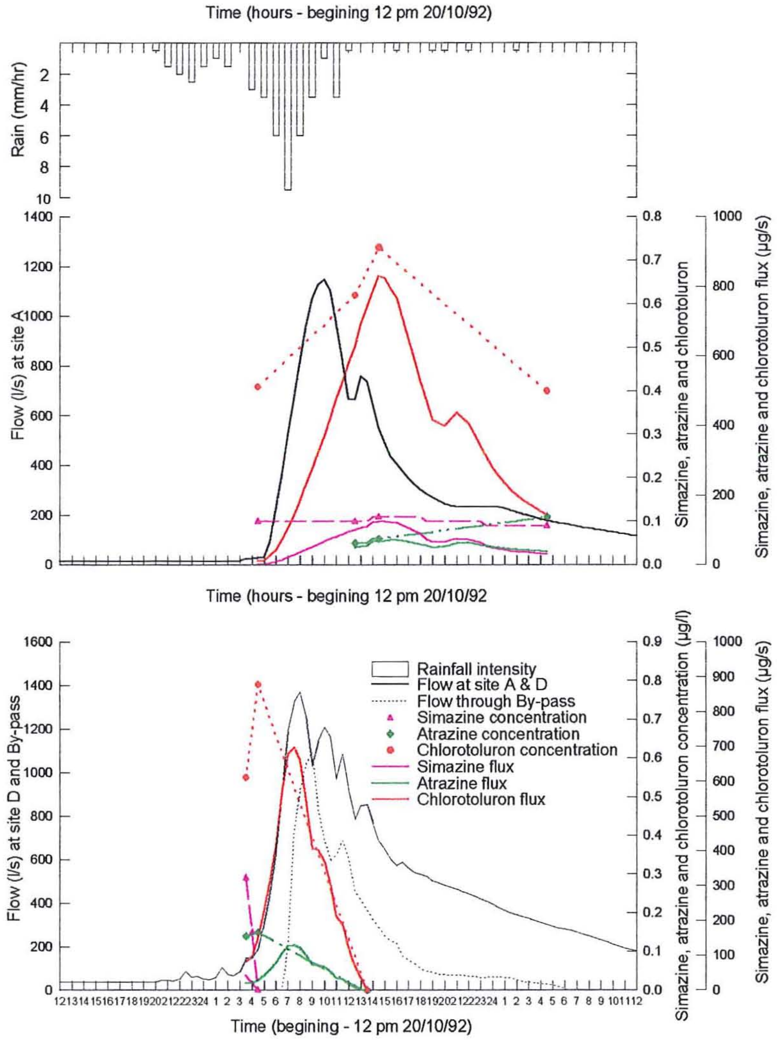

Figure 7-18 Simazine, atrazine and chlorotoluron concentrations (µg/l) and fluxes (µg/s) at site D (lowergraph) and at site A (middle graph) during the storm event occurring on 20/10/92 (JD 294) [Rainfall intensities (upper bar chart) and storm runoff also shown]

At the time of this event, it was considered that given the time lapsed between pesticide applications to the North Weald catchment and the event, there was likely to be only barely detectable amounts of pesticide present in the samples taken. Further, because of various reasons including sample backlog and instrumental problems there was a delay of approximately 2 to 3 months between the sampling and analysis dates. As a result, and for this storm event in particular, the wrong decision was made regarding which and how many samples from the full sample set to analyse. This is shown in Figure 7-18 by the absence of data points around the peak of the hydrograph. As a consequence the information gained from the interpolated concentration and flux data set may not have been fully representative of the true situation.

Of the pesticides in the analysis suite, only simazine, atrazine and chlorotoluron were detected. The absence of isoproturon and diuron may have been due to the significant dilution of the largest runoff event monitored during the programme and to a lesser extent the exhaustion of their sources due to leaching and/or degradation. The concentrations of simazine, atrazine and chlorotoluron in sample one were 0.29µg/l, 0.14µg/l and 0.55µg/l respectively; in the second sample the respective concentrations were 0.29µg/l, 0.15µg/l and 0.79µg/l, and in the third sample none of the three pesticides were detected. Integration of the estimated simazine, atrazine and chlorotoluron flux curves over the sampling duration, showed that 78mg, 2,146mg and 11,728mg respectively were transported through Site D during the storm event. These weights corresponded to event mean concentrations of 0.14µg/l, 0.08µg/l and 0.41µg/l respectively. For the reasons previously outlined, only approximate values can be calculated for the loads determined at Site D with respect to the combined applications within the agricultural sub-catchment and the urbanised catchment. The combined percentage application loss for simazine was $8.2\text{x}10^{-6}\%$ and for chlorotoluron the loss was $8.0\text{x}10^{-3}\%$. These values should be viewed as estimates since a significant pesticide load was probably transported within the considerable by-pass, flow that occurred during this event. Assuming similar mean concentrations in the runoff at Site D and in the by-pass the true herbicide loads and application losses at Site D may have been double the quoted values. A value for atrazine is not given since the details of the source within the agricultural sub-catchment were not known.

7.4.7 Results for the storm event on 9/11/92 (JD 314)

The sixth storm event to be automatically sampled at Site D (Figure 7-19) occurred on 9/11/92 (JD 314). Figure 7-19 shows the concentration (µg/l) curves for simazine, chlorotoluron and diuron that were determined from twenty samples that were taken over the duration of the storm event. For each pesticide, a flux (µg/s) curve is shown which was the product of the concurrent concentration and flow rate values.

Significant runoff was generated throughout the entire North Weald catchment and the hydrographs recorded at Sites A, D and the by-pass channel are plotted in Figure 7-19. The event occurred after 12mm of a rain fell upon the catchment over a nine hour period at a maximum intensity of 3mm/hr. The peak flow rates of the hydrographs recorded at Site D and the by-pass channel were 692l/s and 170/s respectively and both values were augmented by runoff flowing into the urbanised catchment from the agricultural sub-catchment. As was the case with the two previously described storm events (2/10/92 and 20/10/92), the operation of the by-pass channel, which was not sampled, made it impossible to isolate the results from the urbanised catchment from those of the agricultural sub-catchment with respect to pesticide input. Therefore the following section only semi-quantitatively describes the pesticide behaviour within the urbanised catchment.

7.4.7.1 Simazine, chlorotoluron and diuron

The storm event occurred 357 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and 188 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92. The event occurred 426 days after the simazine application (0.346kg) and 12 days after the diuron application (0.461kg) to the railway line, and approximately 275 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment made by the Parks and Recreation Department. The applications made to the agricultural sub-catchment (see Section 7.4.6.1) were also relevant.

Of the pesticides in the analysis suite, only simazine, chlorotoluron and diuron were detected. The absence of isoproturon and atrazine is believed to be due to the exhaustion of their sources as a result of leaching and/or degradation processes. Simazine was only detected twice at low concentrations (<0.10µg/l) in sample 4, which was taken 30 minutes before the hydrograph peak, and sample 18, which was taken 18.5 hours after the hydrograph peak. The initial diuron concentration in the sample taken 2 hours before the hydrograph peak was 0.39µg/l. The concentration then rapidly decreased to 0.06μg/l in sample four which was taken 30 minutes before the hydrograph peak. After this point the diuron concentration fluctuated between 0.1μg/l and no detection for the following 14 samples. The trend in the diuron concentrations was similar to those observed in the previous storm events in which diuron was detected, in that the initial pre-peak flow concentrations were relatively high and then fell rapidly as the flow rate increased. This trend was typical of pesticide transport from hard-surfaced, non-soil areas, and in this case probably represented the rapid transport of diuron form the railway line where it was applied 12 days before the storm event. The chlorotoluron concentration commenced at a value of 0.20μg/l and then decreased to 0.07μg/l in sample three taken 60 minutes before the hydrograph peak. Subsequently the concentration increased to a maximum of 0.34μg/l which coincided with the hydrograph peak. A second chlorotoluron concentration peak occurred centred on sample 8 at a value of 0.20μg/l after which it fell to a steady value between 0.06μg/l and 0.11μg/l.

The timing of the major peak chlorotoluron concentration with the hydrograph peak ensured that the peak flux (225μg/s) coincided with it. However, for diuron the period of greatest load transport rate (108μg/s) occurred 90 minutes prior to the hydrograph peak due to the early high concentration values. Integration of the chlorotoluron and diuron flux curves over the sampling duration indicated that 1,604mg and 788mg respectively were transported through Site D during the storm event. These herbicide weights corresponded to event mean concentrations of 0.14μg/l and 0.09μg/l respectively. Diuron was not detected at Site A (Figure 7-19) and therefore that monitored at Site D was sourced from within the urbanised catchment, most probably from the railway line where 0.461kg was applied (0.461kg) 12 days prior to the storm event. The total diuron flux measured at Site D equates to an application loss of 0.17% with respect to the railway line application.

Although the 0.17% application loss of diuron from the railway line was relatively large compared to the order of loss that may have been expected from a soil based application, the loss was relatively low considering that the application was made to the ballast based railway line that was preferentially drained to the main watercourse.

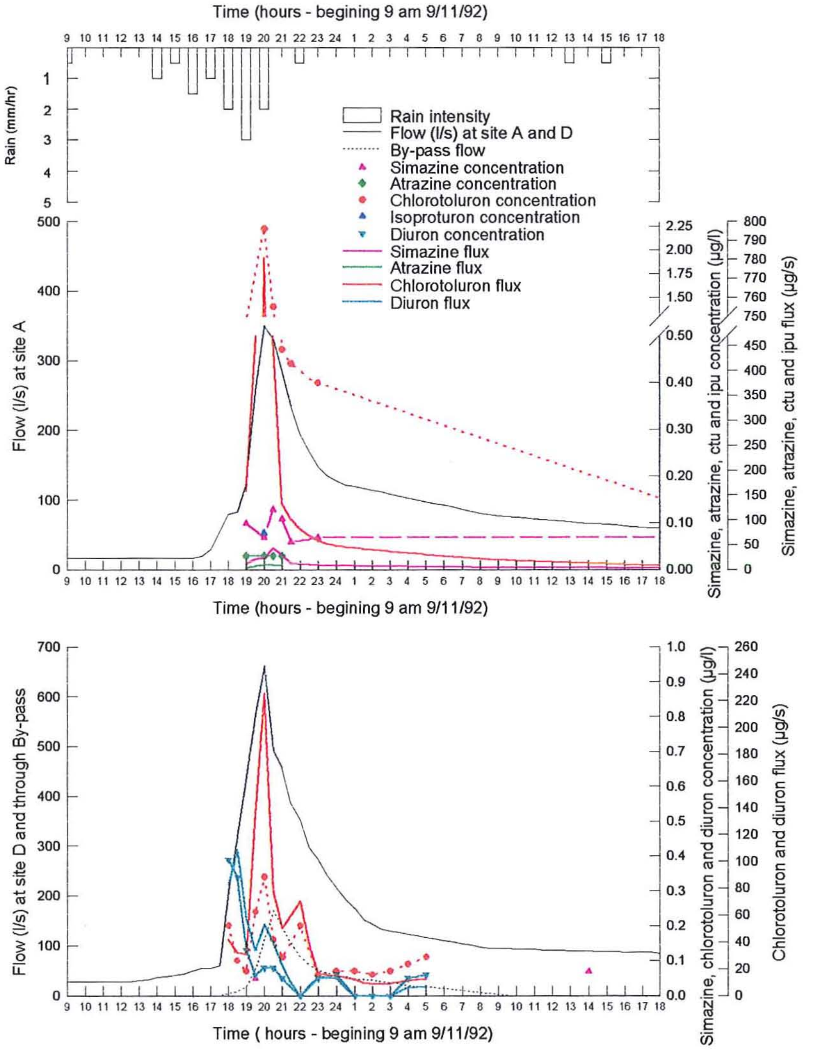

Figure 7-19 **Simazine, chlorotoluron and diuron concentrations (µg/l) and fluxes (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 9/11/92 (JD 314) [Rainfall intensities (upper bar chart) and storm runoff also shown]**

Examination of Figure 5-7 shows that fours days after the diuron application to the railway on 29/10/92, an event occurred on 2/11/92 (JD 307) which unfortunately was not sampled at Site D due to sampler malfunction caused by debris preventing the operation of the sampler trigger switch. Considering the short period of time that had elapsed between the application and the event of 2/11/92, it would have been likely that the application loss during that event would have been significantly greater. Therefore, the amount of diuron that was removed during the 2/11/92 event could have substantially reduced the amount subsequently available for transport in runoff during this event (9/11/92).

Because of the chlorotoluron input from the agricultural sub-catchment application and the minor operation of the by-pass channel, it was difficult to isolate the amount of chlorotoluron that was transported solely from the urbanised catchment. Therefore the load determined at Site D had to be compared to the combined applications and the combined percentage application loss for chlorotoluron was 0.001%. If the mean of the by-pass channel chlorotoluron concentration was assumed to be the same as that determined at Site D, it was estimated that the by-pass load may have been approximately 10% of that determined at Site D.

7.4.8 Results for the storm event on 15/11/92 (JD 320)

The seventh storm event to be automatically sampled at Site D occurred six days after the previously described storm, on 15/11/92 (JD 320). Figure 7-20 shows the concentration (μg/l) curves for simazine, chlorotoluron, isoproturon and diuron that were determined from sixteen samples that were taken over the duration of this storm event. For each pesticide, a flux (μg/s) curve is shown which was the product of the concurrent concentration and flow rate values.

As for the storm event six days earlier, significant runoff was generated throughout the entire North Weald catchment and hydrographs were recorded at Sites A, D and at the by-pass channel. The event occurred after 7.5mm of rainfall over a four hour period at a maximum intensity of 5mm/hr. The peak flow rates of the hydrographs recorded at Site D and the by-pass channel were 795l/s and 110/s respectively. Both these values were augmented by runoff entering the urbanised catchment from the agricultural sub-catchment. Due to the operation of the by-pass channel, which was not sampled, it was not possible to specifically categorise pesticide input from the urbanised catchment. Therefore, the following section only semi-quantitatively describes the pesticide behaviour within the urbanised catchment.

7.4.8.1 Simazine, chlorotoluron, isoproturon and diuron

The storm event occurred 363 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91 and 194 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92. Further, the event occurred 432 days after the simazine application (0.346kg) and 17 days after the diuron application (0.461kg) to the railway line, and 281 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment made by the Parks and Recreation Department. Since the runoff sampled at Site D also contained a major contribution from Site A, applications made to the agricultural sub-catchment may also have been significant for the explanation of pesticide concentrations at Site D. The relevant applications to the agricultural sub-catchment are described previously (Table 7-1).

The reappearance of isoproturon in the runoff generated by this storm event, though at low concentrations, may have been due to the higher peak rainfall intensity event compared to the previous event. Johnson (1995) has previously shown that the amount of isoproturon removed during a given event was proportional to the rainfall intensity of the event. Simazine was only detected once at a concentration of 0.06μg/l in sample 3 which coincided with the hydrograph peak. Its source was probably from the application made to the agricultural sub-catchment combined with that made to the railway line. The diuron concentration started at 0.24μg/l 60 minutes before the hydrograph peak and then rapidly increased to 0.69μg/l in sample two which was taken 30 minutes later. After this point the diuron concentration fell rapidly to a value below the detection limit (0.05μg/l) and then fluctuated between 0.1μg/l and no detection for the following 13 samples. This concentration behaviour approximately replicated the trends observed in the previous storm events in which diuron was detected, in that the initial high pre-hydrograph concentrations rapidly fell as the flow rate of the hydrograph increased. In this storm event it appeared that the diuron concentration peaked 30 minutes before the hydrograph and then decreased to below the detection limit which was a good example of the 'dilution-exhaustion' phenomenon described by Ellis and Revitt (1991). The chlorotoluron concentration in sample one was 0.27μg/l, which then decreased to 0.17μg/l before increasing to 0.43μg/l for sample three which coincided with the hydrograph peak. Subsequently the concentration gradually decreased to a concentration below the detection limit in sample six after which it fluctuated between 0.1µg/l and 0.05µg/l. The chlorotoluron detection was probably due to the combined losses from the agricultural sub-catchment and urbanised catchment applications.

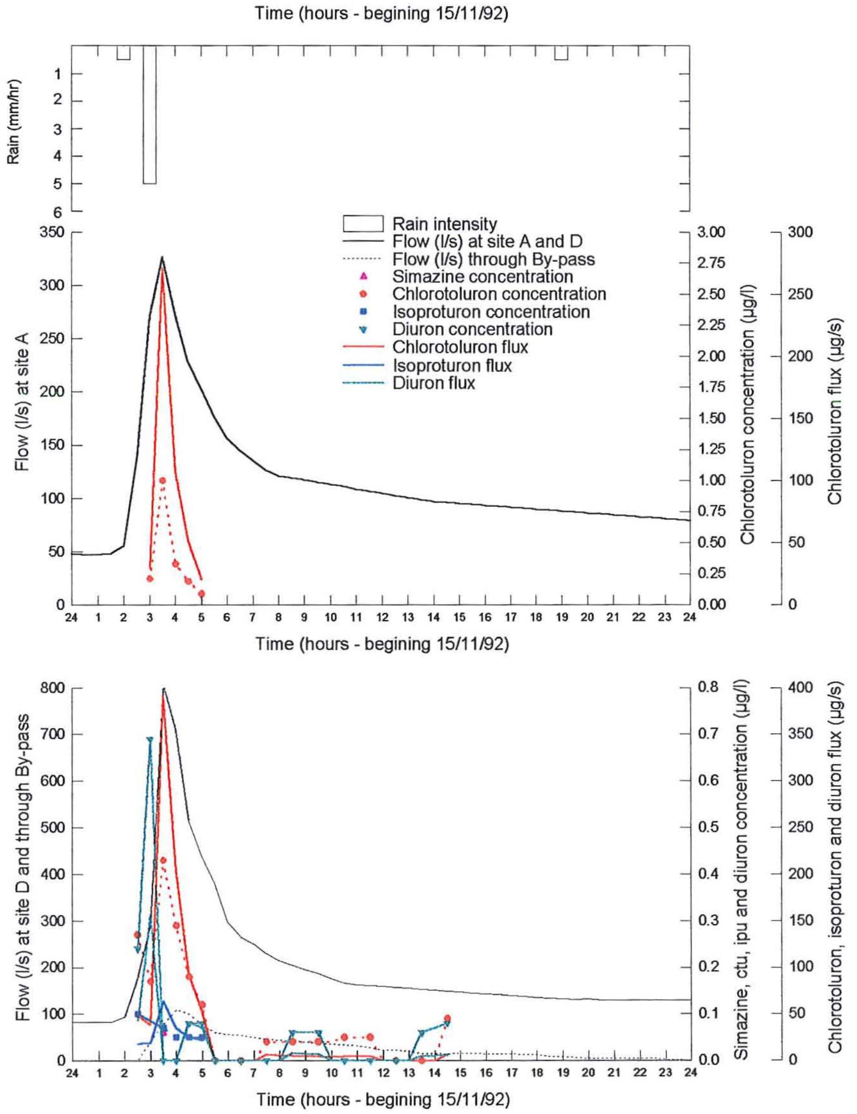

Figure 7-20 **Simazine, chlorotoluron, isoproturon and diuron concentrations (µg/l) and flux (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 15/11/92 (JD320) [Rainfall intensities (upper bar chart) and storm runoff also shown]**

The simultaneous timing of the peak chlorotoluron and isoproturon concentrations and the hydrograph peak, produced maximum chlorotoluron and isoproturon fluxes of 390µg/s and 63µg/s respectively. Due to the occurrence of the peak diuron concentration before the hydrograph peak,the peak diuron flux of 157μg/s occurred 30 minutes before the hydrograph peak. Integration of the chlorotoluron, isoproturon and diuron flux curves over the sampling duration, showed that 1,538mg, 100mg and 524mg respectively were transported through Site D during the storm event; these loads corresponded to event mean concentrations of 0.13μg/l, 0.01μg/l, and 0.07μg/l respectively. Since the runoff in which the chlorotoluron was detected at Site D was from a combination of urban and agricultural sources, it was necessary to express the chlorotoluron load in terms of the combined applications which gave a value of 1.0×10^{-3}%.

Diuron was not detected at Site A and therefore that detected at Site D was from a source within the urbanised catchment, most probably from the railway line where it was applied (0.461kg) 18 days prior to the storm event. The total diuron flux measured at Site D equates to an application loss of 0.11% with respect to the railway line application. If it was assumed that the diuron event mean runoff concentration that passed through the by-pass channel was similar to that determined for site D, then the integration of a flux curve produced for the by-pass hydrograph over the same period would give a diuron mass of 129mg. Incorporating this value the total diuron loss would have been 653mg which is equivalent to a loss of 0.14% with respect to the railway line application.

7.5 Results of storm event monitoring for 1993

The results discussed in this section cover the automatic samples taken between January and March 1993 for the urbanised catchment.

7.5.1 Results for the storm event on 6/1/93 (JD 6)

The eighth storm event to be automatically sampled at Site D occurred on 6/1/93 (JD 6) and the concentration (μg/l) curves for chlorotoluron and diuron that were determined from the eighteen samples that were collected over the duration of the storm event are shown in Figure 7-21. For each pesticide, a flux (μg/s) curve is shown which was the product of the concurrent concentration and flow rate values.

In common with the other storm events that occurred during the 1992-93 winter period, significant runoff was generated throughout the entire North Weald catchment and hydrographs were recorded at Sites A, D and at the by-pass channel. The event occurred after 7.5mm of rain fell upon the catchment over a six hour period at a maximum intensity of 2 mm/hr. The peak flow rate of the hydrographs recorded at Site D and the by-pass channel were 560l/s and 236/s respectively. Both these values were supplemented by runoff flowing into the urbanised catchment from the agricultural sub-catchment. The operation of the un-sampled by-pass channel made it impossible to isolate the herbicide input deriving only from the urbanised catchment. Therefore the following section semi-quantitatively describes the pesticide behaviour within the urbanised catchment.

7.5.1.1 Chlorotoluron and diuron

The storm event occurred 415 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91, 246 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92, and 69 days after the diuron application (0.461kg) to the railway line. The chlorotoluron application (78.330kg) made to the agricultural sub-catchment 415 days before the event was pertinent for the explanation of pesticide behaviour at Site D. An isoproturon application during November 1992 had been planned for the agricultural sub-catchment, but due to prolonged periods of rainfall the land had become too waterlogged to allow tractor access and therefore the timing of the application was delayed until the agricultural sub-catchment had drained sufficiently to allow access.

The disappearance of isoproturon and simazine compared to the previously described storm event may have been due to the lower peak rainfall intensity of this event and/or the exhaustion of the isoproturon source due to degradation or removal. The diuron concentration in sample one which was taken 90 minutes before the main hydrograph peak was 0.17μg/l and the concentration then rapidly decreased to 0.09μg/l in sample two which was taken 60 minutes before the hydrograph peak. After a small increase in concentration to 0.11μg/l in sample four, which coincided with the hydrograph peak, the diuron concentration fell to 0.06μg/l in sample five and to below the detection limit for sample six where it remained for the duration of the sampling period. Chlorotoluron was only detected in the first three samples at concentrations of below 0.1µg/l. The chlorotoluron concentration in sample one was 0.06µg/l, which then decreased to 0.05µg/l for sample two and then to 0.04µg/l for sample three which was taken 30 minutes before the main hydrograph peak.

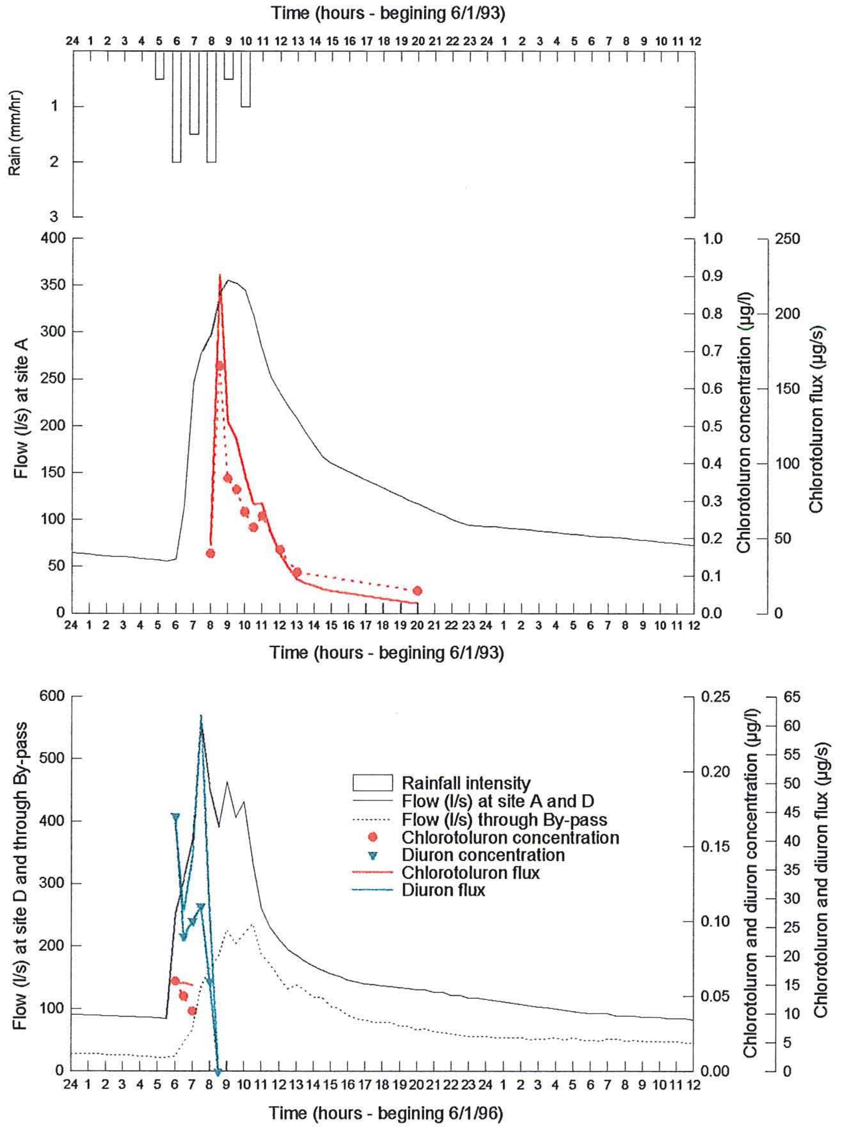

Figure 7-21 Chlorotoluron and diuron concentrations (µg/l) and flux (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 6/1/93 (JD 6) [Rainfall intensities (upper bar chart) and storm runoff also shown]

During the event, the point of maximum diuron load (61µg/s) coincided with the hydrograph peak. However, at the time of peak flow the chlorotoluron concentration was at a minimum and then subsequently rose to a maximum that coincided with the last minor peak of the hydrograph, producing a peak flux value of 43μg/s. Integration of the chlorotoluron and diuron flux curves over the sampling duration, showed that 54mg and 287mg respectively were transported through Site D during the storm event. These herbicide loads corresponded to event mean concentrations of 0.07μg/l and 0.10μg/l respectively. Diuron was not detected at Site A (Figure 7-20) and therefore the amount of this pollutant detected at Site D was sourced from within the urbanised catchment, most probably from the railway line where 0.461kg was applied 69 days prior to the storm event. The total diuron flux measured at Site D equates to an application loss of 0.06% with respect to the railway line application.

If it is assumed that the diuron event mean concentration of runoff that passed through the by-pass channel was similar to that determined for site D, then the integration of the flux curve produced for the by-pass hydrograph over the same period would give a diuron mass of 61mg. When combined with the diuron mass that was transported though Site D, this gives a total diuron load of 348mg and an application loss of 0.07% with respect to the railway line application. As discussed for previous storm events, the combined effect of the chlorotoluron input from the agricultural sub-catchment and the operation of the by-pass channel made it impossible to isolate the amounts of chlorotoluron that were transported solely from the urbanised catchment and also to specify values for application loss. However, in terms of the combined application, the chlorotoluron load determined at Site D corresponded to an application loss of $3.0\text{x}10^{-4}\%$. This value ignores the loss via the by-pass channel which it was estimated would have probably increased the loss value to $4.0\text{x}10^{-4}\%$, based on the by-pass runoff volume and assuming a similar mean chlorotoluron concentration to that observed at Site D.

7.5.2 Results for the storm event on 1/4/93 (JD 91)

The rainfall depths for February and March 1993 (Table 5.1) were significantly lower than the average monthly rainfall values provided by the Soil Survey Land Resource Centre, and consequently no significant storm events occurred during this period. Further, during this relatively dry period the soil moisture content of the agricultural sub-catchment decreased. This reduced the water logged state of the soil sufficiently to allow tractor access to the fields and hence to enable the isoproturon application that was originally planned for the autumn of 1992, to proceed. The ninth storm event to be automatically sampled at Site D occurred on 1/4/93 (JD 91) and this is diagrammatically shown in Figure 7-22. The Figure shows the concentration (μg/l) curves for atrazine, isoproturon and diuron that were determined from the seventeen samples that were collected over the duration of the storm event. For each pesticide, a flux (μg/s) curve is shown which was the product of the concurrent concentration and flow rate values.

The event occurred after 17.5mm of rain fell upon the catchment over an eight hour period at a maximum intensity of 5mm/hr. This generated runoff throughout the North Weald catchment including the by-pass channel. The peak flow rates of the hydrographs recorded at Site D and the by-pass channel were 620l/s and 288l/s respectively and both these values were supplemented by runoff flowing into the urbanised catchment from the agricultural sub-catchment. The operation of the by-pass channel, which was not sampled, made it difficult to isolate the urbanised catchment from the agricultural sub-catchment and to determine the amount of pesticide detected at Site D that was transported only from the urbanised catchment. Therefore the following section only semi-quantitatively describes the pesticide behaviour within the urbanised catchment.

7.5.2.1 Atrazine, isoproturon and diuron

The storm event occurred 500 days after the chlorotoluron application (70kg) to the British Telecom land on 18/11/91, 331 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92 and 154 days after the diuron application (0.461kg) to the railway line on 29/10/92. In addition, the event occurred approximately 418 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment made by the Parks and Recreation Department during the week ending 8/2/92. Relevant agricultural sub-catchment applications included chlorotoluron (78.330kg) applied 521 days before the event; isoproturon (39.692kg) applied 57 days before the event; and simazine (9.027kg) applied on 28/11/91, 490 days previously (Table 7-1).

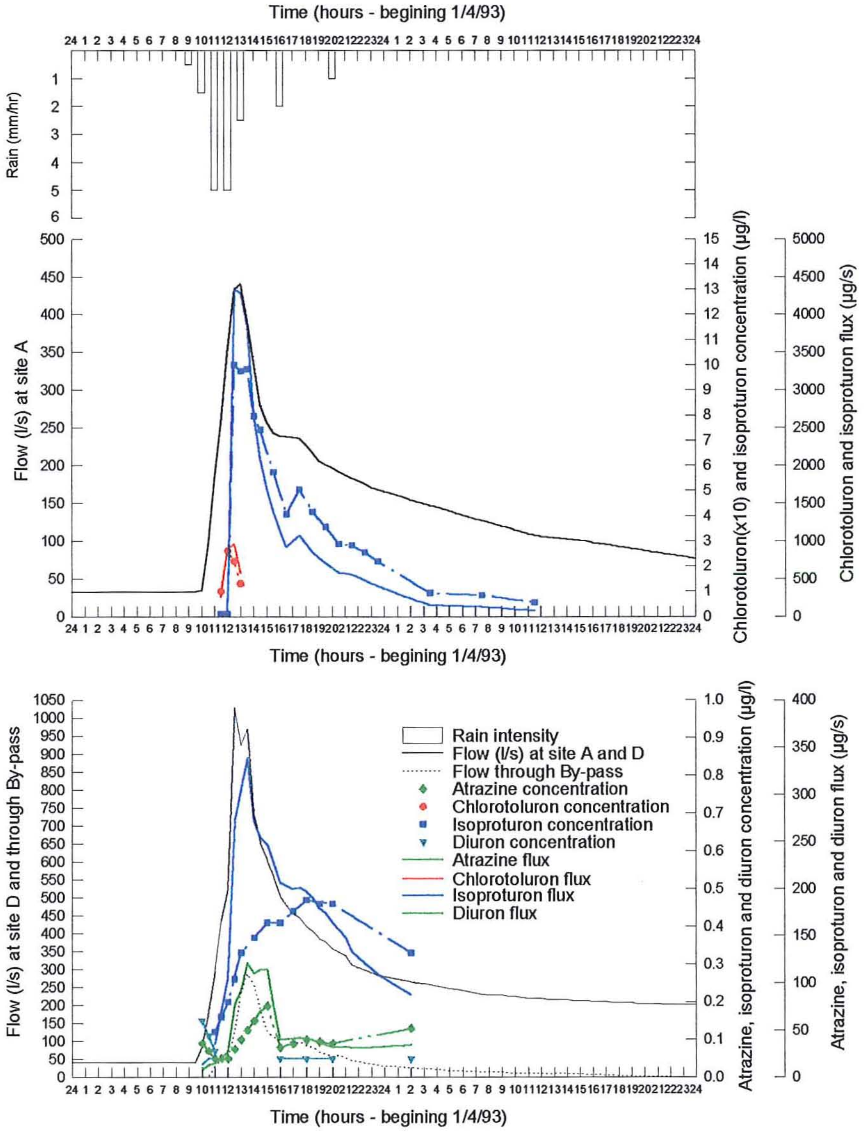

Figure 7-22 **Atrazine, isoproturon and diuron concentrations (µg/l) and fluxes (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 1/4/93 (JD 91) [Rainfall intensities (upper bar chart) and storm runoff also shown]**

Of the pesticides in the analysis suite, atrazine, isoproturon and diuron were detected at Site D. The reappearance of isoproturon was attributed to the application made to the agricultural sub-catchment 57 days prior to the event. The reappearance of atrazine was unexpected considering that the only identified applications to the urbanised catchment were made by the Parks and Recreation Department over one year previously. Due to the restriction on the non-agricultural use of the simazine and atrazine, the Department had stated that for 1993 atrazine would be replaced by propyzamide. However, the detection of atrazine approximately five months after its previous detection at Site D suggested that the conversion to propyzamide may not have taken place. During this event chlorotoluron was detected in runoff at Site A but not at Site D. The disappearance of chlorotoluron at Site D compared to the previously described event on 6/1/93 could have been the result of the enhanced degradation of the urban compared to the agricultural source. If this was the case, the concurrent chlorotoluron input from the agricultural sub-catchment would have been diluted with chlorotoluron-free runoff from the urbanised catchment reducing the Site A chlorotoluron concentration to below the detection limit at Site D. The atrazine concentration in sample one which was taken two-and-a-half hours before the main hydrograph peak was 0.09μg/l. The concentration then decreased to 0.05μg/l in the sample taken 30 minutes before the hydrograph peak, after which the concentration gradually increased to 0.19μg/l for sample nine collected approximately two-and-a-half hours after the hydrograph peak. The concentration then fell to 0.08μg/l and thereafter gradually increased to 0.13μg/l in sample seventeen. Isoproturon was first detected in sample three collected an hour-and-a-half before the hydrograph peak and at a concentration of 0.12μg/l. From this point onwards the isoproturon concentration gradually increased to 0.47μg/l for sample twelve which was taken five-and-a-half hours after the main hydrograph peak. Subsequently the isoproturon concentration fell to 0.33μg/l in sample seventeen taken fourteen hours after the hydrograph peak. This rather unusual pattern of behaviour for the isoproturon concentration is further discussed in Section 7.6.4. The highest diuron concentration of 0.15μg/l was determined in sample one falling to 0.07μg/l in sample two. Diuron was then only intermittently detected within a range of 0.05-0.07μg/l until sample seventeen.

The period of highest isoproturon mass transport (338μg/s) occurred 60 minutes after the hydrograph peak coincident with that of atrazine (121μg/s). The diuron flux peaked two hours before the hydrograph peak at 20μg/s. Integration of the atrazine, isoproturon and diuron flux curves over the sampling duration, showed that 2,716mg, 9,316mg and 67mg respectively were transported through Site D during the storm event corresponding to event mean concentrations of 0.1μg/l, 0.35μg/l and 0.004μg/l respectively. Diuron was not detected at Site A (Figure 7-22) and therefore that detected at Site D was sourced from within the urbanised catchment, probably from the railway line where 0.461kg was applied 154 days prior to the storm event. The total diuron flux measured at Site D equates to a loss of 0.01% with respect to the railway line application. If it is assumed that the diuron event mean runoff concentration that passed through the by-pass channel was similar to that determined for site D, then the integration of the flux curve produced for the by-pass hydrograph over the same period would have given a diuron mass of 6mg. When combined with the diuron mass that was transported though Site D, this gives a total diuron loss of 73mg and an application loss of 0.015% with respect to the railway line application.

The total mass of isoproturon (9,316mg) leaving the urbanised catchment was low compared to the amount (64,829mg) that was imported from the agricultural sub-catchment (see Section 6.3.2.1). Given the relatively minor volume of the by-pass flow during the event, it was unlikely that the discrepancy in loadings at the two sites could be explained by the unaccounted for by-pass load. The reasons for this are discussed in Section 7.6.4.

7.5.3 Results for the storm event on 25/4/93 (JD 115)

The ninth and final storm event to be automatically sampled at Site D occurred on 25/4/93 (JD 115). The concentration (μg/l) curves for isoproturon and diuron determined in the eighteen samples taken over the duration of the storm event are shown in Figure 7-23. Atrazine was detected only once in sample three. Apart from atrazine, for each herbicide, a flux (μg/s) curve is also shown which was the product of the concurrent concentration and flow rate values.

The event occurred after 12.5mm of rain fell upon the catchment over a twelve-hour period at a maximum intensity of 2.5 mm/hr resulting in the generation of runoff throughout the North Weald catchment including the by-pass channel. The temporal distribution of the flow produced two hydrograph peaks (Figure 7-23) which were recorded at both Sites A and D. The peak flow rates of the hydrographs at Site D were 320l/s and 265l/s and for the by-pass channel they were 96l/s and 76l/s. As with the previously described event, both these values were supplemented by runoff flowing into the urbanised catchment from the agricultural sub-catchment. The operation of the by-pass channel, which was un-sampled, made it impossible to isolate the urbanised catchment from the agricultural sub-catchment and hence to determine the amount of pesticide detected at Site D which arose only from within the urbanised catchment.

7.5.3.1 Atrazine, isoproturon and diuron

The storm event took place 354 days after the diuron application (0.867kg) by the Roads and Highways department on 5/5/92, 177 days after the diuron application (0.461kg) to the railway line on 29/10/92 and approximately 442 days after the atrazine application (0.208kg) to grassed amenity areas of the urbanised catchment made by the Parks and Recreation Department during the week ending 8/2/92. Since the runoff sampled at Site D also contained a major contribution from Site A, applications made to the agricultural sub-catchment may also have been significant for the explanation of pesticide concentrations. Relevant applications included chlorotoluron (78.330kg) applied 545 days before the event and isoproturon (39.692kg) applied 81 days before the event (see Table 7-1).

Three of the pesticides in the analysis suite (atrazine, isoproturon and diuron) were detected at Site D. The appearance of isoproturon was attributed to the application made to the agricultural sub-catchment 81 days prior to the event. Atrazine was detected only once in sample three (0.07μg/l) and probably originated from the same source as the previous detection of atrazine at Site D. This involved the suspected use of atrazine rather than propyzamide by the Parks and Recreation Department during February 1993 (see Section 7.5.2.1). The absence of chlorotoluron detection at Site D though it was detected at Site A was probably the result of the dilution of the Site A runoff as it passed through the urbanised catchment. This assumes that the runoff sampled at Site D contained negligible residues of the chlorotoluron previously applied to the BT land 524 days earlier (Table 7-1) and that therefore the chlorotoluron entering the urbanised catchment from the agricultural sub-catchment was diluted by chlorotoluron-free runoff from the urbanised catchment.

Isoproturon was first detected in sample one which was taken 30 minutes before the first hydrograph peak, at a concentration of 0.14μg/l. From this point forward to sample eleven, taken

6.5 hours later, the isoproturon concentrations showed a gradual upward trend but with marked oscillations in the form of troughs and valleys producing four distinct peaks.

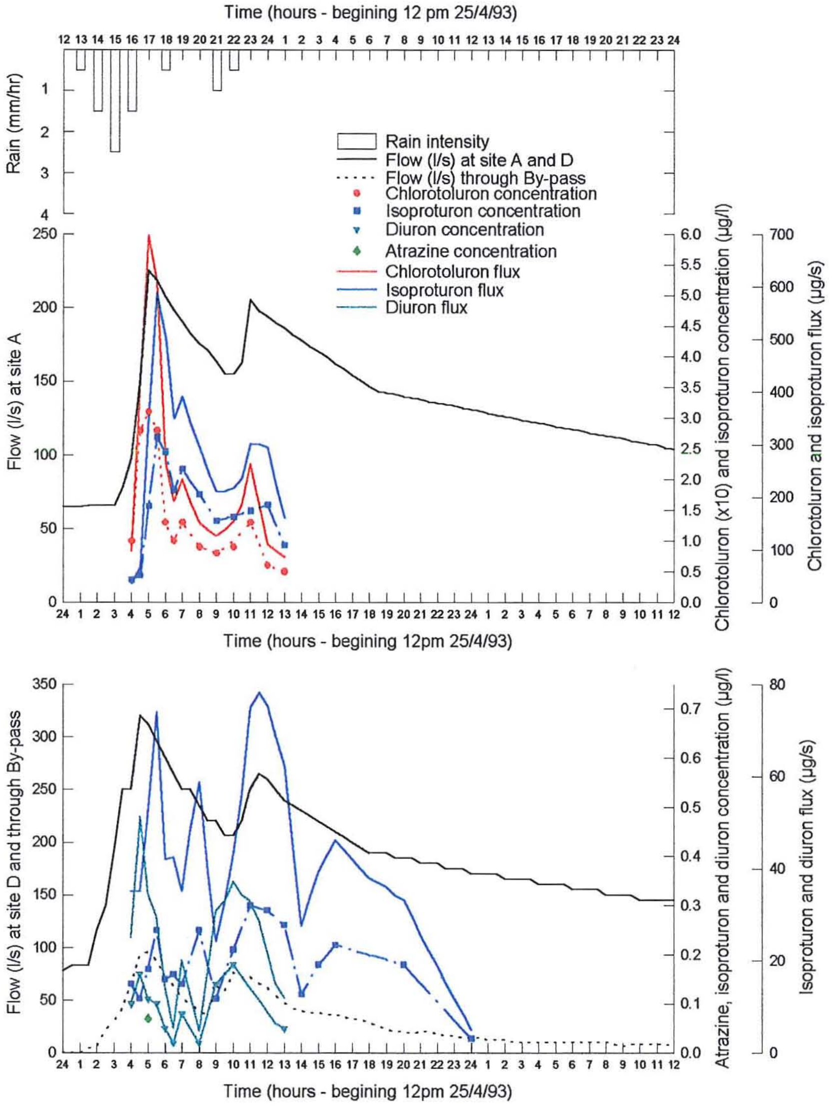

Figure 7-23 Isoproturon and diuron concentrations (µg/l) and fluxes (µg/s) at site D (lower graph) and at site A (middle graph) during the storm event occurring on 25/4/93 (JD 115) [Rainfall intensities (upper bar chart) and storm runoff also shown]

Subsequently the concentration declined to 0.12µg/l in sample fourteen before increasing again to another peak value of 2.2µg/l in sample sixteen. The distribution of the isoproturon concentrations over this storm event was somewhat unusual and unseen in the previous events recorded at Site D where isoproturon was detected. It may have been a function of the distinctive hydrograph which consisted of two sequential peak flows superimposed on a uniformly high value throughout the event. Similarly, the diuron concentration pattern was unique for this event with three peaks (maximum value 0.18µg/l) being observed between an initial concentration of 0.1µg/l and final detection in sample thirteen (0.05µg/l)

Due to the varying nature of the isoproturon concentrations, four flux peaks of 74µg/s, 58µg/s, 78µg/s and 46µg/s were observed, with the first and third coinciding with the two hydrograph peaks. Similarly, the varying nature of the diuron concentration, produced three flux peaks of 51µg/s, 20µg/s and 37µg/s, with the first of these coinciding with the first hydrograph peak. Integration of the isoproturon and diuron flux curves over the sampling duration, indicated that 2,947mg and 795mg respectively were transported through Site D during the storm event. These weights corresponded to event mean concentrations of 0.18µg/l and 0.09µg/l respectively. The isoproturon load discrepancy between Sites A and D, which was observed during the previous event on 1/4/93, was also observed here and is further discussed in Section 7.6.4. Diuron was not detected at Site A (Figure 7-23) and therefore that detected at Site D was from a source within the urbanised catchment, most probably from the railway line where 0.461kg was applied 178 days prior to the storm event. The total diuron flux measured at Site D equated to an application loss of 0.17% with respect to the railway line application. If it is assumed that the diuron event mean concentration of runoff that passed through the by-pass channel was similar to that determined for site D, then the integration of the flux curve produced for the by-pass hydrograph over the same period would give a diuron mass of 189mg. The combined diuron masses transported through Site D and the by-pass channel represents a total diuron loss of 984mg and an application loss of 0.21% with respect to the railway line application.

7.6 Discussion and interpretation of storm event runoff data from the urbanised catchment outlet

The storm event herbicide data described in Sections 7.4 and 7.5 are summarised in Tables 7-6 to 7-9. Table 7-6 shows the hydrological data for the eleven storm events sampled at Site D during the course of the monitoring programme. The dates on which the storm events occurred are also represented using the Julian day convention.

Table 7-6 Hydrological data for eleven storm events sampled at Site D during the course of the monitoring programme

JD	Date	RI	RV	ADP	LAG	PF	TR	BFV	DRV	PBFV	PR	WB	ED
106	15/4/92	2	9.5	na	70	55	0.63	0.29	0.35	45	55	7.4	23.5
119	28/4/92	3	18.5	36	165	161	3.89	1.11	2.78	29	71	15	24
122	1/5/92	3.5	9.5	60	70, 130	178	1.98	0.58	1.4	29	71	14.8	11.5
150	29/5/92	6	25.5	643	100	330	17.4	5.59	11.8	32	68	46	13.5
276	2/10/92	5.5	31.5	50	140	408	7.74	2.9	4.84	37	63	69	16.5
294	20/10/92	9.5	49.5	214	51	1468	15.9	1.9	14	12	88	28	17.5
314	9/11/92	3	12	164	175	426	7.9	2.71	5.19	34	66	43	12.5
320	25/11/92	5	7.5	80	78	560	3.20	1.31	1.89	56	59	43	7.3
6	6/1/93	2	7.5	18	140	367	6.22	2.4	3.82	39	61	51	18
91	1/4/93	5	17.5	16	130	515	6.05	0.85	5.2	14	86	29.7	18.5
115	25/4/93	2.5	8	na	105	412	11.4	7.78	3.63	68	22	45	18

Where:

RI	Rainfall intensity (mm/hr)	RV	Rainfall volume (mm)
LAG	Rainfall-runoff lag time (minutes)	PF	Peak flow rate (ls^{-1})
BFV	Baseflow volume (mm)	DRV	Direct runoff volume (mm)
TR	Total runoff volume (mm)	WB	Water balance (%)
ED	Event duration[direct runoff] (hrs)	PBFV	Percentage baseflow volume
PR	Percentage runoff volume	ADP	Antecedent dry period (hrs)
na	not available		

Table 7-7 shows the known amount of each herbicide transported through Site A and D during the duration of the monitored storm events. As mentioned in the description of the storm events in Sections 7-4 and 7-5, for seven of the eleven monitored events the by-pass channel was in operation. For events corresponding to Julian Days 276, 314, 320, 91 and 115, the volume of the by-pass flow was approximately 10% of the total Site D flow; for event 294 the by-pass volume was approximately 40% and for event 6 the by-pass volume was approximately 30% of that at Site D.

Table 7-7 Summary of storm event herbicide loadings (µg) at Sites A and D

		Storm event loading (µg)								
Event	Date	A	D	A	D	A	D	A	D	D
(JD)		Sim	Sim	Atra	Atra	Ctu	Ctu	Ipu	Ipu	Diu
106	15/04/92	ns	147,900	ns	213,000	ns	91,300	ns	10,050	242,600
119	28/04/92	ns	1,080,000	ns	1,988,000	ns	773,600	ns	922,500	2,723,000
122	01/05/92	265,419	611,378	133,444	632,314	333,026	892,698	438275	830,774	382,868
150	29/5/92	ns	2,981,000	ns	2,310,000	ns	7,688,000	ns	3,342,000	390.933g
276	02/10/92	3,261,841	6,694,000	362,140	4,625,000	15,650,163	12,106,000	3361696	3,686,000	2,226,000
294	20/10/92	2,861,553	3,903,000	1,625,589	2,146,000	16,850,312	11,728,000	nd	nd	nd
314	09/11/92	478,862	nd	40,139	nd	3,630,597	1,604,000	nd	nd	932,000
320	15/11/92	nd	nd	nd	nd	835,072	1,538,000	nd	100,000	524,000
6	06/01/93	nd	nd	nd	nd	2,069,868	415,000	nd	nd	287,000
91	01/04/93	nd	nd	nd	2,716,000	409,285	nd	64,829,043	9,316,000	67,000
115	24/04/93	nd	nd	nd	442,000	767,101	nd	9,409,006	2,947,346	355,000

A - value at Site A, D - value at Site D, Sim - Simazine, Atra - Atrazine, Ctu - Chlorotoluron, Ipu - Isoproturon, Diu - Diuron, nd - no detection, ns - not sampled

Although the flow rate of the runoff travelling through the by-pass channel was monitored, the waters were not sampled for the determination of herbicide concentrations. Therefore, it was not possible to determine the amount of herbicide that was transported through the channel during the storm events and consequently it was not possible to derive an accurate value for the total load of each pesticide that was exported from the urbanised catchment. Consideration was given to estimating the by-pass herbicide load by multiplying the by-pass flow rate by the event mean concentration determined at Site D. However, in most situations, the error in assuming that the Site D event mean concentration was applicable to the by-pass channel was considered to be greater than the error associated with ignoring the operation of the by-pass channel. Therefore, the amount of herbicide exported from the urbanised catchment during a storm event was approximated to that measured at Site D. For comparison purposes, Table 7-7 also shows the amount of herbicide exported from the agricultural sub-catchment into the urbanised catchment for each storm event. The data in Table 7-7 is also shown graphically in Figures 7-24, 7-28, 7-31, 7-35 and 7-38. Table 7-8 shows the peak herbicide concentrations determined at Site D for each of the eleven storm events. For comparison purposes the concurrent peak concentrations determined at Site A are also shown. The data shown in Table 7-8 is also shown graphically in Figures 7-26, 7-29, 7-33, 7-36 and 7-39 for simazine, atrazine, chlorotoluron, isoproturon and diuron respectively.

Table 7-8 Summary of storm event maximum pesticide concentrations (µg/l) at Sites A and D

		Maximum storm event concentration (µg/l)								
Event	Date	A	D	A	D	A	D	A	D	D
(JD)		Sim	Sim	Atra	Atra	Ctu	Ctu	Ipu	Ipu	Diu
106	15/04/92	ns	0.67	ns	0.68	ns	0.33	ns	0.22	1.06
119	28/04/92	ns	0.47	ns	0.68	ns	0.29	ns	0.48	1.33
122	01/05/92	0.29	0.20	0.21	0.23	0.79	0.43	1.00	0.34	0.25
150	29/5/92	ns	2.23	ns	1.28	ns	4.51	ns	3.27	238.39
276	02/10/92	0.33	0.53	0.09	0.84	1.62	0.91	0.27	0.50	0.96
294	20/10/92	0.11	0.29	0.11	0.15	0.73	0.79	nd	nd	nd
314	09/11/92	0.13	0.07	0.03	nd	2.23	0.34	0.08	nd	0.39
320	15/11/92	nd	0.06	nd	nd	1.00	0.43	nd	0.10	0.69
6	06/01/93	nd	nd	nd	nd	0.66	0.06	nd	nd	0.17
91	01/04/93	nd	nd	nd	0.19	0.26	nd	10	0.47	0.15
115	24/04/93	nd	0.07	nd	0.07	0.31	nd	2.69	0.30	0.18

A - value at Site A, D - value at Site D, Sim - Simazine, Atra - Atrazine, Ctu - Chlorotoluron, Ipu - Isoproturon, Diu - Diuron, nd - no detection, ns - not sampled

Table 7-9 shows the event mean concentrations for each of the herbicides detected at Site D, and also at Site A, during the monitoring programme. The data shown in Table 7-9 is also shown graphically in Figures 7-27, 7-30, 7-34, 7-37 and 7-40 for the individual pollutants. Ideally an objective of this research would have been to correlate the storm event hydrological data with the hydrochemical data, which were both characteristic of the runoff and known pesticide applications within the urbanised catchment. This would have provided some indications of the significant hydrological and hydrochemical factors that influenced elevated pesticide concentrations during storm events. However, because it was not possible to accurately isolate the hydrological and hydrochemical data for Site D due to a combination of the operation of the by-pass channel and the problems with peak flow rate estimation (associated with 10% error, see Section 5.3.2), it was considered that it would be relatively uninformative to correlate these two sets of data for Site D, as was done for Site A (see Section 6.4.3). Therefore, in the following sub-sections the hydrochemical data for each herbicide determined at Site D is semi-quantitatively discussed with respect to concurrent data for Site A and where possible inferences are drawn regarding the movement of pesticides within the urbanised catchment.

Table 7-9 Summary of storm event mean herbicide concentration at Sites A and D

		Storm event mean concentration (µg/l)								
Event	Date	A	D	A	D	A	D	A	D	D
(JD)		Sim	Sim	Atra	Atra	Ctu	Ctu	Ipu	Ipu	Diu
106	15/04/92	ns	0.40	ns	0.58	ns	0.24	ns	0.03	0.66
119	28/04/92	ns	0.26	ns	0.48	ns	0.18	ns	0.22	0.65
122	01/05/92	0.21	0.14	0.1	0.11	0.25	0.17	0.34	0.12	0.11
150	29/5/92	ns	1.08	ns	0.84	ns	2.81	ns	1.22	142.00
276	02/10/92	0.2	0.33	0.06	0.23	0.98	0.62	0.21	0.19	0.11
294	20/10/92	0.1	0.14	0.07	0.08	0.59	0.41	nd	nd	nd
314	09/11/92	0.07	0.05	0.03	nd	0.57	0.14	nd	nd	0.09
320	15/11/92	nd	nd	nd	nd	0.45	0.13	nd	0.01	0.07
6	06/01/93	nd	nd	nd	nd	0.23	0.1	nd	nd	0.07
91	01/04/93	nd	nd	nd	0.1	0.2	nd	3.64	0.35	0.004
115	24/04/93	nd	nd	nd	nd	0.13	nd	1.63	0.18	0.09

A - value at Site A, D - value at Site D, Sim - Simazine, Atra - Atrazine, Ctu - Chlorotoluron, Ipu - Isoproturon, Diu - Diuron, nd - no detection, ns - not sampled

7.6.1 Simazine

The occurrence of simazine at Site D was principally governed by the simazine application (9.027kg) to the agricultural sub-catchment on 10/9/91 and the simazine application (0.346kg) to the railway line on 28/11/91. The first storm event at Site D in which simazine was detected occurred 139 days after the agricultural sub-catchment application and 218 days after the railway line application (on 15/4/92) and had a peak concentration of 0.67µg/l. The last storm event at Site D in which simazine was detected at a concentration above the limit of the EC Drinking Water Directive (0.1µg/l) occurred on 20/10/92. The peak simazine concentration of this storm event was 0.29µg/l, and it took place 406 days after the railway line application and 327 days after the application to the agricultural sub-catchment (see Table 7-8 and Figure 7-26). During the course of the monitoring programme, the maximum simazine concentration detected at Site D was 2.23µg/l, which occurred during the storm event of 29/5/92 (JD150). On this occasion the flow at Site D was not supplemented by runoff from the agricultural sub-catchment and therefore the source of the simazine was most certainly the application (0.346kg) made to the railway line; the behaviour of simazine during this event is further discussed below.

Of the eleven storm events which were monitored at Site D, those occurring on 15/4/92 (JD106), 28/4/92 (JD119) and 29/5/92 (JD150) did not contain any significant runoff from the agricultural catchment. This was due to the soil moisture deficit which existed at the time consuming the majority of the incident rainfall that fell onto the agricultural sub-catchment. Further, for these three storm events, the by-pass channel was not in operation and therefore the runoff and detections at Site D were largely representative of the urbanised catchment. For these three storm events, the simazine that was detected at Site D was most certainly transported from the simazine application made to the railway line on 10/9/91. For the remaining eight storm events, where simazine was detected at Site D, the source was most probably a combination of herbicide transport from the agricultural sub-catchment and the railway line application.

Figure 7-24 shows the simazine loads transported during monitored storm events at Sites A and D. At Site A, events JD106, JD119 and JD150 were not sampled due to absence of runoff, and during events JD320-JD115 no simazine detections were made. At Site D, events JD226, JD95 and JD99 were not sampled due to sampler malfunction and during events JD314-JD91 and JD115 no simazine detections were made. Where detections were made at both sites the load at Site D was always in excess of the load at Site A, which represented the significant simazine contribution to the overall load at Site D from the urbanised catchment. For events JD122 and JD276, where the operation of the by-pass was relatively minor with respect to the runoff volume at Site D, the simazine load at Site D was approximately 200% of that at Site A showing that the urbanised catchment matched the simazine load contribution from the agricultural sub-catchment. Overall, for the storm events which could be compared, it appeared that the two catchments provided similar simazine loads although the amount of simazine applied to the agricultural sub-catchment was approximately 26 times higher than that applied to the urbanised catchment.

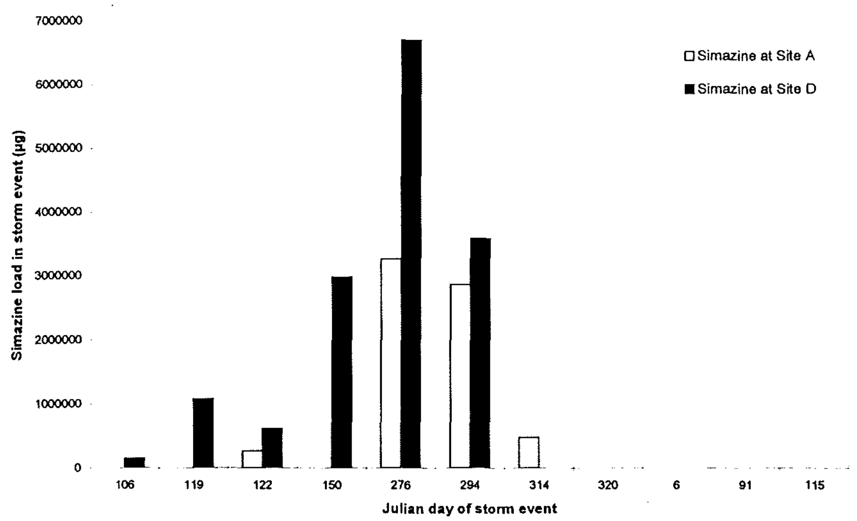

Figure 7-24 Simazine loads during monitored storm events at Sites A and D

Figure 7-25 shows the percentage loss with respect to simazine applications for all storm events monitored at Site D where simazine was detected. Where the flow at Site D was known to be mainly composed of runoff from the urbanised catchment, the percentage loss was expressed in terms of the railway line application (0.346kg). However, when the flow at Site D was known to be composed of runoff from the entire North Weald catchment, the percentage runoff was expressed in terms of the agricultural sub-catchment application (9.027kg) and the railway line application.

Generally, for those events where the Site D flow was mainly urban (events JD106, JD119 and JD150), the application loss values were significantly higher than those instances where the Site D flow was composed of both agricultural and urban runoff. The relatively low application loss value for event JD106 could be explained by the very dry nature of the urbanised catchment at the time which produced the lowest runoff volume and peak flow value of the eleven monitored storm events (see Table 7-6). The percentage simazine application loss values for the storm events composed of both urban and agricultural runoff ranged from 6.0×10^{-3}% to 7.0×10^{-2}%. These values represented typical application losses for simazine and agreed with the values produced for the agricultural catchment, where a range of 3.0×10^{-3} to 3.6×10^{-2}% was found as well as with simazine data from other studies. For example, Williams *et al* (1995) found simazine application loss values ranging from 2.8×10^{-2} to 9.2×10^{-2}% for the Rosemaund agricultural catchment where similar masses of simazine were applied. The Rosemaund catchment was of a similar soil type and scale to the North Weald catchment.

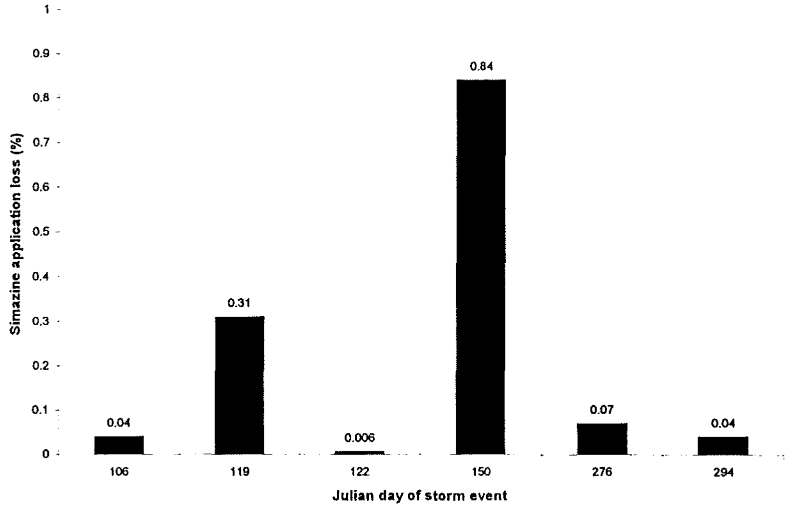

Figure 7-25 Simazine loss (%) with respect to amount of application for storm event detections (numbers on bars represent percentage application loss)

By comparison, the percentage simazine application loss values for the storm events composed mainly of urban runoff were significantly higher (0.04% to 0.84%). When applied to railway embankment material composed of coarse gravel, Torstensson (1994) found that diuron was seventy times more mobile and had a half-life ten times longer than when applied to an agricultural clay soil. Therefore, it was probable that the simazine applied to the North Weald railway line exhibited a similar increase in mobility and half-life, which may have accounted for the relatively high range of application losses obtained.

Figures 7-26 and 7-27 show the peak and event mean simazine concentrations for the eleven storm events monitored at Site D. Generally the range of peak simazine concentrations for the events composed mainly of urban runoff (JD106, JD119 and JD150) were higher (0.47–2.23µg/l) than those containing both urban and agricultural runoff (0.06–0.53µg/l). A similar contrast exists for the ranges of event mean concentrations which were higher for urban runoff only events (0.26–1.08µg/l) compared to those derived from both urban and agricultural runoff (0.05–0.33µg/l). The higher values for the storm events composed mainly of urban runoff are consistent with the higher percentage application loss values for these storm events. In semi-quantitative terms, this indicates that for a given volume of runoff (generated per unit area), a higher concentration of simazine was produced for the urbanised catchment, compared to the combined area of the agricultural and urbanised catchments. This can be primarily attributed to the greater mobility of simazine applied to the railway line ballast material compared to soil applications, which agrees with the findings of Torstensson (1994).

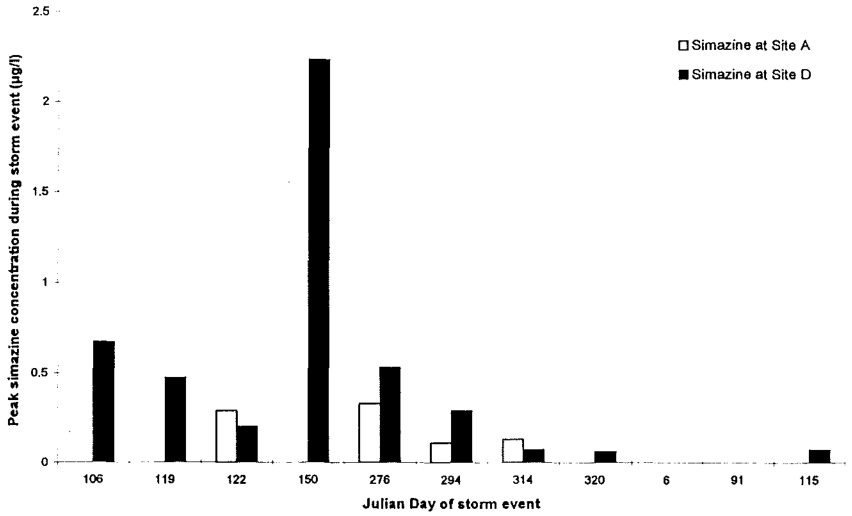

Figure 7-26 Peak simazine concentrations during monitored storm events at Sites A and D

The gradual decrease in the simazine event mean concentrations with time (Figure 7-27) was indicative of the continuous degradation of simazine at the agricultural and urban application sites. The anomalously high value of the event of Julian day 150 was the result of relatively high intensity rainfall (Table 7-6) and the production of runoff only from the urbanised catchment which was subject to limited dilution. Johnson (1995) has described how increasing rain intensity leads to higher losses of isoproturon from a clay-soil lysimiter; in this case simazine may have behaved in a similar manner.

It is difficult to infer what effect the nature of the application substrate had upon the respective fates of the simazine applied to soil in the agricultural catchment and that applied to limestone clinker in the urbanised catchment, since the point of detection in runoff was common to both application sites. With respect to half-life, it was probable that, in situ, the simazine applied to the limestone clinker would have persisted longer than that applied to soil given the lower organic matter content of the clinker. With respect to transport potential, due to the lower clay and organic matter content of the clinker, the simazine applied to the ballast would have been more mobile and hence transported from the application site more readily than from a soil application. This mechanism would have enabled simazine to travel, relatively unimpeded, both to surface waters and groundwater via infiltration through the foundation and drainage system of the railway line.

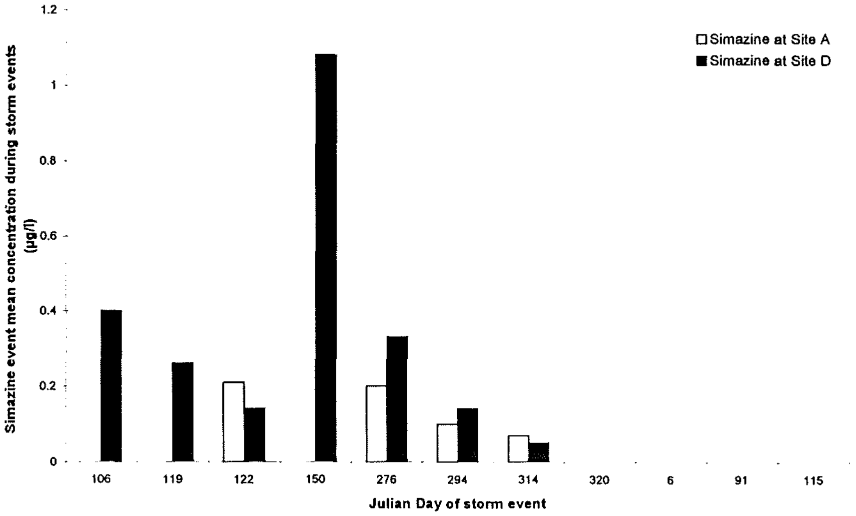

Figure 7-27 **Simazine event mean concentrations (µg/l) during monitored storm events at Sites A and D**

7.6.2 Atrazine

The occurrence of atrazine at Site D was principally governed by the atrazine application (0.208kg) made to the urbanised catchment during the week ending 8/2/92 by the Epping Forest District Council-Parks and Recreation Department and again by a suspected application during February 1993. However, it appeared that there was also a source of atrazine present within the agricultural sub-catchment which was suspected to be runoff from a non-agricultural application made to the M11 motorway which bordered the western edge of the sub-catchment (Section 6.4.1). Further, the results of the artificial rainfall-runoff experiments carried out on samples of railway line clinker suggested that the railway line may also have been a source of atrazine, albeit a very minor one.

The first storm event at Site D in which atrazine was detected (15/4/92) occurred 67 days after the application to the urbanised catchment and had a peak concentration of 0.68μg/l. The last storm event at Site D in which atrazine was detected, at a concentration above the limit of the EC Drinking Water Directive (0.1μg/l), occurred on 20/10/92. The peak atrazine concentration of this storm event, which took place 255 days after the Parks and Recreation Department application, was 0.15μg/l (Table 7-8 and Figure 7-29). During the course of the monitoring programme, the maximum atrazine concentration detected at Site D was 1.28μg/l, which occurred during the storm event of 29/5/92 (JD150). On this occasion the flow at Site D was not supplemented by runoff from the agricultural sub-catchment so the source of the atrazine was certainly the Parks and Recreation Department application (0.208kg).

The events occurring on 15/4/92 (JD106), 28/4/92 (JD119) and 29/5/92 (JD150) did not contain any significant runoff from the agricultural catchment due to the soil moisture deficit at the time and the by-pass channel was not in operation. Therefore, the atrazine detected at Site D was wholly representative of the urbanised catchment. Figure 7-28 shows the atrazine load monitored during storm events at Sites A and D. At Site A, events JD106, JD119 and JD150 were not sampled due to absence of runoff and during events JD320-JD115 atrazine was not detected. At Site D, events JD226, JD95 and JD99 were not sampled due to sampler malfunction and during events JD314-JD6 atrazine was not detected.

When detections were made at both Sites A and D, the load at Site D was always in excess of that at Site A due to the significant atrazine contributions to the overall load from the urbanised catchment. For events JD122 and JD276, where the operation of the by-pass was relatively minor with respect to the runoff volume at Site D, the atrazine load at Site D was considerably higher than that at Site A especially for event JD276. This indicated the ability of the urbanised catchment to produce a significantly higher atrazine load compared to the agricultural sub-catchment. However, due to the absence of details on the source of atrazine in the agricultural sub-catchment it is difficult to draw any definite conclusions regarding the relative behaviour of atrazine applied to the agricultural and the urban sub-catchments.

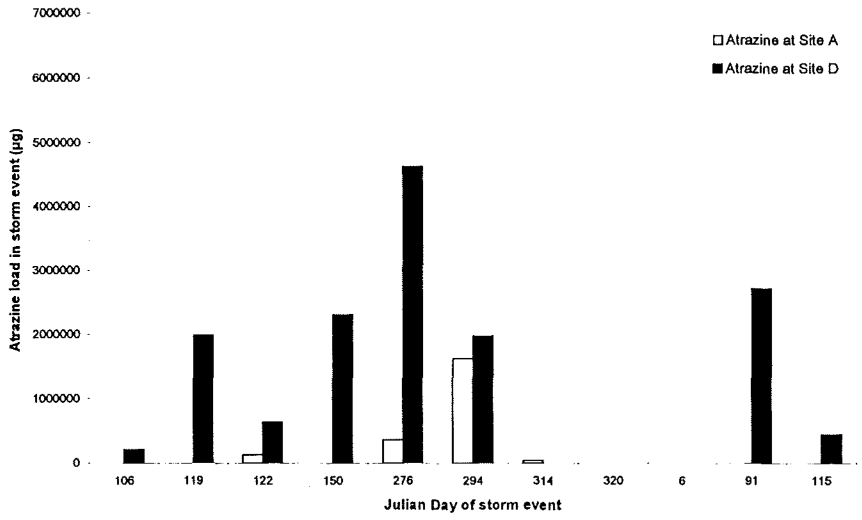

Figure 7-28 Atrazine loads during monitored storm events at Sites A and D

For the storm events (JD106, JD119 and JD150), the atrazine detected at Site D was most certainly only transported from the Parks and Recreation Department applications, whereas for the remaining eight storm events, atrazine detections at Site D were likely to be influenced by the unidentified application in the agricultural sub-catchment. For the three storm events relating to JD106, JD119 and JD150, the percentage application loss values were 0.10%, 0.96% and 1.11% respectively, with respect to the Parks and Recreation Department application (0.028kg). For the remaining eight storm events for which atrazine was detected at Site D, calculations of percentage application losses were hindered by the lack of information on the unidentified application of atrazine located in the agricultural sub-catchment. Similarly to the relatively high simazine losses from the railway line application described above (Section 7.6.1), the percentage application loss values for atrazine were higher than those found for soil applications by other workers conducting similar studies. For example, Williams *et al* (1995) found atrazine loss values in the range of $1.4\text{x}10^{-4}$ to 0.2% for atrazine applied to fields within the Rosemaund catchment. The higher than expected atrazine application loss values determined at Site D were probably the result of applications to substrates untypical of the soil environment and more typical of gravelly amenity areas that were relatively low in organic matter content. Hence by, analogy to the simazine transport from the railway line (Section 7.6.1) and the findings of Torstensson (1994), the atrazine applied by the Parks and Recreation Department appeared to be more mobile than would have been predicted from its behaviour in a typical soil environment. This has also been found by other studies (Williams *et al*, 1991 and Williams *et al*, 1995). Unfortunately, when acquiring information to construct the pesticide application data base for the urbanised catchment (see Table 7-1), details of the types of surface to which amenity applications were made by the Parks and Recreation Department were unavailable. However, given the atrazine application loss data for storm events JD106, JD119 and JD150, it was suspected that they were untypical of agricultural soils but composed of sand and gravel or possibly tarmacadam and located in areas from which runoff was relatively unimpeded by soil during travel to a flow channel.

Figures 7-29 and 7-30 show the peak and event mean atrazine concentrations for the eleven storm events monitored at Site D. Generally the range of peak atrazine concentrations for the events composed mainly of urban runoff (JD106, JD119 and JD150) were higher (0.68–1.28µg/l) than those containing both urban and agricultural runoff (0.07–0.84µg/l). Similarly the event mean concentrations were higher for urban runoff only with a range of 0.48–0.84µg/l compared to 0.08–0.23µg/l. This pattern agrees with that found for simazine, and indicates in semi-quantitative terms, that for a given volume of runoff generated per unit area, a higher concentration of atrazine was produced for the urbanised catchment, compared to the combined area of the agricultural and urbanised catchments.

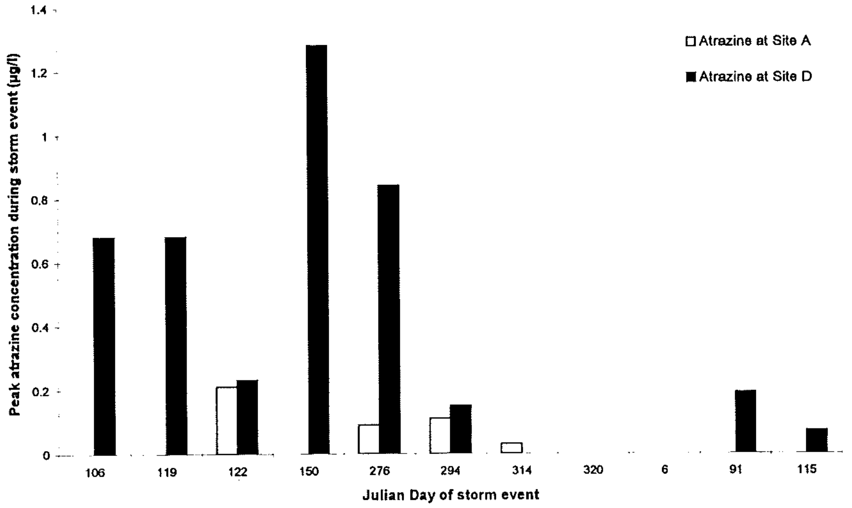

Figure 7-29 Peak atrazine concentrations during monitored storm events at Sites A and D

This could be attributed to the greater mobility of atrazine applied by the Parks and Recreation Department to suspected non-soil areas compared to the mobility of atrazine applications to agricultural soil environments. However, without specific details of the atrazine source within the agricultural sub-catchment, it is difficult to infer with absolute certainty that this was the true situation.

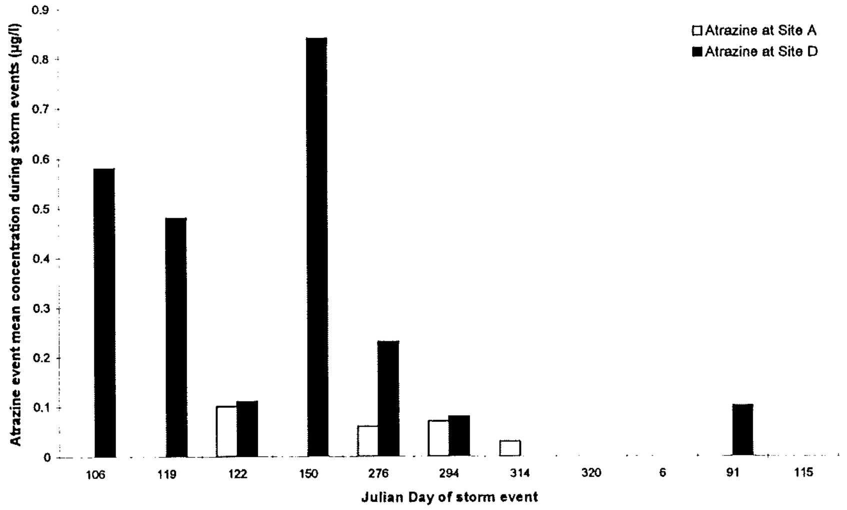

Figure 7-30 Atrazine event mean concentrations during monitored storm events at Sites A and D

7.6.3 Chlorotoluron

With respect to known applications, the occurrence of chlorotoluron at Site D was principally governed by the chlorotoluron application (70kg) made to the British Telecom land area (Figure 7-1) of the urbanised catchment on 18/11/91 and the application (78.333kg) made to the agricultural sub-catchment on 28/10/91. Also, as previously discussed (Section 7.3) the results of the artificial rainfall-runoff experiments carried out on samples of railway line ballast, suggested that the railway line may also have been a source of chlorotoluron, although probably a very minor one.

The first storm event at Site D (15/4/92) in which chlorotoluron was detected occurred 149 days after the application to the urbanised catchment and 170 days after the agricultural sub-catchment application. It had a peak chlorotoluron concentration of 0.33µg/l. The last storm event at Site D, in which chlorotoluron was detected at a concentration above the limit of the EC Drinking Water Directive (0.1µg/l), occurred on 15/11/92. The peak chlorotoluron concentration during this storm event was 0.43µg/l and it took place 363 days after the urbanised catchment application and 384 days after the agricultural sub-catchment application (Table 7-8 and Figure 7-33).

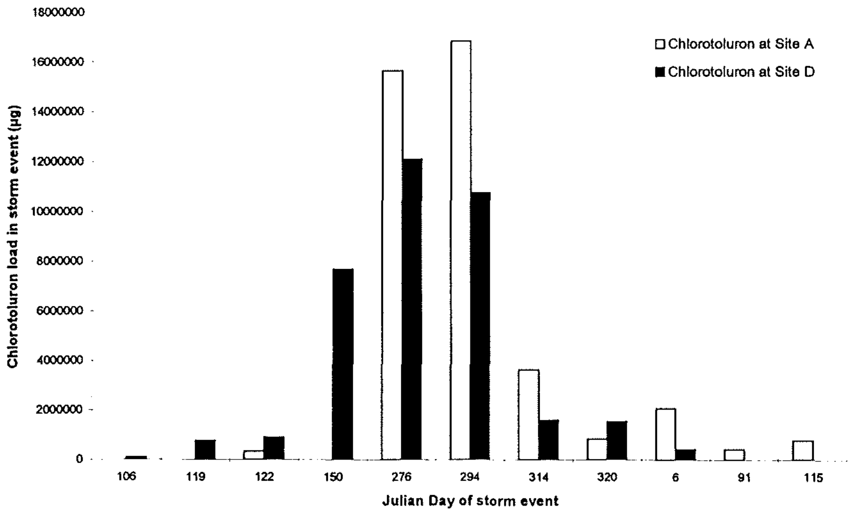

Figure 7-31 Chlorotoluron load during storm events monitored at Sites A and D

During the course of the monitoring programme, the maximum chlorotoluron concentration detected at Site D was 4.51µg/l during the storm event of 29/5/92 (JD150). Since the flow at Site D was not augmented by runoff from the agricultural sub-catchment during this event, the source of the chlorotoluron was identified as the application made to the British Telecom land. Table 7-7 and Figure 7-31 show the chlorotoluron loads determined for each storm event at Sites A and D.

At Site A, events corresponding to JD106, JD119 and JD150 were not sampled due to the absence of runoff and at Site D and events JD226, JD95 and JD99 were not monitored due to sampler malfunction. For event JD122, the expected higher chlorotoluron load was found at Site D compared to Site A, as a consequence of the throughput of the Site A load in addition to the chlorotoluron load from the urbanised catchment. However, for the three events between JD276 to JD314 and JD6 the opposite situation occurred with the Site A chlorotoluron load consistently exceeding the Site D load. Examination of the relevant hydrographs and pollutographs in Figures 7-16, 7-18, 7-19 and 7-21, suggests that the discrepancy in chlorotoluron load between Sites A and D may have been possibly accounted for by the load being diverted through the by-pass channel which was flow-gauged but not sampled for herbicides.

Considering the similar amounts of chlorotoluron that were applied to cropped areas of the agricultural sub-catchment and urbanised catchment at approximately the same time, it would be reasonable to infer that the chlorotoluron detections at Site D would have persisted for a similar period to those at Site A. However, as shown in Table 7-7 this situation was not observed as the last chlorotoluron detection at Site D occurred approximately three months before that at Site A. This disparity may be explained if the soil retention was higher and the half-life lower for the chlorotoluron applied to the urbanised catchment compared to that for the chlorotoluron applied to the agricultural sub-catchment. This may have been the result of slightly differing soil chemistries and/or field management practice which may have produced differing soil organic matter contents. Levanon *et al* (1993) suggested that for a given pesticide, higher soil organic matter content would enhance sorption and biodegradation resulting in lower pesticide leaching. If this was the situation, then for a given storm event, the chlorotoluron load entering the urbanised catchment from the agricultural sub-catchment would have interacted with urban runoff of generally lower chlorotoluron concentration. As the monitoring programme progressed, eventually the amount of chlorotoluron present in the urban runoff may have decreased to marginal levels, and in this situation the chlorotoluron in the agricultural runoff entering the urbanised catchment would have been diluted to levels below detection limits at site D.

Table 7-10 and Figure 7-32 show the percentage chlorotoluron application losses determined at Site D compared to those at Site A. The Site A values were calculated relative to the chlorotoluron application (78.333kg) made to the agricultural sub-catchment on 28/10/91. The Site D values were calculated relative to the combined urbanised and agricultural sub-catchment applications except for events JD106, JD119 and JD150 which were mainly composed of urban runoff.

Table 7-10 Percentage chlorotoluron loss determined at Site D compared to loss determined at Site A

Event (Julian day)	Event	Chlorotoluron loss determined at Site A (%)	Chlorotoluron loss determined at Site D (%)
106	15/04/92	ns	0.0001#
119	28/04/92	ns	0.0010#
122	01/05/92	0.0004	0.0006
150	29/05/92	ns	0.0110#
226	13/08/92	0.0034	ns
276	02/10/92	0.0200	0.0082
294	20/10/92	0.0215	0.0073
314	09/11/92	0.0046	0.0011
320	15/11/92	0.0011	0.0010
6	06/01/93	0.0026	0.0003
91	01/04/93	0.0005	ns
95	05/04/93	0.0007	ns
99	09/04/93	0.0024	ns
115	24/04/93	0.0010	ns

ns- not sampled, # for events JD106, JD119 and JD150 at site D, the flow was mainly composed of urban runoff, therefore the percentage loss was expressed in terms of urbanised catchment chlorotoluron application only

No account was made for the herbicide load that was possibly diverted through the by-pass channel and therefore any inferences drawn must be viewed from a semi-quantitative perspective. The data show that the ranges for the percentage application losses of the three events monitored at Site D, which were composed mainly of urban runoff (JD106, JD119 and JD150), were not markedly different to those that contained a combination from both urban and agricultural runoff. This possibly highlights the common type of soil-based application substrate. The range for the urban-runoff-only storm events was 1.0×10^{-4}–1.1×10^{-2}% compared to 3.0×10^{-4}–8.2×10^{-3}% for the events containing both urban and agricultural runoff. This contrasts to the situation for simazine and atrazine where the three urban-runoff-only events had noticeable higher application loss value ranges.

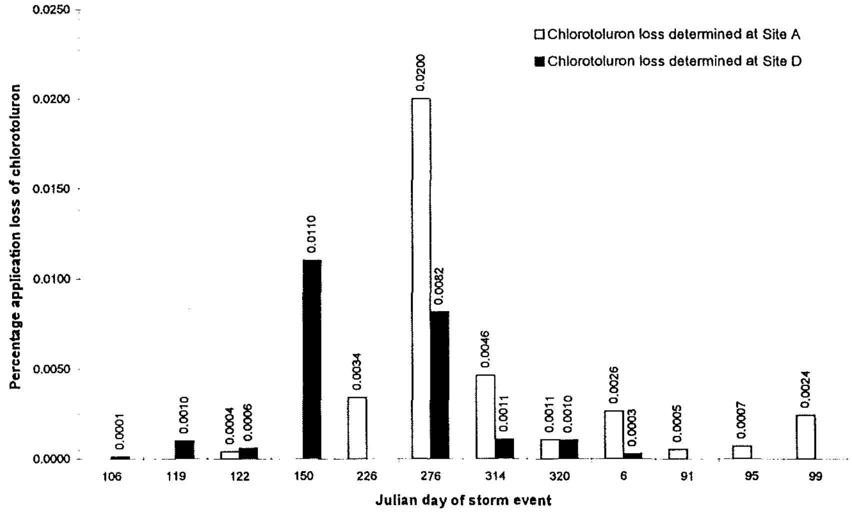

Figure 7-32 Percentage application losses of chlorotoluron at Site D and Site A during monitoring programme [Flow at Site D for events 106, 119 & 150 composed mainly of urban runoff, therefore % loss expressed with respect to urban chlorotoluron application only. Numbers on bars relate to percentage application loss]

Figures 7-33 and 7-34 show the peak and event mean chlorotoluron concentrations for the eleven storm events monitored at Site D during the course of the monitoring programme (see also Table 7-8 and 7-9). Generally the range of peak chlorotoluron concentrations (0.29-4.51µg/l {0.29-0.33µg/l excluding the event JD150 value}) for the events composed mainly of urban runoff (JD106, JD119 and JD150) were equivalent to those of events derived from both urban and agricultural runoff (0.06-0.91µg/l).

Similarly the ranges for the event mean concentrations were similar with ranges of 0.18-2.81µg/l (0.18-0.24µg/l excluding the event JD150 value) and 0.1-0.62µg/l respectively. The anomalously high peak and event mean concentrations for storm event JD150 were probably the result of the intense rainfall which occurred and which has been reported by Johnson (1995) to give rise to proportionately higher pesticide runoff losses.

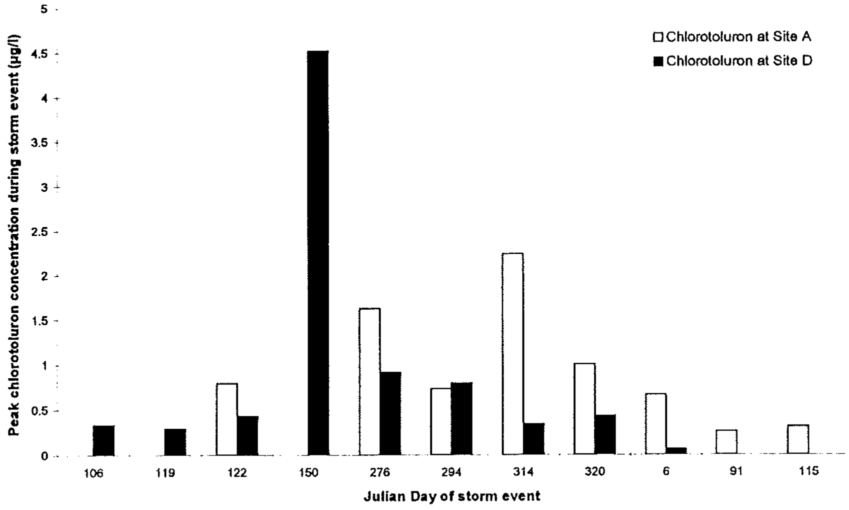

Figure 7-33 Peak chlorotoluron concentrations during monitored storm events at Sites A and D

Excluding the data for storm event JD150, the general similarity of urban and urban-and-agricultural runoff peak and event mean concentration range data agrees with the common type of soil-based application in the agricultural sub-catchment and the urban catchment.

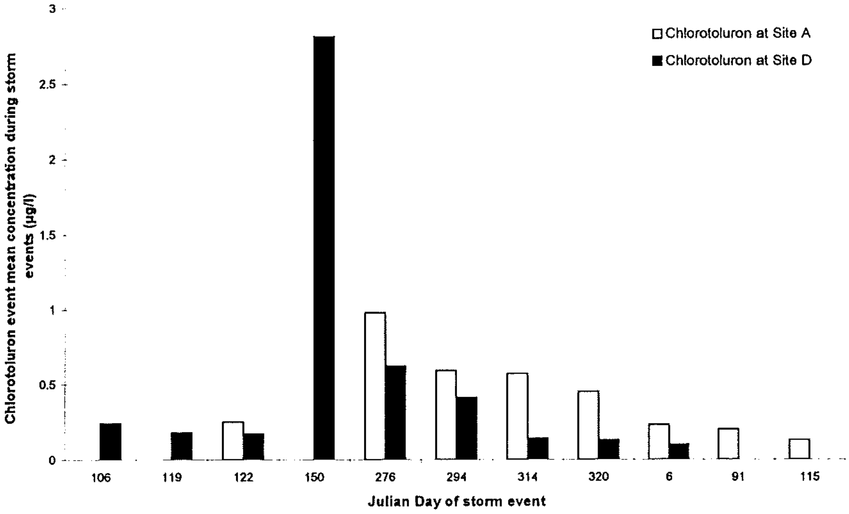

Figure 7-34 Chlorotoluron event mean concentrations during monitored storm events at Sites A and D

Comparison of the chlorotoluron peak and event mean concentration data for specific events shows that the Site A data were generally greater than the Site D data (Figures 7-33 and 7-34). This behaviour probably resulted from the enhanced degradation of the chlorotoluron applied to the urbanised catchment which would have meant that the chlorotoluron leaving the agricultural sub-catchment would have mixed with urban runoff of generally lower chlorotoluron concentration, thus lowering the mean concentration determined at Site D compared to that at Site A.

7.6.4 Isoproturon

The occurrence of isoproturon at Site D was principally governed by the isoproturon applications made in 1991 and 1993 to the agricultural sub-catchment. These were, 13.055kg applied on 28/10/91; 25.250kg applied on 6/11/91; 22.475kg applied on 16/11/91 and 39.692kg applied on 3/2/93. Therefore, the occurrence of isoproturon at Site D can be considered relative to two application periods corresponding to the winter of 1991 (three separate applications) and early spring of 1993 (one application). The data from storm events monitored at Site D which were composed mainly of urban runoff, showed that there was an unidentified source of isoproturon present in the urbanised catchment. The results of manual sampling within the urbanised catchment suggested that this source may have been the British Telecom land, since on 29/5/92 isoproturon was found in ditch water draining from this area, at a concentration of 34.56μg/l (Section 7.2.1).

The first monitored storm event at Site D in which isoproturon was detected (15/4/92) occurred 151-170 days after the 1991 winter application to the agricultural sub-catchment and had a peak concentration of 0.22μg/l (Table 7-8 and Figure 7-36). The last monitored storm event at Site D in which isoproturon was detected at a concentration above the limit of the EC Drinking Water Directive (0.1μg/l), occurred on 24/4/93. The peak isoproturon concentration of this storm event was 0.30μg/l, and it took place 81 days after the agricultural sub-catchment application on 3/2/93 (Table 7-8 and Figure 7-36). During the course of the monitoring programme, the maximum isoproturon concentration detected at Site D was 3.27μg/l during the storm event of 29/5/92 (JD150). Since the flow at Site D on this occasion was mainly composed of runoff from the urbanised catchment, the source of the isoproturon was probably an unidentified application made within the urbanised catchment.

For these three storm events (JD106, JD119 and JD150), the isoproturon that was detected at Site D was sourced entirely within the urbanised catchment from the unidentified application. From the pollutographs of these storm events, especially those for event JD106 (Figure 7-7) and event JD150 (Figure 7-13), it appeared likely that the isoproturon was transported from a soil environment rather than a hard-surface environment, in accordance with the label recommendation of isoproturon products which were approved only for agricultural use by the Ministry of Agriculture, Fisheries and Food. This suggestion agrees with the manual sampling data, from which it appeared probable that the source of the isoproturon was the British Telecom land where arable crops were grown. The fact that runoff was generated from soiled areas of the urbanised catchment but not the agricultural sub-catchment may have been associated with the slope of the British Telecom land area which was greater than any area within the agricultural sub-catchment. Wauchope (1978) and Buttle (1989) have reported that as the slope of a soiled area increases so does the area's capacity to generate runoff.

Figure 7-35 and Table 7-7 show the levels of the isoproturon loads during storm events monitored at Sites A and D. For events JD106, JD119 and JD150, the only significant runoff and consequently a monitored isoproturon load was recorded at Site D. For storm events JD122 and JD276, storm event runoff was sampled from both Sites A and D; for event JD122 the isoproturon load found at Site D was approximately double that found at Site A but for event JD276 the isoproturon loads at both sites were similar. The latter situation was despite the fact that if the isoproturon load that was probably transported through the by-pass channel was taken into account, the combined load for the urbanised catchment would have probably been considerable greater than that of Site A. In general, for the storm events from JD106 to JD6, the overall trend appeared to show that higher isoproturon loads were found at Site D compared to site A. This suggests that the amount of the unidentified isoproturon application made to the British Telecom area was similar to that applied to the agricultural sub-catchment during the 1991 winter. Apart from a minor isoproturon detection at Site D for event JD320, isoproturon was not detected at Sites A or D after the JD276 storm event until after the Spring 1993 isoproturon application when it was detected during the storm event of 1/4/93. This was probably the result of *in-situ* isoproturon degradation and off-site transport from the agricultural sub-catchment and the unidentified urban catchment applications. Because the details of the isoproturon application made to the urbanised catchment were unknown, it was difficult to express the isoproturon load found at Site D in terms of percentage application losses.

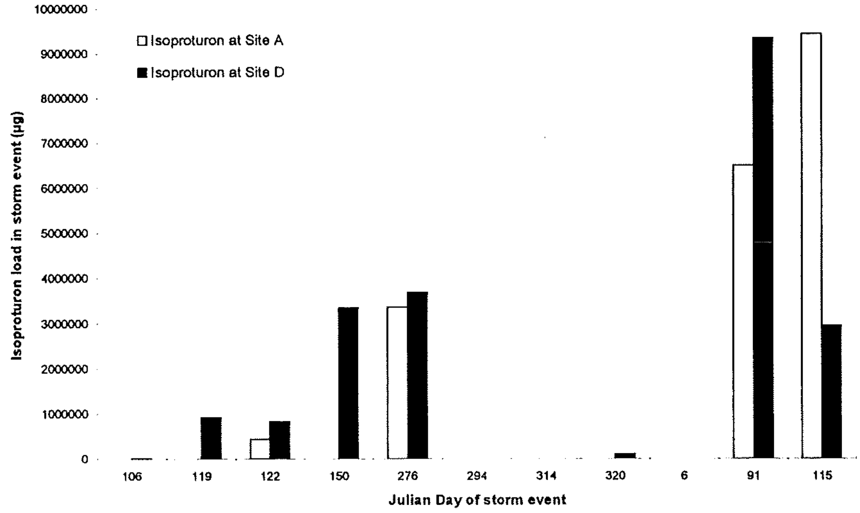

Figure 7-35 Isoproturon load during storm events monitored at Sites A and D [Load for event JD91 at Site A divided by a factor of 10]

After the Spring 1993 isoproturon application to the agricultural sub-catchment, the magnitudes of the subsequent isoproturon loads found at Sites A and D for events JD91 and JD115 did not appear to follow the pattern of occurrence found in previous events (Table 7-7 and Figure 7-35). Events JD95 and JD99 were not sampled at Site D due to sampler malfunction. For event JD91, the isoproturon load found at Site A was approximately seven times that found at Site D and for event JD115, approximately three times the isoproturon load was found at Site A compared to Site D. Assuming that the mean concentration of the by-pass channel runoff was comparable to that of the runoff at Site D, it seemed improbable that the difference in isoproturon load could have been completely accounted for by the operation of the by-pass channel. Because in both cases, the runoff volume that passed through the by-pass channel was only 10-20% of the runoff volume that passed through Site D. Between January and March 1993, the Roads and Highways Department applied approximately 500kg of de-icing salt to the urbanised catchment (Gibbons *pers comms*, 1994). Therefore, the difference in load may be possibly explained if the runoff generated within the urbanised catchment had a high salt concentration as a result of de-icing salt applications. If this was the case, then for JD91 and JD115 storm events, the runoff draining from the agricultural sub-catchment would have mixed with the urbanised catchment runoff of significantly higher ionic strength which may have caused the isoproturon to precipitate from the combined runoff solution by the 'salting-out' effect and therefore significantly reduce the isoproturon concentration in the runoff that passed through Site D.

Figures 7-36 and 7-37 show the peak and event mean isoproturon concentrations monitored at Sites A and D during the period of the monitoring programme. For the storm events from JD106 to JD320 which relate to the 1991 winter isoproturon application to the agricultural sub-catchment, isoproturon detections were observed more often at Site D compared to Site A. This may have been due to the faster response of the relatively steeply sloped British Telecom land compared to the flatter agricultural sub-catchment. This would have reduced the period of time between rainfall interception and runoff and consequently produced a relatively higher isoproturon concentration (Baker *et al.* 1982).

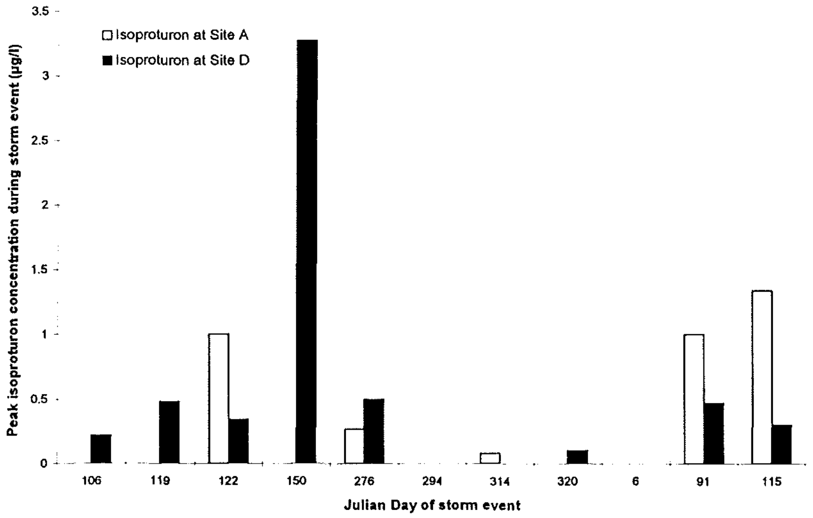

Figure 7-36 Peak isoproturon concentrations during monitored storm events at Site A and D
[Events 91 and 115 divided by a factor of 2]

Isoproturon was monitored simultaneously at both sites for only two events. For the first, event (JD122) both the peak and event mean concentration data at Site A were higher than those at Site D (peak concentration: 1.00μg/l and 0.34μg/l, and event mean concentration: 0.34μg/l and 0.12μg/l respectively). Whilst, for the second event (JD276) the peak concentration at Site D was higher than that at A (0.5μg/l and 0.27μg/l respectively) whereas the situation with the event mean concentration data was reversed (0.21μg/l and 0.19μg/l). A review of the data shown in Figure 7-16 suggests that a detailed comparison of these two events may be unwarranted. Unlike the event of JD122 where fourteen samples were collected, the interpretation of the variation of concentration for event JD276 was based on four samples which may not have accurately reflected the concentration and flux behaviour of isoproturon during the course of the event.

For the case of storm event JD150, where the flow at Site D was mainly composed of urban runoff, the anomalously high isoproturon concentration was probably the result of relatively high rainfall intensity for the event. As previously mentioned, Johnson (1995) found that a fourfold increase in rainfall intensity produced a tenfold increase in isoproturon concentration. For the storm events JD91 and JD115, that occurred in Spring 1993, the peak and event mean isoproturon concentrations monitored at Site A were higher than those at Site D which was likely to be attributable to dilution.

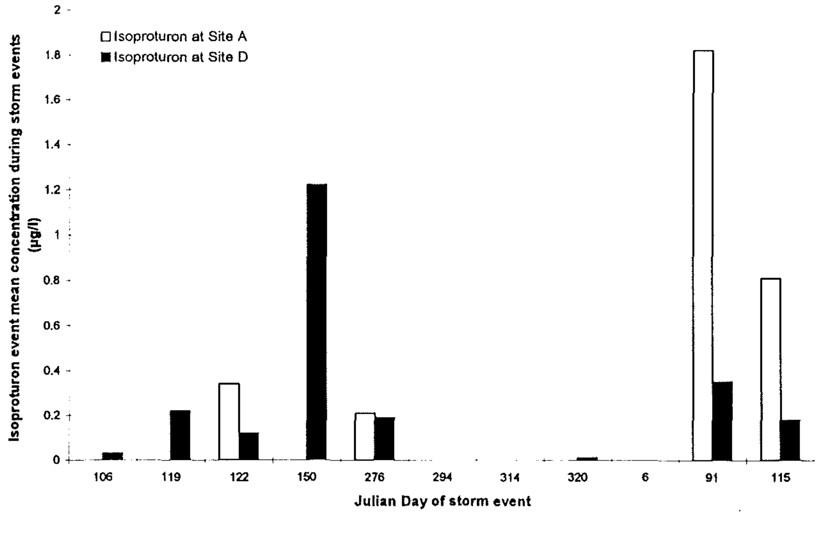

Figure 7-37 Isoproturon event mean concentrations during monitored storm events at Site A and D [Events 91 and 115 divided by a factor of 2]

7.6.5 Diuron

The occurrence of diuron at Site D was wholly governed by the diuron applications made in 1992 to the urbanised catchment. During this period no applications were made to the agricultural sub-catchment. The applications in the urbanised catchment were 0.083kg during the week ending 8/2/92 by the Parks and Recreation Department to amenity areas; 0.800kg on 5/5/92 by the Roads and Highways Department to roadside verges; and 0.461kg on 29/10/92 by London Underground to the track ballast of the railway line.

The first storm event at Site D (15/4/92; JD106), in which diuron was detected, occurred approximately 67 days after the Parks and Recreation Department application (0.083kg) and had a peak concentration of 1.06µg/l (Table 7-8 and Figure 7-39). The last storm event at Site D, in which diuron was detected at a concentration above the limit of the EC Drinking Water Directive (0.1µg/l), occurred on 24/4/93. The peak diuron concentration of this storm event was 0.18µg/l, and it took place 178 days after the London Underground application (0.461kg) on 29/10/92 (Table 7-8 and Figure 7-39). The maximum diuron concentration detected at Site D, during the course of the monitoring programme, was 238.39µg/l. This value was determined during the storm event of 29/5/92 (JD150) which occurred 24 days after the Roads and Highway Department application (0.800kg). Table 7-11 shows the percentage diuron application loss data for the monitored storm events at Site D during the monitoring period. These data are also shown diagrammatically in Figure 7-38. The diuron application loss data in Table 7-11 have been divided into three chronological sections which correspond to the main causative diuron application.

Table 7-11 Percentage diuron application loss at Site D with diuron application data

Diuron application (kg)	Application date	Event Julian day	Event date	Diuron load at Site D (µg)	Diuron application loss at Site D (%)
0.083[1]	w/e 8/2/92	106	15/04/92	242,600	0.2923
		119	28/04/92	2,723,000	3.2807
		122	01/05/92	382,868	0.4613
0.800[2]	5/5/92	150	29/05/92	390,933,000	45.100
		226	13/08/92	ns	ns
		276	02/10/92	2,226,000	0.2567
		294	20/10/92	nd	nd
0.461[3]	29/10/92	314	09/11/92	788,000	0.1709
		320	15/11/92	524,000	0.1137
		6	06/01/93	287,000	0.0623
		91	01/04/93	67,000	0.0145
		115	24/04/93	355,000	0.0770

[1] Parks and Recreation Department; [2] Roads and Highways Department; [3] London Underground; nd: not detected, ns: not sampled

The ranges for the application loss data corresponding to the three different types of diuron applications were:

Diuron application	Range for percentage application loss
• Parks and Recreation Department (0.083kg)	0.29-3.28%
• Roads and Highways Department (0.800kg)	nd-45.1%
• London Underground (0.461kg)	0.06-0.17%

Overall, it appeared that the three ranges for percentage application losses, specific to each of the sequential diuron applications, were generally much higher than those associated with similar phenylurea herbicide applications made to agricultural catchments (Williams *et al*, 1995; Gomme *et al*, 1991). For example, in this study the isoproturon and chlorotoluron percentage application loss ranges for the agricultural sub-catchment were nd-0.16% and $4.0\text{x}10^{-4}$-0.021% respectively. During a comparable study based at the Rosemaund catchment, Williams *et al* (1995) found that the percentage application loss of isoproturon was in the range $3.0\text{x}10^{-5}$-0.014%. Although the diuron data-sets obtained after each of the diuron applications were not extensive, their inter-comparison is still informative with respect to the factors affecting diuron transport in storm event runoff. The percentage application loss data for each sequential diuron application shows that the highest losses were from the Roads and Highways Department application and then by the Parks and Recreation Department application, followed by the London Underground application. It was highly probable that, for the storm events that followed each diuron application, the prevailing meteorological conditions were not constant, different periods of time had elapsed between application and sample collection and not all significant storm events were sampled. However, it is proposed that the type of substrate to which each of the three diuron applications were made, probably had a major effect upon the load and concentration of diuron lost in the storm events following each application. This is based on the physical nature of each substrate which would have had a significant effect upon the retention and persistence of the applied diuron. The probable mechanisms underlying the loss of diuron subsequent to each application are discussed below.

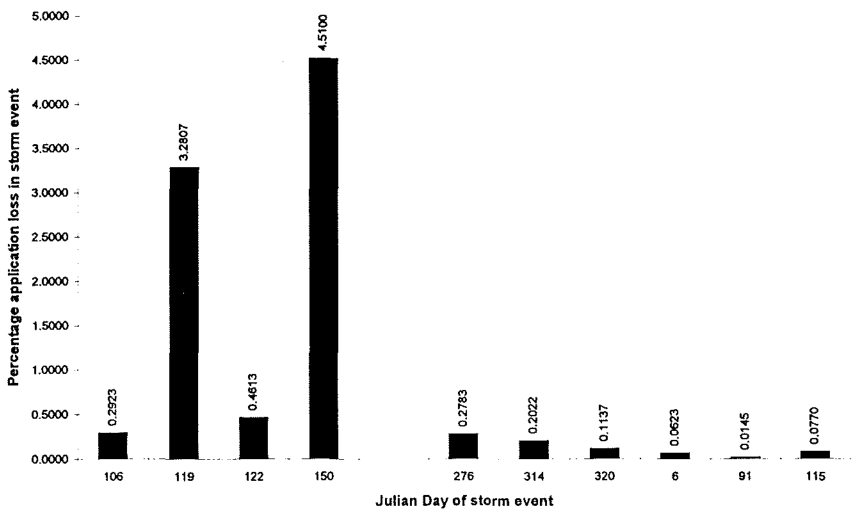

Figure 7-38 Percentage diuron application loss during monitored storm events at Site D
[Value for storm event 150 divide by 10. Numbers on bars relate to percentage application loss]

The diuron application by the Roads and Highways Department on 5/5/92 was made to the roadside kerbstones and backwalls of the majority of the roads in North Weald. By their nature, most engineered hard surfaces possess low infiltration rates, rapid drainage, and low water holding capacity (see Section 3.1.4). Further, the construction of hard surfaces is generally characterised by the use of dense inorganic materials including stone aggregate, sand, and concrete which preclude the accumulation of organic matter which would otherwise partially retain an applied pesticide. The contrasting surface hydrology of hard surfaces in relation to that of soils, would suggest that a pesticide would be unlikely to infiltrate downwards into the immediate surface of the material where possible sorption sites are present. In contrast, with the onset of rainfall, the relatively unretained pesticide is more likely to move rapidly with the surface water into the nearest drainage system (Heather and Carter, 1996). The roadside kerbstones and concrete paving stones of the urbanised catchment, were typical hard-surfaces and with minimal accumulation of organic matter would have had very little opportunity to retain the applied diuron during a storm event. Also, the negligible organic matter content of the hard-surface would have greatly minimised the loss of the diuron through microbial degradation and with respect to a soil environment, the diuron would have shown enhanced persistence. Therefore, with the onset of the first storm event and the absence of any significant retention combined with a relatively high aqueous solubility (42mg/l; Table 4-2), the diuron would have been readily transported from the site of application to the nearest entry of the storm sewer system and subsequently into the main watercourse whilst experiencing the minimum of retention and degradation. Given such favourable circumstances for leaching and off-site transport, it is not surprising that the diuron applied by the Roads and Highways Department on 5/5/92 produced an application loss of 45.1% during the first significant storm event after application.

The amount of diuron available for transport in subsequent storm events would have been considerably reduced and the period for which diuron would have been detected in storm runoff after the application would have been much shorter than for a soil based application experiencing similar meteorological conditions. Unfortunately this behaviour was not clearly shown after the JD150 storm event at Site D due to a combination of a prolonged period of dry weather and because the second storm event following the diuron application was not sampled due to sampler malfunction. However, the percentage application loss for storm event JD276 was only 0.27% due to the combined effects of exhaustion of supply and time since application (150days).

The diuron application made by the Parks and Recreation Department during the week ending 8/2/92 was reported to have been made to grassed public amenity areas to supplement mechanical grass cutting operations where access for mowers was restricted and also to the grass verges of public footpaths. Although the diuron was reported by the Parks and Recreation Department to have been made to grassed areas, the pattern of diuron concentration data in the pollutographs relating to storm events JD106, JD119 and JD122, following the application (Figures 7-7, 7-9 and 7-11), was more typical of that associated with movement form a hard-surface environment than a soil based environment. Also, the range of percentage application loss values was greater than that associated with a soil based application. Therefore, it was probable that the diuron was applied to a number of different substrate types ranging from typical soil based environments to hard-surface environments. These would include vegetation occurring within or next to hard-surface environments, such as weeds growing through pavement cracks or street furniture, and the grass verges of public footpaths. With a relatively broad range of application substrates, the capacity for the applied diuron to infiltrate the surface and be retained by the substrate would probably have been within a range typical of those associated with agricultural environments and hard-surface environments. For example, where the diuron was applied to the grass verge of a tarmacadam footpath, once the diuron had leached from the grass/soil substrate it would readily be carried in runoff to the nearby footpath during a storm event. From the hard-surfaced footpath it would be rapidly transported into the urban drainage system and then into the main watercourse in a manner similar to that described above for the diuron applied to roadside verges by the Roads and Highways Department. Alternatively, where the diuron was applied to control vegetation surrounding an obstruction present within a grassed area that was not accessible to grass mowers, its fate and transport would have been more typical of that of a herbicide applied to a soil substrate.

The diuron applied to the railway line by London Underground Limited on 29/10/92 was essentially made to the ballast material that composed the foundation of the railway line. The construction of a railway track foundation involves an upper layer of heavy ballast overlying a dense substrate to allow rapid surface drainage (Heather and Carter, 1996). In some cases, the surface drainage could be channelled into an engineered drainage system but more usually it would be channelled into a soakaway area allowing the surface runoff to bypass the pesticide attenuating upper soil profile and to infiltrate into the unsaturated zone and eventually the groundwater (Gomme *et al*, 1992). Aldous and Turrel (1994) found significant concentrations of atrazine present in the unsaturated zone six metres below a site immediately adjacent to a railway line which suggested that the atrazine applied to the railway track had efficiently penetrated the unsaturated zone and moved into the saturated zone and groundwater. It was known from discussions with London Underground that the railway line at North Weald did not have an engineered drainage system and that, where necessary, surface drainage was channelled into soakaways (D Mole *pres comms*, 1993). Therefore, given the low percentage application losses of the diuron applied to the railway line compared to the other applications, it was likely that the majority of the applied diuron was transported downwards into the unsaturated zone rather than being transported laterally within surface runoff to the main watercourse. This proposal would agree with the work of Torstensson (1994) who found that 33 days after an application to a Swedish railway line, diuron was detected at a concentration of approximately 100μg/l at depths of between 50 and 75 cm depth below the surface of the railway track.

The peak and event mean diuron concentration data for each storm event monitored are shown in shown in Figures 7-39 and 7-40. In both figures the data for storm event JD150 have been divided by a factor of 100 to minimise the suppression of the data for the other storm events.

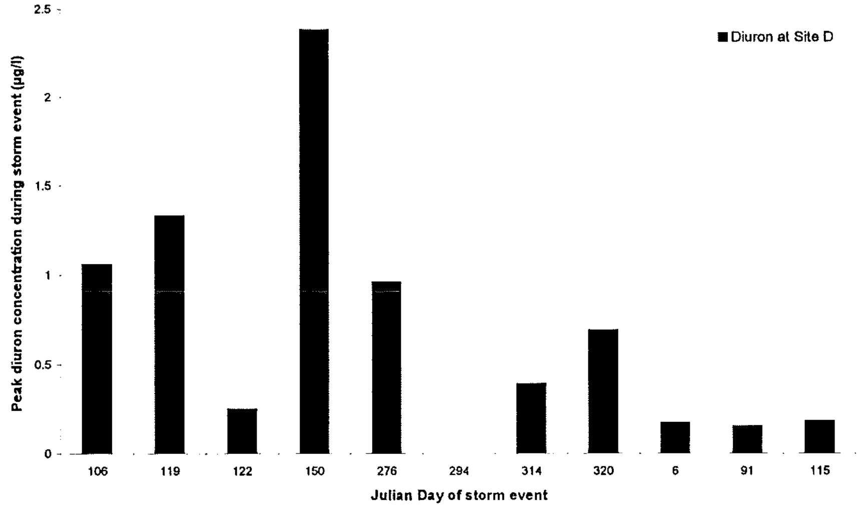

Figure 7-39 Peak diuron concentrations during monitored storm events at Site D [Peak concentration during storm event on 150 divided by a factor of 100]

The range of peak and event mean diuron concentrations relating to each of the three sequential diuron applications are shown below.

Diuron application	Peak concentration range	Event mean concentration range
Parks and Recreation Department (0.083kg)	0.25-1.33(µg/l)	0.11-0.65(µg/l)
Roads and Highways Department (0.800kg)	nd-238.39(µg/l)	nd-142.00(µg/l)
London Underground (0.461kg)	nd-0.69(µg/l)	nd-0.09(µg/l)

The data show that for each sequential diuron application, highest concentrations were found following the Roads and Highways Department application followed by the Parks and Recreation Department application, and then by the London Underground application. This order copies that of the percentage application loss data described above.

The peak and event mean diuron concentration data for the Parks and Recreation and London Underground applications were comparable with the equivalent data for simazine and atrazine which were known to have been applied to the urbanised catchment (Tables 7-8 and 7-9). Of the three storm events that were monitored subsequent to the Parks and Recreation Department's application, events JD106 and JD119 were composed mainly of urban runoff whereas event JD122 was composed of both agricultural and urban runoff. The comparison of the diuron load and corresponding concentration data for the JD106 and JD122 events show that the extra dilution provided by the additional agricultural runoff during the JD122 event, significantly reduced the peak and event mean diuron concentrations of this event with respect to the JD106 event. Thus, 242,600µg of diuron was transported during the JD106 event which had peak and event mean concentrations of 1.06µg/l and 0.66µg/l respectively; whereas 382,868µg of diuron was transported during the JD122 event but the peak and event mean concentrations were 0.25µg/l and 0.11µg/l respectively.

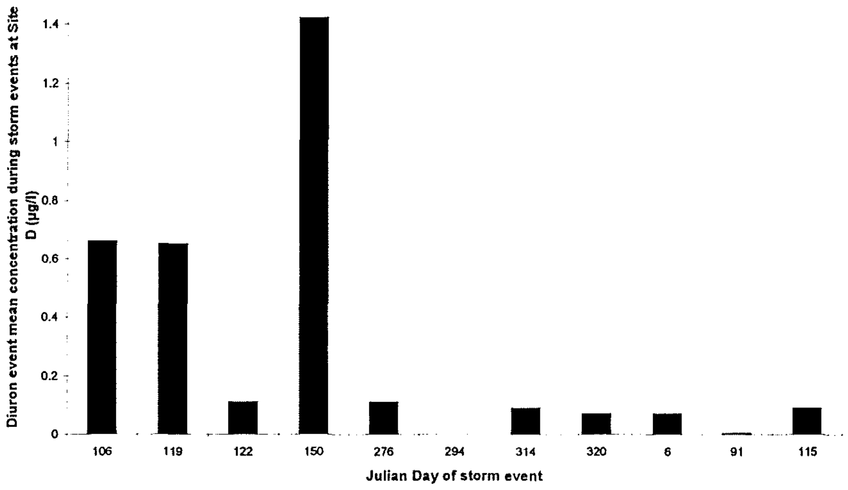

Figure 7-40 Diuron event mean concentrations during monitored storm events at Site D
[Peak concentration during storm event 150 divided by a factor of 100]

The peak and event mean diuron concentrations obtained for the first storm event to occur after the diuron application made by the Roads and Highways Department, were 238.39µg/l and 142µg/l respectively. These concentrations were the highest recorded, amongst all the pesticides monitored during the entire duration of the monitoring programme and together with the percentage application loss value of 45.1%, illustrate the efficiency and rapidity with which a herbicide applied to a hard-surface can be transported during a storm event. The diuron peak and event mean concentrations in the next monitored storm event on 2/10/92 (JD276) were considerably lower at 0.96μg/l and 0.11μg/l respectively. The nature of the kerbstones and concrete paving slabs to which the diuron was applied, would have presented a minimum retention relative to a soil substrate. Therefore, the majority of available diuron that was present prior to the JD150 event was probably transported during the JD150 event leaving a relatively minor diuron residue available for transport in subsequent storm events.

CHAPTER EIGHT

8. Pesticide fate, prediction and protection of receiving waters

This chapter begins with an overview of the behaviour of pesticides applied to the agricultural sub-catchment and urbanised catchment. Differences in behaviour are identified and discussed in terms of persistence in runoff, application loss, and impact on receiving surface waters. The chapter proceeds with an investigation of the modelling of the runoff data produced during the monitoring programme, using approaches based on chemical fugacity and multi-linear regression analysis. Where appropriate, comparisons are made with modelling exercises carried out on data from similar catchment runoff experiments. The chapter concludes with an examination of the methods available for reducing pesticide use, and for lessening the impact of pesticide use on receiving waters.

8.1 Comparison of pesticide fate and transport in the agricultural and urban environments

This section compares and contrasts the observed behaviours of pesticides applied to the agricultural sub-catchment and the urbanised catchment at North Weald. Only those pesticides that could be specifically identified to either of the catchments, with known application rates and application dates, have been examined. Therefore, with respect to the agricultural sub-catchment, this included data for chlorotoluron, isoproturon and simazine following their applications to soil sown for arable crops; for the urbanised catchment the relevant pesticide data was for the diuron applications made by the Parks and Recreation Department, the Roads and Highways Department and the London Underground. Although a number of other pesticides were determined at Site D, including atrazine, simazine, isoproturon and chlorotoluron, only diuron was known to be specifically applied to the urbanised catchment. In the cases of other pesticides, it was considered very likely that both catchments were probable sources and therefore comparison of data determined at Sites A and D would have been meaningless.

8.1.1 Persistence in event runoff of pesticides applied to the agricultural sub-catchment and urbanised catchment

Figure 8-1 shows the persistence in event runoff of pesticides applied to the agricultural sub-catchment and urbanised catchment during the period of the monitoring programme. The data were taken from Tables 6-7 and 7-7 (see Sections 6.4 and 7.6 respectively). In this instance, 'persistence in event runoff' (PER) refers to the period between pesticide application and the date of the last detection of the pesticide in storm-event runoff, rather than the persistence in soil. As previously discussed in Section 3.0, the general meaning of 'persistence' in the *literature* refers to the period of time that a pesticide remains present at the site of application. This normally applies to a soil profile and is a balance between the rate at which a pesticide is degraded on-site and the rate at which the pesticide is removed off-site by various transport processes including, for example, volatilisation and transport in storm event runoff.

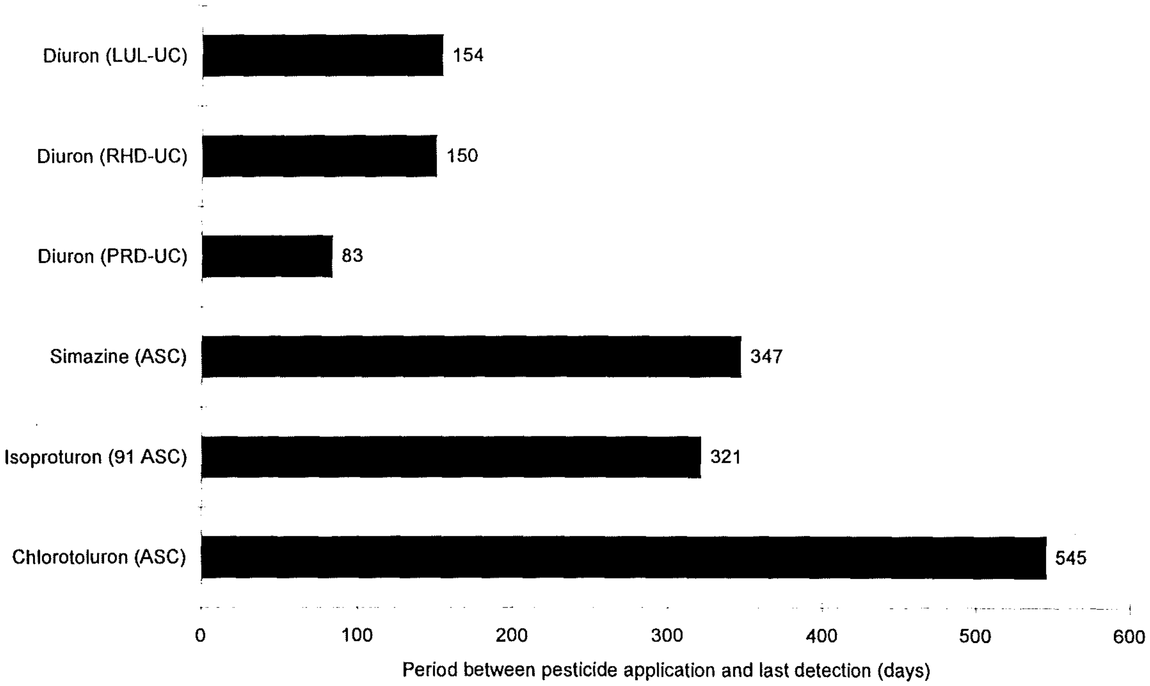

Figure 8-1 Persistence in event runoff of pesticides applied to the agricultural sub-catchment and urbanised catchment [LUL-UC: diuron application made by London Underground; RHD-UC: diuron application made by Roads and Highways Department; PRD-UC: diuron application made by Parks and Recreation Department; ASC: application to agricultural sub-catchment; Isoproturon (91 ASC): isoproturon application made to agricultural sub-catchment in autumn 1991], [Numbers on bars refer to persistence in event runoff]

For the diuron application (0.083kg) made by the Parks and Recreation Department, the PER value shown of 83 days is likely to be an underestimate of the true value. The herbicide was applied during the week ending 8/2/92 and the PER value related to the period up to the detection during the storm event on 1/5/92 (JD122). However, diuron was also detected during the following storm event on 29/5/92, which was largely the result of the diuron application (0.800kg) by the Roads and Highways Department on 5/5/92. It was unlikely that the Parks and Recreation Department's diuron application had fully degraded by the time of the storm event on 29/5/92 and it was probable that the source of the diuron detected on 29/5/92 was in part the result of the Parks and Recreation application as well as that of the Roads and Highways Department. Obviously due to the more recent and larger diuron application, it was impossible to quantify the amount of diuron that was residual from the Parks and Recreation Department's application. Therefore, the true PER value may well be similar to that found for the other diuron applications in the urbanised catchment.

Of the two isoproturon applications, only that of autumn 1991 was considered in terms of persistence in event runoff. This was because for the spring 1993 application, the last storm event to be monitored occurred 81 days after that date and, based on the persistence of the autumn 1991 application, it was very likely that residues from this application would have persisted in event runoff beyond 81 days. For this reason the value would not have been representative.

The values given in Figure 8-1 show that the simazine, chlorotoluron and isoproturon applied to the agricultural sub-catchment persisted significantly longer in event runoff than the three diuron applications made to the urbanised catchment. It should be noted that the values should be treated with a degree of caution since the four pesticides were applied on different dates and were therefore subject to different meteorological conditions. For the agricultural sub-catchment, the persistence in event runoff of simazine, isoproturon and chlorotoluron was in the same order as their respective soil half-life values of 70-110 days, 20-46 days and 135-143 days (see Table 4-2, Section 4.4.1). The chlorotoluron appeared to persist in event runoff approximately 35% longer than simazine which was in exact concurrence with the mean of their respective half-lives. Although the persistence in event runoff of isoproturon was less than that of simazine and chlorotoluron, it was not at the level which would have been inferred from their respective half-lives. This may have been due to the drier-than-average 1991 winter/spring period which may have decreased the rate of biodegradation of isoproturon more than that of simazine and chlorotoluron, due to its possible application to a drier location of the agricultural sub-catchment. Nicholls *et al* (1993) reported that increasing the soil moisture content from 40% to 100% with respect to field capacity produced a five-fold increase in isoproturon degradation.

The relatively low persistence of diuron at the sites of application and subsequently in event runoff, would have been determined by a combination of *in situ* degradation loss and loss by off-site transport. In terms of soil half-life, the diuron applied to the urbanised catchment would have been expected to persist in event runoff for a similar period to that exhibited by simazine. However, as the type of surface to which the diuron was applied became characterised by hard-surfaces, the more it would become devoid of organic matter and impervious (see Section 7.6.5). This would apply particularly to the diuron application made by the Roads and Highways Department to roadside kerbstones. In the absence of organic matter, it was probable that photolysis and hydrolysis would become the dominant application-site loss mechanisms in place of biochemical degradation. Further, the substrate retention would have decreased and become untypical of that inferred from a soil-based application. This agrees with the work of González-Pradas *et al* (1994) who, from an experiment on the variation of diuron sorption on organic matter amended calcareous soils, reported that a reduction in the organic matter content from 1.66% to 0.18% subsequently reduced the diuron K_d value from 37 to 2.2.

Little work has been reported in the literature on the rate of diuron hydrolysis and photolysis. Montgomery (1990) reported the hydrolysis half-life of diuron in natural waters to be approximately 150 days and Jirkovský *et al* (1997) determined the half-life of diuron in aqueous solution to be 231 days. In addition, Durand *et al* (1990) have reported that the photolysis of diuron in aqueous solution was quenched by the presence of chloride ions. Jirkovský *et al* (1997) also reported the photolysis kinetics for diuron coated onto different grade sands, clays and iron (III) oxide that were continually exposed to a 400 Watt mercury arc lamp (λ >290nm) whilst contained in a rotating round-bottomed flask. A half-life value of 22 hours was found for natural sand (particle size 150-200μm) and of 96 hours for ground sand (particle size <50 μm); a value of 100 hours was found for montmorillonite and a value of 200 hours for kaolin; on iron (III) oxide the rate of transformation was reported as 'extremely slow, just detectable after 100 hours'. The longer half-life of kaolin compared to montmorillonite was attributed to the light absorption of the iron (III) content. As a crude estimation, in the absence of further data, it can be assumed that the photolysis half-life of diuron applied to a concrete or tarmacadam hard-surface, may be within the range of values found by Jirkovský *et al* (1997).

Relating the photolysis rate induced by a mercury lamp to environmental photolysis conditions depends on a number of factors including the distance from the sun, altitude of the sun, the length of the day and the level of cloud cover. Based on the work of Jirkovský *et al* (1997), as an approximate estimation, during the spring and summer period of the monitoring programme it can be assumed that the average period of sunshine was approximately five hours per day which would equate to a photolysis half-life value in the range of approximately 4 to 40 days based on the data described above (values derived by relating the range of half-life data to the hours of daily sunshine) . However, Shaw (1991) has estimated that the average net solar energy varies from 40 Wm^{-2} in July to -120 Wm^{-2} in January for European latitudes. Therefore, assuming a linear relationship between light intensity and photolysis rate (Wolfe *et al*, 1990), the photolysis half-life of diuron applied to a hard surface during the spring/summer period of the monitoring programme would have been between 40 and 400 days (values derived through taking into account the relative energy [watts] of the mercury lamp compared to solar energy.

This wide range for the estimated half-life of diuron photolysis probably also takes into account the overall half-life for diuron persistence when applied to the various substrates of the urbanised catchment. The degree of hydrolysis would depend on the specific characteristics of the urban environment. On a hard surface, hydrolysis would only be expected to occur during a storm event as at other the times rainfall rapidly drains away leaving a dry surface. Alternatively, a gravel or ballast substrate would retain moisture for a longer period and ensure aqueous hydrolysis was more significant. Photolysis was more likely to act continually and be more significant on flat hard surfaces that offered little protection from the solar energy of the sun compared to the more angular surface of gravel or ballast.

As the application substrate became more characteristic of a hard-surface, the progressive absence of organic matter combined with lower infiltration would have greatly reduced the opportunity for diuron to be partitioned and partially retained by the application substrate. This, as well as affecting the mechanism of on-site degradation, would have also affected the magnitude of loss in surface runoff. Considering that the level of diuron retention and partition on application substrates with hard-surface characteristics would have been minimal, it was probable that the majority of diuron present at the onset of a storm event would have been available for removal in the event runoff. This contrasts with a soil-based application substrate, where for phenylurea and triazine herbicides, only the pesticide present in the soil water would be available for off-site transport in storm event runoff. Following the storm event, soil-water/soil-particle re-equilibration would have recharged the soil-water pesticide concentration.

In summary, the behaviour of diuron in runoff when applied to a hard surface in the urbanised catchment was dependent on *in situ* degradation, most probably by hydrolysis and photolysis, and off-site removal by transport in storm event runoff. It was possible that the hard-surface degradation half-life was similar to the soil half-life, though the dominant degradation mechanisms were likely to be different. The absence of organic matter and pervious surfaces would have significantly restricted opportunities for retention on the application substrate. It was therefore probable that the bulk of the diuron application residue would have been removed in the runoff of the first post-application storm event. The timing of the rainfall event would in most instances, have been on a significantly shorter time scale than that relating to the *in situ* degradation. Therefore, in general the persistence of a pesticide applied to a hard-surface substrate, as opposed to a soil substrate, would be critically dependent on the timing of post application rainfall rather than on the degradation kinetics at the site of application. It is plausible that as the nature of the urban substrate was more soil-like (i.e. gravel) then the substrate retention would have become more significant and persistence in storm event runoff would have become more prolonged.

8.1.2 Total percentage application loss of pesticides applied to the agricultural sub-catchment and urbanised catchment

Figure 8-2 shows the total percentage application loss of pesticides applied to the agricultural sub-catchment and urbanised catchment during the monitoring period. The data were taken from Tables 6-8 and 7-7 (see Sections 6.4 and 7.6 respectively). Total percentage application loss refers to the summation of the pesticide loads determined in each monitored event with regard to the amount of pesticide originally applied. For the reasons already discussed in relation to pesticide persistence in storm event runoff, the value stated in Figure 8-2 for the Parks and Recreation Department's application (4.03%) may have been an under-estimation and the true value may have been slightly higher. The isoproturon runoff data for the 1991 and 1993 applications are shown in Figure 8-2. For the spring 1993 application, the true isoproturon percentage loss value was probably higher than that given, since residues from the application would also have been detected in storm events following the last monitored storm event in the agricultural sub-catchment on 25/4/93 (JD115).

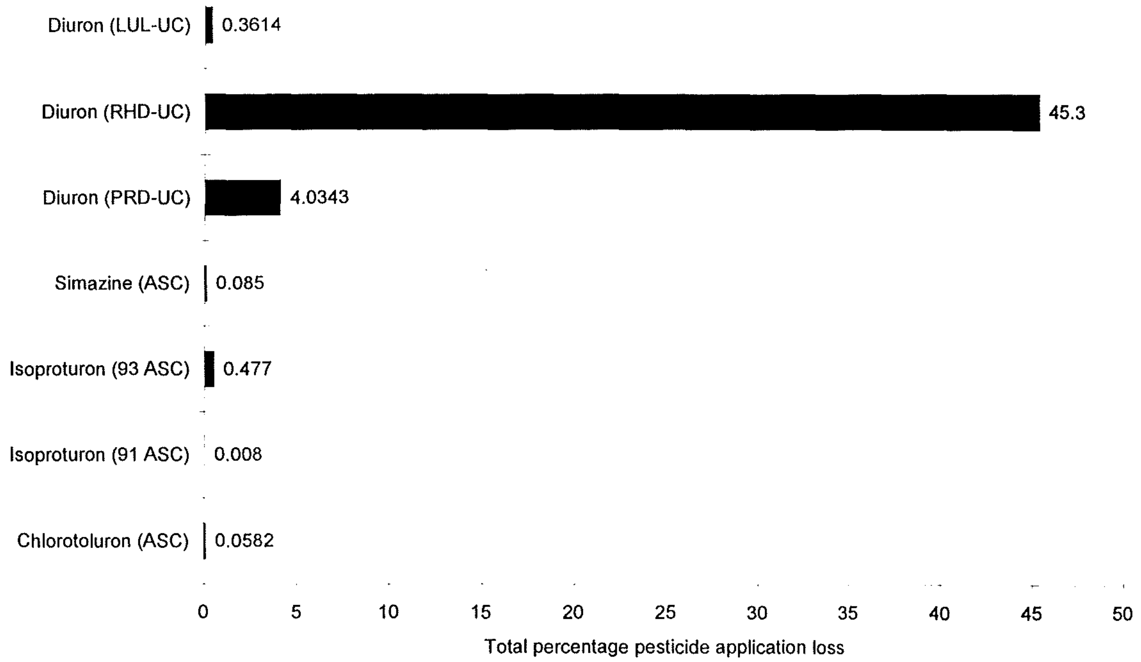

Figure 8-2 Total percentage application loss of pesticides applied to the agricultural sub-catchment and urbanised catchment [Isoproturon (93 ASC): isoproturon application made in spring 1993; Isoproturon (91 ASC): isoproturon application made in autumn 1991, for other codes see Figure 8-1, values on bars represent total application loss]

Generally, the data in Figure 8-2 show that the simazine, chlorotoluron and isoproturon applications made to the agricultural sub-catchment demonstrated lower levels of application loss compared to the diuron applications made to the urbanised catchment. This was despite the fact that approximately a hundred times more pesticide was applied to the agricultural sub-catchment. The application loss values are not directly comparable as the four pesticides were applied on different dates and were therefore subject to different meteorological conditions. Within the agricultural sub-catchment, the differences between the two isoproturon applications essentially showed the importance of the period between application and the occurrence of the first post-application storm event. This has been fully discussed in Section 6.4.2 and is only briefly referred to here. Because of the lower-than-average rainfall after the autumn 1991 application, the first significant runoff to be sampled did not occur until 1/5/92 (JD122) which was six months after the application. During this period the bulk of the isoproturon application probably degraded *in situ*. However, for the spring 1993 isoproturon application, the first post-application storm event, which was also sampled, occurred within eight weeks of the application. As a consequence, the total of the monitored losses for the spring 1993 isoproturon application was approximately sixty times greater than that for the autumn 1991 application (Figure 8-2).

The highest application loss found within the agricultural sub-catchment (0.477%) was for the spring 1993 isoproturon application. In terms of pesticide losses in runoff from agricultural catchment applications, this value was higher than most values reported in the literature for similar experiments carried out in the UK. For example, it was approximately twenty-six times greater than that determined for a similar experiment carried out on isoproturon losses from the clay-soil-based catchment at Rosemaund Farm (Williams *et al*, 1995). However, compared to the magnitude of diuron losses from the urbanised catchment it was relatively insignificant. It was two orders of magnitude lower than the highest diuron application loss value of 45.1% (for the application made by the Roads and Highways Department) and one order of magnitude lower than the second-highest diuron application loss value of 4.0343% (for the Parks and Recreation Department's application). There was however, equivalence with the loss from the London Underground application (0.3614%).

The significantly higher losses from applications made to the urbanised catchment were probably a feature of the hard surface content of the catchment's substrate compared to the soil substrate of the agricultural applications. With minimal substrate retention, once applied, the diuron would have started degrading, but at any time would have been largely free to be transported off-site in the runoff of the first post-application storm event to occur. The order of diuron application loss relative to each application, was probably a reflection of the type of surface to which the diuron was applied, in conjunction with favourable surface hydrology, which would have facilitated the rapid movement of runoff to the main watercourse. The highest loss, resulting from the Roads and Highways Department's application, was made to concrete kerbstones located adjacent to entries to the storm sewer network connected to the water course. As previously described, this classic hard surface would have afforded the minimum of retention and infiltration and would have rapidly moved diuron-bearing surface water to the nearest roadside drain and hence to the main watercourse. The diuron application made by the Parks and Recreation Department was probably made to a range of surfaces including soil, concrete and tarmac, and would have exposed the diuron to more opportunities for retention and infiltration (Section 7.6.5). Overall this would have produced lower application loss levels than expected from a total hard-surface application but higher than that anticipated from a soil substrate application.

The diuron application loss from the London Underground application on 29/10/92 (JD303) was comparable with that of the spring 1993 isoproturon application to the agricultural sub-catchment despite the fact that approximately eighty times more isoproturon was applied (see Figure 8-2; Table 7-1). As discussed in Section 7.6.5, due to sampler malfunction, a storm event which occurred four days after the London Underground application (see Figure 5-7) was not sampled, therefore it was possible that the absence of a removed load from this event would have lowered the overall application loss value. Further, it was likely that rain falling onto the railway track would have rapidly infiltrated downwards via soakaways into the groundwater and that the volume of contaminated surface runoff would have been relatively minimal compared to the volume of contaminated infiltrating rainwater (see Section 7.6.5). If this had not travelled downwards, it could have produced a significant diuron load in the surface runoff of post application storm events.

8.1.3 Peak and event mean concentrations of pesticides applied to the agricultural sub-catchment and urbanised catchment

Figure 8-3 shows the peak and maximum event mean concentrations of pesticides monitored in runoff from to the agricultural sub-catchment and urbanised catchments during storm events. These data were extracted from Tables 6.7, 6.9, 7.8 and 7.9 (see Sections 6.4 and 7-6). The event mean concentration refers to the total pesticide load transported during a given period divided by the runoff volume over the same period; it can be significantly different from the peak concentration since it is dependent on the timing of the peak concentration relative to the peak runoff. Table 8-1 shows the peak and maximum event mean pesticide concentrations together with associated application and fate data.

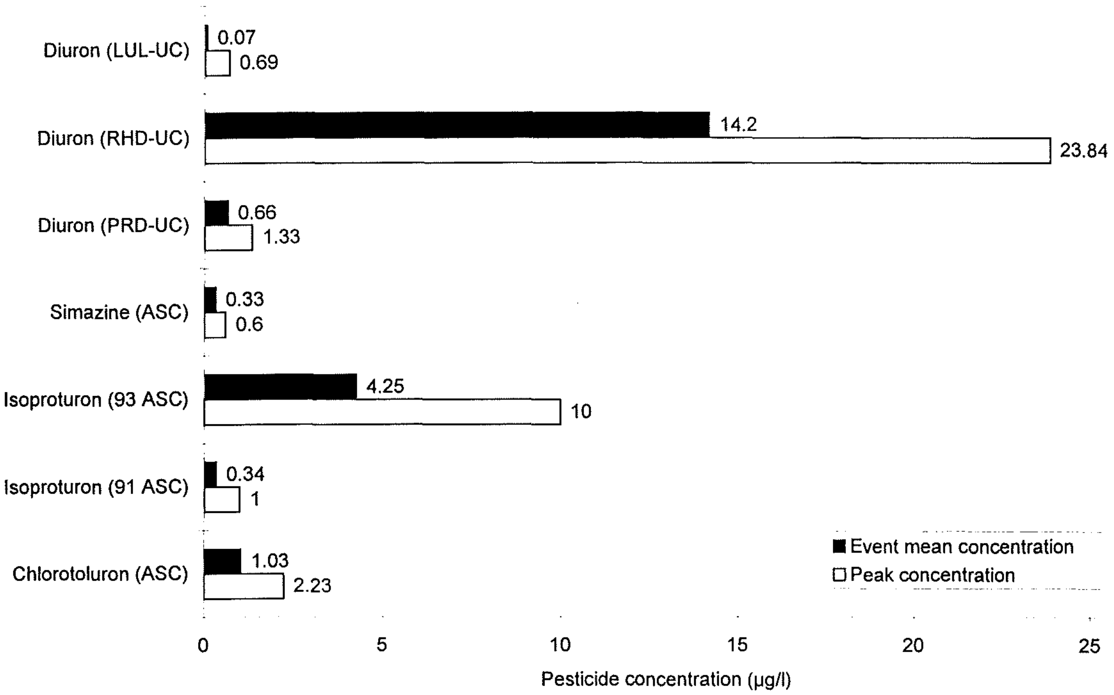

Figure 8-3 Peak and event mean concentrations of pesticides monitored in runoff from the agricultural sub-catchment and urbanised catchments [Data for diuron (RHD-UC) divided by factor of ten; values on bars represent concentration]

The data in Figure 8-3 are dominated by the concentrations relating to the Roads and Highways Department's diuron application, (RHD-UC). Comparisons between the two catchment types are somewhat obscured by the different degradation and retention characteristics of the herbicides that were applied at different times. However, overall the data show that the diuron applications made to the urbanised catchment produced peak and maximum event mean concentration data that were equal to and greater than those originating from the agricultural sub-catchment. This was despite their applications in quantities that were approximately two orders of magnitude lower than those applied to the agricultural sub-catchment. It is suggested that the principal factor that influenced the fate in surface waters of pesticides applied to the catchment as a whole, was the extent to which the application substrates were characterised by impervious hard-surfaces.

Table 8-1 Maximum event mean concentrations of pesticides applied to the agricultural sub-catchment and urbanised catchment with associated application and fate data

Pesticide	Amount applied (kg)	Soil Half-life $t_{1/2}$ (days)	K_{oc}	Time to event from application	Max emc (μg/l)	Max conc (μg/l)
Simazine	9.027	60	130	308	0.33	0.6
Isoproturon (1991)	60.78	25	107	117	0.34	1.00
Isoproturon (1993)	39.692	25	107	65#, 57*	4.25	10
Chlorotoluron	78.330	140	206	378	1.03	2.23
Diuron (LUL)	0.461	90	288	17	0.07	0.69
Diuron (RHD)	0.867	90	288	24	142	238.4
Diuron (PRD)	0.083	90	288	80	0.66	1.33

Isoproturon (1991): autumn 1991 application; Isoproturon (1993): spring 1993 application; pesticides shown in italics applied to agricultural sub-catchment, those not shown in italics applied to urbanised catchment; Max emc: maximum event mean concentration; Max conc: maximum concentration; #: for max emc; *: for peak conc

This effect is most clearly illustrated by comparing the Roads and Highway Department's diuron application within the urbanised catchment with the spring 1993 isoproturon application to the agricultural sub-catchment (Table 8-1). Although the amount of isoproturon applied was forty-five times that of diuron, the first post-application storm event produced a peak diuron concentration that was over twenty-three times higher and an event mean concentration that was thirty-three times higher. Although this is not an absolute comparison since the periods between application and the storm events were different and the half-lives of the two pesticides were different, the effect of an application to an impervious hard-surfaced substrate with low organic matter content compared to a pervious soil substrate with relatively high organic matter content is clearly demonstrated. This behaviour agrees with the data shown in Figure 8-2 which show that generally the post-application losses of pesticide applications made to the urbanised catchment were much higher than those made to the agricultural sub-catchment, and therefore would have subsequently lead to higher runoff concentrations. In principle, the observed behaviour of pesticides applied to the urbanised and agricultural sub-catchment concurs with the work of Kreuger and Törnqvist (1998). These workers carried out a multiple-regression analysis of pesticide application quantity, concentration, physico-chemical and fate data from a discrete surface water monitoring survey carried out within a small agricultural catchment ($9km^2$) in southern Sweden. They found that the key variable that determined mean concentration in streamflow for each pesticide was the quantity of pesticide originally applied to the catchment. In the North Weald catchment, this factor would also have generally explained the magnitude of pesticide concentrations. However, in the case of an urbanised catchment a further factor would have been required that expressed the availability for transport in runoff of a pesticide based on the retention characteristics of the application substrates involved. For example, in terms of availability for transport in runoff, this would equate to 10kg of soil-applied pesticide to 100 grammes of hard-surface-applied pesticide due to the significantly lower pesticide retention characteristics of the latter substrate.

Another factor that would have led to higher peak concentrations in the urbanised catchment compared to the agricultural sub-catchment, for a given amount of pesticide application, was the hydraulic route of the runoff water. The rapid response to rainfall of a hard surface would have delivered the pesticide-bearing runoff to the main water course at a time prior to the peak runoff, thus tending to increase the observed concentration of the diuron in the watercourse at that time. Once the whole catchment had responded to the rainfall, the concentration would have experienced a dilution exhaustion effect (Ellis and Revitt, 1991) and consequently decreased during the period of the main hydrograph-peak. An example of this effect can be seen in Figure 7-14.

In summary, the underlying factor that differentiated the behaviour of pesticides applied to the agricultural sub-catchment and the urbanised catchment, as illustrated in Figures 8-1, 8-2 and 8-3, was the level of pesticide retention by the application substrate. Those substrates with the highest level of hard-surface character possessed the lowest degree of retention which led to the highest post-application losses, the largest peak concentrations and event mean concentrations and the lowest period of persistence in storm event runoff.

8.2 Pesticide transport modelling

As initially discussed in Section 3.2, the requirement to predict the behaviour of pesticides in the environment is essentially driven by the excessive costs of running extensive field trial monitoring programmes and also the need to understand the fate of a pesticide after application to a substrate in the environment. Modelling also enables the estimation of the probability of adverse effects on the environment, including surface and groundwater contamination (Wagnet and Rao, 1990). Computer models attempt to simulate the real world and hence the behaviour of a pesticide. Generally there are two approaches to modelling—statistical and deterministic (Gustafson, 1995). The statistical approach, which tends to be site specific, may involve the analysis of an experimental data-set and the identification of the dominant independent variables, for example rainfall intensity, that determine the key dependent variable such as event mean concentration. For the deterministic approach, the prediction of pesticide fate is based on the simulation of the physical and chemical processes that affect the fate of the pesticide in the application environment. A relatively large amount of data specific to the pesticide is required such as the meteorology and the application site details. This section examines both modelling approaches. The deterministic method adopted is based on the concept of pesticide fugacity and the statistical procedure is based on the use of multi-linear regression analysis.

8.2.1 Modelling pesticide movement in runoff using SoilFug

The following text provides a brief description of the principles behind chemical fugacity environmental modelling and the SoilFug model. A more detailed discussion on this modelling approach is given by Mackay (1991) who pioneered the application of fugacity to environmental modelling and Di Guardo *et al* (1994) who designed the fugacity-based SoilFug model which operates in the Windows™ PC operating system.

Fugacity is a thermodynamic function which can be thought of as the escaping tendency of a pesticide, which will move from one phase to another in an attempt to establish an equal fugacity in both phases. For each compartment of the environment a fugacity capacity can be defined, which measures how much fugacity a phase can hold. Fugacity capacities are derived from partition coefficients based on the solubility of a pesticide in air, water and octanol (used to represent the organic phases of the environment). The fugacity depends on the properties of the chemical as well as on the properties of the environment. The ratio of two values for different phases gives the partition coefficient between the two phases. This simplifies the calculations as only one value per phase is needed rather than partition coefficients between all pairs of phases.

Fugacity (f), with units of pressure, is considered as the measure of a pesticide's tendency to escape from one medium, until it is in equilibrium with adjoining media. Fugacity is equivalent to partial pressures within ideal gases and at low pressures can be considered as representative of the real environment. Fugacity is related to concentration by the equation $C = Z\ f$, where Z is the fugacity capacity. The concept of fugacity has been related to heat capacity by the following analogy;

HEAT CONCENTRATION (J m^{-3}) = HEAT CAPACITY (J m^{-3} K^{-1}) X TEMPERATURE (K)
CONCENTRATION (mol m^{-3}) = FUGACITY CAPACITY (mol m^{-3} Pa^{-1}) X FUGACITY (Pa)

Mackay (1991) combined the use of fugacity with the concept of the unit world, in which the environment is composed of a number of compartments each of which represents an environmental phase. It is assumed that each compartment is homogeneous and that the properties of the compartment, and the concentration of the chemical, are equivalent throughout the compartment.

A fugacity model can be applied with different levels of complexity depending on the process to be simulated. At the simplest level, a fixed amount of chemical is partitioned between the compartments of the model at equilibrium and no removal processes are considered. This approach is referred to as a Level I fugacity model and is the basis of the SoilFug model. The model considers the field environment to be made up of four compartments: soil air, soil water, organic matter and mineral matter. The depth of the soil is set to 50cm; this is considered to be the average depth which soil-water has to travel before reaching the field drainage system. Rainfall events are treated differently from the periods between events. During the 'before rain event' periods, which are treated the same as between event periods, only degradation and volatilisation operate; the runoff component is added to the 'during rain event' periods. During the 'before rain event' periods, the water content of the soil is considered to be equal to field capacity, which is a constant value and simplifies the calculations. For a rain event, the volume of water in the soil is increased by the rainfall and a new volume calculated with a maximum possible value equal to the total porosity of the soil so that the soil air volume is reduced to zero.

After application, the pesticide is partitioned between the different phases. For the period up to the first storm event, degradation and volatilisation are allowed to proceed. Degradation acts on the total soil volume and volatilisation is accounted for by diffusion through the soil air and the air layer above the soil. The amount of pesticide remaining at the end of this period is redistributed through the compartments of the system. During a rainfall period, the compartment volumes are recalculated as described above. In this case three process are allowed to act; degradation, volatilisation and runoff. With the onset of a storm event, the pesticide present in the soil water is flushed out of the soil profile and, together with the excess rainfall, travels to a drainage channel. The amount of pesticide removed by the runoff and the volume of soil water and excess rainfall leads to the calculation of a concentration in the drainage water and hence to a concentration in the stream which is the mean concentration for the storm event. The amount of pesticide remaining in the soil environment at the end of the storm event period is repartitioned amongst the environmental compartments and the cycle then begins again (see Figure 8-4).

In the following sub-sections, the SoilFug model has been used to predict the event mean concentrations of pesticides detected in storm-event runoff leaving the agricultural sub-catchment and the urbanised catchment. For the agricultural sub-catchment, this includes the autumn 1991 application of simazine, chlorotoluron and isoproturon and the spring 1993 application of isoproturon. The prediction of isoproturon concentrations is compared with that obtained from the Rosemaund catchment using the same modelling approach (Turnbull *et al*, 1995). For the urbanised catchment, the feasibility of using the model to predict the transport of diuron in urban runoff from hard surfaces, is examined.

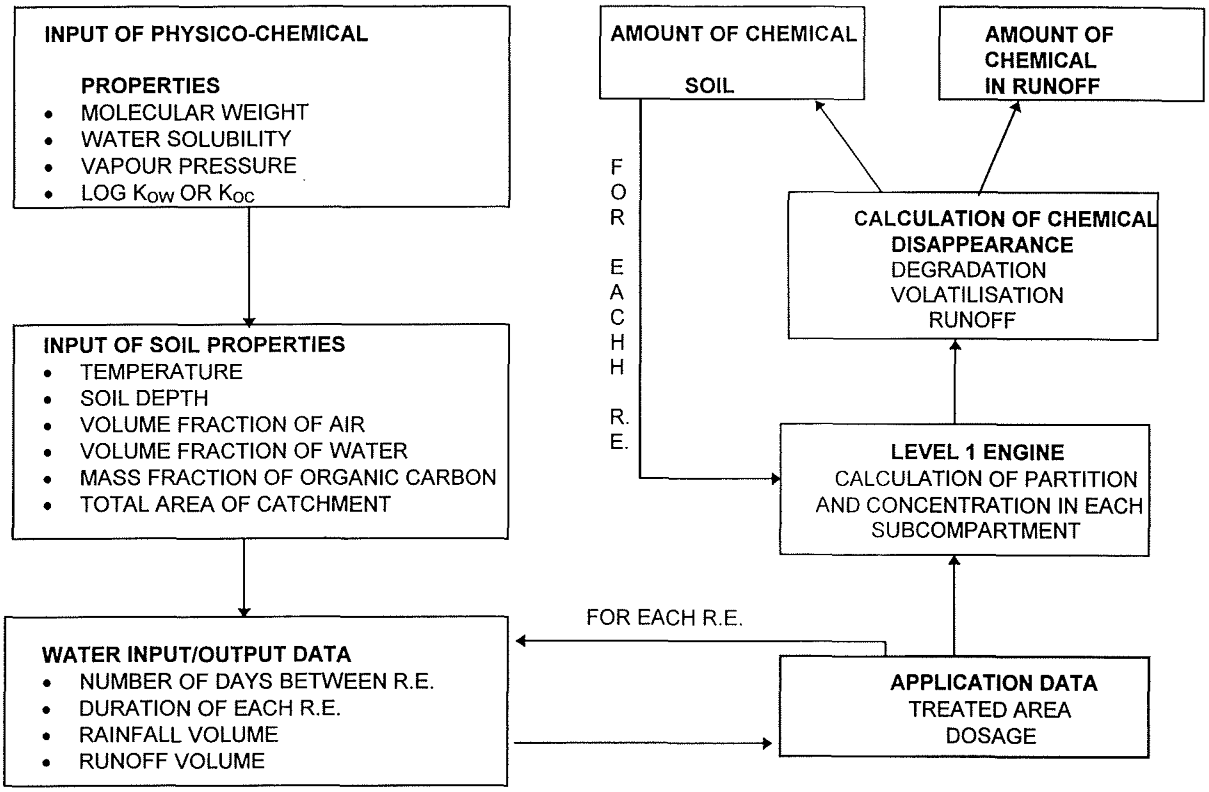

Figure 8-4 Schematic diagram of the SoilFug model (R.E. - rainfall event) [from DiGuardo et al, 1994]

8.2.2 Modelling of chlorotoluron transport in runoff from the agricultural sub-catchment using SoilFug

Table 8-2 shows the physico-chemical, environmental fate, catchment and application details used for modelling of the chlorotoluron. The chemical properties and some of the soil properties were obtained from Table 4-2; the soil data relating to depth, volume fraction of air and water at field capacity were obtained from Shaw (1991). The organic matter content of the soil of the agricultural sub-catchment was not directly measured. However, from the literature relating to similar pesticide runoff studies, a value of 4.5% which was determined as part of the work carried out at Brimstone Farm (Jones *et al*, 1995) was chosen. This choice was based on the fact that the soil survey of both sites identified similar soil series and also because both sites were under similar farm management. The chlorotoluron application data was taken from Table 6-2. The soil temperature was set at a typical value for soils for SE England although on investigation the model output was found to be relatively insensitive to soil temperature, presumably because of the low volatility of the pesticide.

Table 8-2 Physico-chemical, fate, catchment and application details for the autumn 1991 chlorotoluron application

Chemical Properties		
Molecular weight: 212.7	Aqueous solubility: 70 gm^{-3}	Vapour pressure: 1.7x10^{-6} Pa
Log K_{ow}: 2.29		
Soil Properties		
Soil half-life: 139 days	Catchment area: 160 ha	Soil temperature: 12 °C
Soil depth: 0.5 m	Diffusive depth of soil: 0.25 m	Volume fraction of air: 0.09
Volume fraction of water: 0.41	Mass fraction of organic carbon: 0.045	
Application data		
Area treated: 26.11 ha	Treatment rate: 3 kg/ha	Period before first event: 186 days

Table 8-3 shows the rainfall and runoff data used for the modelling exercise for each of the storm events following the autumn 1991 chlorotoluron application. As reported by Turnbull (1995), the allocation of the start and end of the storm events has a major effect on the runoff volume and subsequently the event mean concentration. Therefore, the runoff volume data shown refers to the value used to calculate the actual event mean concentration. The Table also shows the elapsed period between the chlorotoluron application and the occurrence of a given storm event. Table 8-4 and Figure 8-5 show the mean chlorotoluron concentrations predicted by the model and compare them with the measured event mean concentrations for each storm event.

Table 8-3 Rainfall and runoff volumes of the modelled storm events relating to the autumn 1991 chlorotoluron application

Event (Julian day)	Period from application (days)	Rainfall (mm)	Runoff (mm)	Event Julian day	Period from application (days)	Rainfall (mm)	Runoff (mm)
122	186	9.5	0.83	6	436	7.5	5.62
226	290	23.5	1.6	91	521	17.5	1.28
276	340	17.5	9.9	95	525	8	2.15
294	358	49.5	17.85	99	529	30.5	10.08
314	378	12	4	115	545	9.5	3.69
320	384	7.5	1.12				

In accordance with the guidelines relating to the level of model performance considered to be useful for surface water exposure assessment of plant protection products (Adriaanse *et al*, 1997), the SoilFug model was designed to simulate mean storm event pesticide concentrations to within one order of magnitude. Examination of Table 8-4 shows that the modelling results for every storm event except the first (JD122) fall within the range of one order of magnitude between measured and predicted data. Also the comparison of the real and modelled data shows that the SoilFug model over-predicted the mean chlorotoluron concentration for each storm event. Similar behaviour was observed from an exercise carried out on the pesticide runoff data produced from the Rosemaund catchment study (Di Guardo *et al*, 1994; Turnbull *et al*, 1995). The tendency of the model to over-predict mean pesticide concentrations was considered to be a useful feature, given that the model was designed to be a screening tool and that, when used to assess the risk of surface water contamination, the model would tend to provide a worse case scenario.

The measured event mean concentration for the first event on Julian Day 122 was significantly lower than the values of the immediately following storm events and was next matched during a storm event that occurred almost one year later on Julian day 91-1993. This phenomenon may have been the result of the temporal soil-sorption behaviour of chlorotoluron (see Section 6.4.2). The anomalously dry period between the chlorotoluron application and the first storm event would have allowed pesticide molecules to become bound to vacant sites on soil surfaces that were normally occupied by water molecules. After the first storm event on Julian Day 122, the general wetness of the agricultural sub-catchment would have increased and the influx of more polar water molecules would have displaced the sorbed chlorotoluron molecules into soil solution, thus leading to a higher mass of chlorotoluron available for transport in the following storm event. The SoilFug model does not take into account such temporal variation in the pesticide-soil sorption isotherm and therefore has predicted a higher mean chlorotoluron concentration for the first (Figure 8-5).

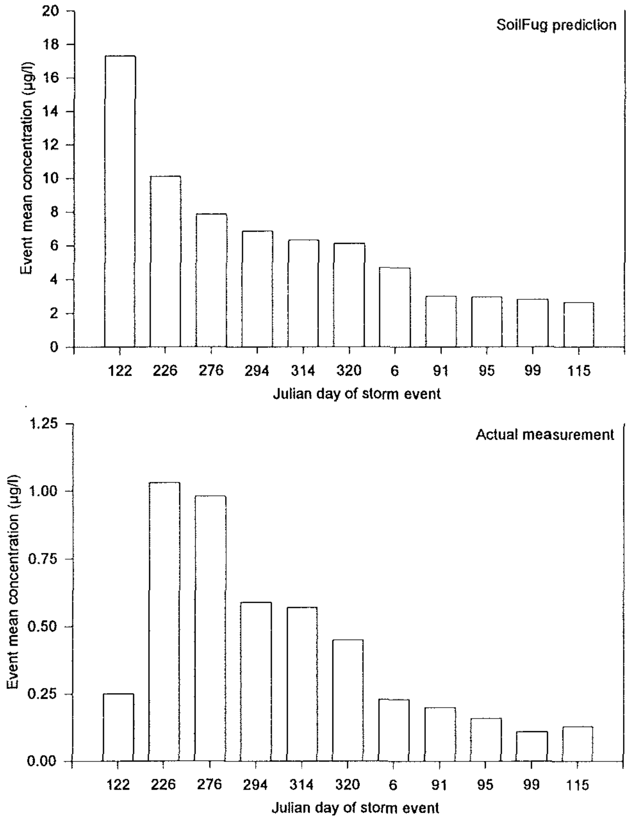

Figure 8-5 Comparison of SoilFug predictions to values of actual measured chlorotoluron event mean concentrations in runoff subsequent to the autumn 1991 application

Examination of the data in Table 8-4 also show that the extent of model over prediction appeared to increase with time. Pignetallo and Huang (1991) and Beck *et al* (1995) have found that the fraction of pesticide associated with restricted sites within the soil structure, increased with the period between application and sampling and thus increased the 'apparent' soil partition coefficient K_{app}. The SoilFug model has no provision for temporal changes in soil partition coefficient and therefore would have assumed that the temporal chlorotoluron distribution between soil and soil-water was constant. However, in practice the fraction of chlorotoluron present in soil-water would have decreased with time and the model would therefore have progressively over-predicted the mean storm event chlorotoluron concentration as the age of the chlorotoluron residue increased.

Table 8-4 Comparison of measured and modelled chlorotoluron event mean concentration data for the period of the monitoring programme

Storm event (Julian day)	Actual emc (µg/l)	SoilFug emc (µg/l)	Storm event (Julian day)	Actual emc (µg/l)	SoilFug emc (µg/l)
122	0.25	17.3	6	0.23	4.68
226	1.03	10.1	91	0.20	3.01
276	0.98	7.85	95	0.16	2.96
294	0.59	6.86	99	0.11	2.81
314	0.57	6.32	115	0.13	2.62
320	0.45	6.12			

emc; event mean concentration (µg/l)

8.2.3 Modelling of simazine event mean concentrations in runoff from the agricultural sub-catchment using SoilFug

Table 8-5 lists the physico-chemical, environmental fate, catchment and application details used for modelling simazine behaviour. The application data were taken from Table 6-2. Table 8-6 shows the rainfall and runoff data used for the modelling exercise and also the period between the simazine application and the occurrence of appropriate storm events. Table 8-7 and Figure 8-6 show the mean simazine concentrations predicted by the modelling exercise and compare these to the measured event mean concentrations for each storm event. As can be seen from Table 8-7, the agreement between the measured data and the modelled data was very good, with the exception of the data relating to the first event on Julian day JD122.

The modelled value for the first event was over five times greater than the measured value but was still within the 'one order of magnitude' guideline of Adriaanse *et al* (1997). As was found for chlorotoluron, the measured event mean simazine concentration for the first storm event was lower than that for the following event on Julian day 226, after which the event mean concentrations decreased progressively. The reason for this behaviour could again be explained by the initial association of simazine molecules with active sites on the soil surface. These were subsequently displaced by water molecules into the soil water as the catchment became wetter after first storm event, and consequently became available for transport in the runoff of the following event.

Table 8-5 Physico-chemical, fate, catchment and application details for the autumn 1991 simazine application

Chemical Properties		
Molecular weight: 201.7 Log Kow: 2.24	Aqueous solubility: 5 gm^{-3}	Vapour pressure: $810x10^{-9}$ Pa
Soil Properties		
Soil half-life: 60 days Soil depth: 0.5 m Volume fraction of water: 0.41	Catchment area: 160 ha Diffusive depth of soil: 0.25 m Mass fraction of organic carbon: 0.045	Soil temperature: 12 °C Volume fraction of air: 0.09
Application data		
Area treated: 7.85 ha	Treatment rate: 1.15 kg/ha	Period before first event: 155 days

Table 8-6 Rainfall and runoff volumes for the modelled storm events relating to the autumn 1991 simazine application

Event (Julian day)	Period from application (days)	Rainfall (mm)	Runoff (mm)
122	155	9.5	0.78
226	259	23.5	1.61
276	309	17.5	10.2
294	327	49.5	17.88
314	347	12	4.27

Table 8-7 Comparison of measured and modelled simazine event mean concentration data for the period after the autumn 1991 application

Event (Julian day)	Measured emc (µg/l)	SoilFug emc (µg/l)
122	0.21	1.21
226	0.33	0.35
276	0.2	0.19
294	0.1	0.15
314	0.07	0.12

To a much lower extent than for chlorotoluron, the results of the simazine modelling showed a tendency to over-predict the event mean concentration. This suggests that the effect of pesticide residue ageing upon the apparent soil partition coefficient was more significant for chlorotoluron than simazine and may be due to their differing organic carbon partition coefficient values of 175-206 and 130 respectively (Table 4-2).

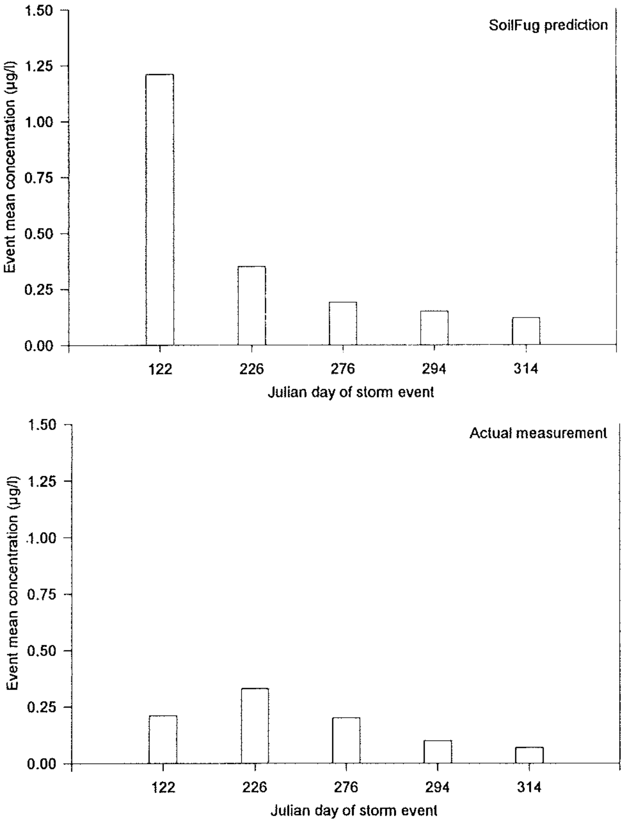

Figure 8-6 Comparison of SoilFug predictions with values of measured simazine event mean concentrations in runoff subsequent to the autumn 1991 application

As described by Di Guardo *et al* (1994), the SoilFug model was used to simulate the event mean concentrations of simazine residues determined in runoff from the Rosemaund catchment. In this case the model was used to predict the mean concentrations determined during storm events that occurred between 33 and 107 days after an application of 6.21kg of simazine. This compares to the North Weald data-set in which the determination was between 155 and 347 days after an application of 9.025kg of simazine. A good agreement was claimed between measured and modelled data for the Rosemaund catchment (Figure 8-7). The Rosemaund catchment had many similarities to the to the agricultural sub-catchment at North Weald in that it was of a similar area, 151ha compared to 160 ha, and was of a similar clay composition although the soil of the agricultural sub-catchment was heavier and had a higher organic matter content. Consequently both catchments possessed a similar soil hydrology which favoured surface runoff over infiltration to ground water.

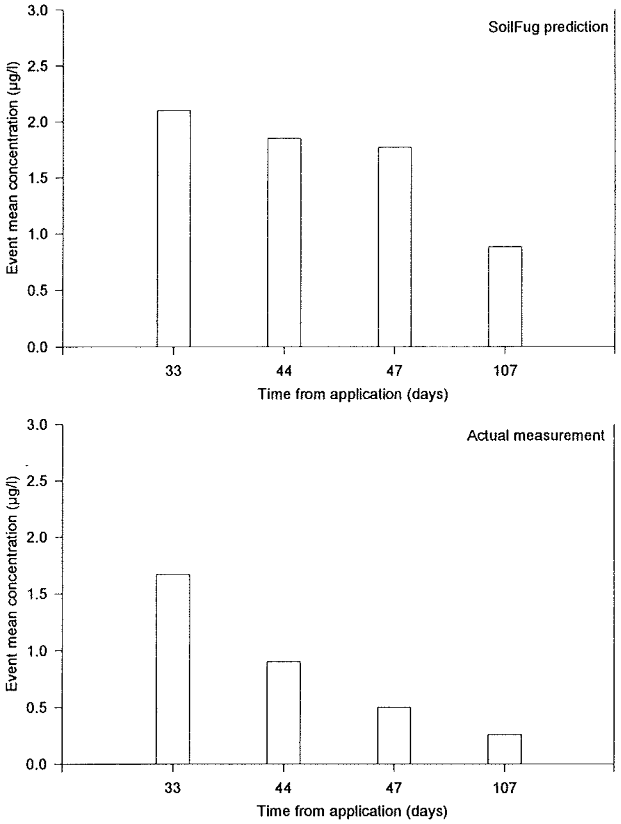

Figure 8-7 Comparison of SoilFug predictions with values of measured simazine event mean concentrations in runoff determined at the Rosemaund catchments (Di Guardo *et al*, 1994)

The similar performance of the model when applied to both catchments suggests that the estimated parameters for the North Weald catchment (soil half-life and soil organic-matter content) were in the correct range. Further, it suggests that the ability of the model to predict the aquatic fate of simazine applied to clay-soil catchments was transferable and adds credibility to the robustness and usefulness of the model.

8.2.4 Modelling of isoproturon event mean concentrations in runoff from the agricultural sub-catchment using SoilFug

The two isoproturon applications made to the North Weald agricultural sub-catchment in autumn 1991 and spring 1993, allow the performance of the SoilFug Model to be assessed on data-sets of different ages. The former data-set was obtained between 186 and 340 days after application and the latter between 57 and 81 days after application.

8.2.4.1 Autumn 1991 isoproturon application

Table 8-8 shows the physico-chemical, environmental fate, catchment and application details which have been used for the modelling of the isoproturon data-set.

Table 8-8 Physico-chemical, fate, catchment and application details for the autumn 1991 isoproturon application

Chemical Properties

Molecular weight: 206.3
Aqueous solubility: 55 gm^{-3}
Vapour pressure: 3.3×10^{-6} Pa
Log K_{ow}: 2.24

Soil Properties

Soil half-life: 55 days
Catchment area: 160 ha
Soil temperature: 12 °C
Soil depth: 0.5 m
Diffusive depth of soil: 0.25 m
Volume fraction of air: 0.09
Volume fraction of water: 0.41
Mass fraction of organic carbon: 0.045

Application data

Area treated: 45.2 ha
Treatment rate: 1.345 kg/ha
Period before first event: 177 days

The isoproturon application data was taken from Table 6-2. Table 8-9 shows the rainfall and runoff data used for the modelling exercise and also the period between the isoproturon application and the occurrence of a given storm event. Figure 8-8 and Table 8-10 show the event mean isoproturon concentrations predicted by SoilFug in comparison with the measured event mean concentrations for each storm event that occurred after the autumn 1991 application. The measure of fit between the measured and modelled data was reasonably good except for the data relating to the first event on JD122.

Table 8-9 Rainfall and runoff volumes for the modelled storm events relating to the autumn 1991 isoproturon application

Event (Julian day)	Period from application (days)	Rainfall (mm)	Runoff (mm)
122	186	9.5	0.80
226	290	23.5	1.61
276	340	17.5	9.9

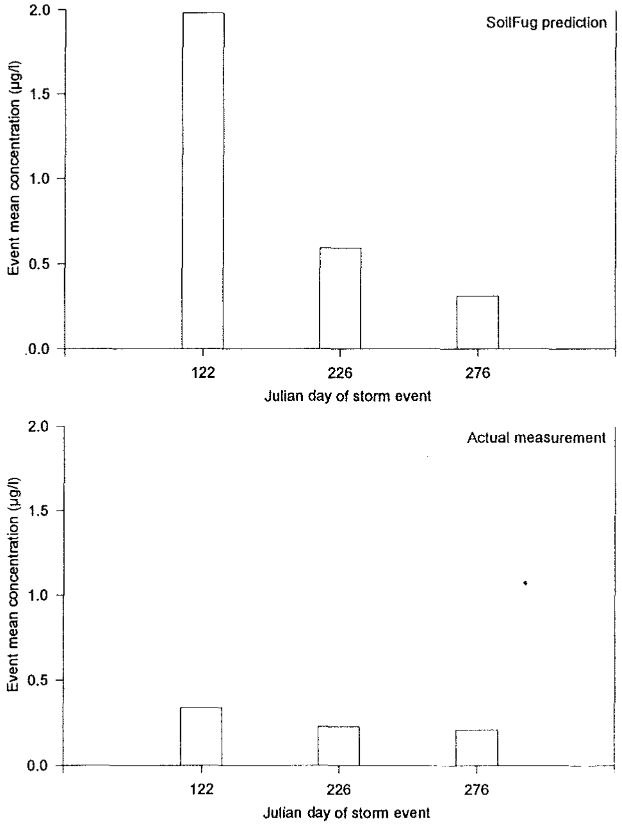

Figure 8-8 Comparison of SoilFug predictions to values of actual measured isoproturon event mean concentrations in runoff subsequent to the autumn 1991 application

Measured and modelled values for the first storm event were within one order of magnitude and for the following two events on Julian Days 226 and 276, the agreement was within a factor of 2.5. Again, the model showed a tendency to over-predict the mean pesticide concentration, especially in relation to the first storm event. Unlike the pattern of the measured data for chlorotoluron and simazine, the event mean concentration for the first isoproturon storm event was not significantly lower than that for the following events due to their association with active sites on the relatively dry soil. The isoproturon was applied at approximately the same time as the chlorotoluron and the simazine and would therefore have experienced the same meteorology and soil moisture regime. It is suggested that isoproturon was not susceptible to the same effect because of its lower K_{oc} value of 107 compared to 175-206 and 130 for chlorotoluron and simazine, respectively.

Table 8-10 Comparison of measured and modelled isoproturon event mean concentration data for the period after the autumn 1991 application

Event (Julian day)	Measured emc (µg/l)	SoilFug emc (µg/l)
122	0.34	1.98
226	0.23	0.59
276	0.21	0.31

8.2.4.2 Spring 1993 isoproturon application

Table 8-11 shows the physico-chemical, environmental fate, catchment and application details used for the modelling of the second isoproturon data-set relating to the spring 1993 application. Table 8-12 shows the rainfall and runoff data used and also the period between the isoproturon application and the occurrence of the storm events.

Table 8-11 Physico-chemical, fate, catchment and application details for the spring 1993 isoproturon application

Chemical Properties		
Molecular weight: 206.3 Log K_{ow}: 2.24	Aqueous solubility: 55 gm^{-3}	Vapour pressure: $3.3x10^{-6}$ Pa
Soil Properties		
Soil half-life: 55 days Soil depth: 0.5 m Volume fraction of water: 0.41	Catchment area: 160 ha Diffusive depth of soil: 0.25 m Mass fraction of organic carbon: 0.045	Soil temperature: 12 °C Volume fraction of air: 0.09
Application data		
Area treated: 23.61 ha	Treatment rate: 1.681 kg/ha	Period before first event: 57 days

Table 8-12 Rainfall and runoff volumes for the storm events relating to the spring 1993 isoproturon application

Event (Julian day)	Period from application (days)	Rainfall (mm)	Runoff (mm)
91	57	17.5	7.85
95	61	8	6.32
99	65	30.5	11.91
115	81	9.5	3.61

Figure 8-9 and Table 8-13 show the event mean isoproturon concentrations predicted by SoilFug in comparison with the measured event mean concentrations for each storm event. For each storm event the agreement between the measured and modelled data was good and within one order of magnitude.

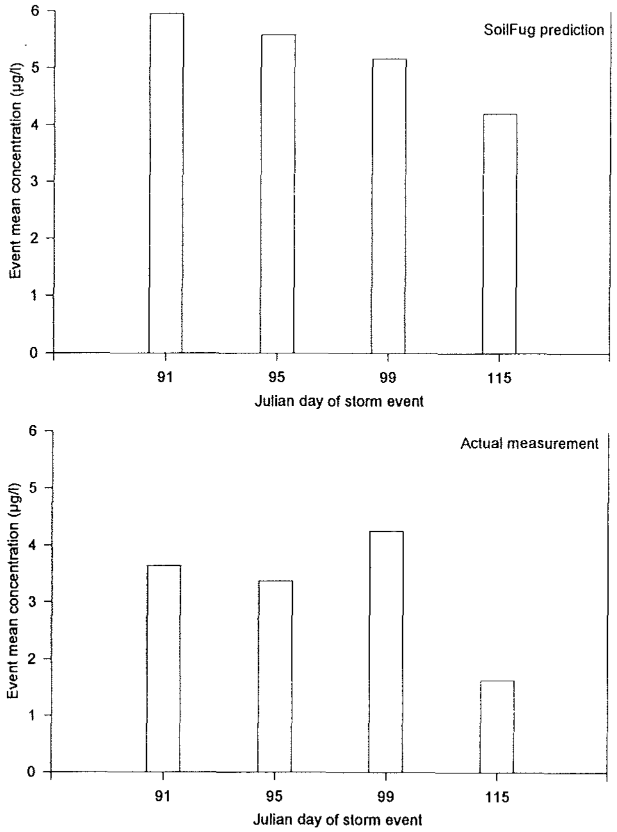

Figure 8-9 Comparison of SoilFug predictions to values of actual measured isoproturon event mean concentrations in runoff subsequent to the spring 1993 application

For the first three events the agreement was within a factor of 1.6 and for the fourth event within a factor of 2.5. Consistent with the previously modelled events, the model showed a tendency to over-predict the mean concentrations. In this case the average over-prediction was approximately 60% compared to 220% for the isoproturon events of autumn 1991.

Table 8-13 Comparison of measured and modelled isoproturon event mean concentration data for the period after the spring 1993 application

Event (Julian day)	Measured emc (µg/l)	Modelled emc (µg/l)
91	3.64	5.95
95	3.37	5.58
99	4.25	5.16
115	1.63	4.19

The design of the model involved a number of assumptions to aid its simplicity (Di Guardo *et al*, 1994), which could have induced systematic errors into the simulations that would have become more apparent as time proceeded. Therefore, the gradual increase in the level of over-prediction would be expected since the periods between pesticide application and events was approximately three times greater for the events subsequent to the autumn 1991 isoproturon application compared to the spring 1993 application.

The SoilFug model has been used to simulate the event mean concentrations of isoproturon residues determined in runoff from the Rosemaund catchment (Di Guardo *et al*, 1994b). However, the modelling exercise was not directly comparable with that for North Weald. This was because the model was applied to runoff data that was generated from up to three time-separated applications rather than a single application as was the case at North Weald. In addition, the catchment areas modelled were somewhat different from those of the agricultural sub-catchment at North Weald. Overall the level of fit between the SoilFug prediction and the measured data was good, with agreement generally within one order of magnitude. Interestingly, as the modelled area of the Rosemaund catchment decreased, so the prediction error appeared to increase. This may suggest that a scaling factor was present whereby local variations in, for example, soil hydrology and composition become more important as the modelled area was reduced. As a consequence the model results that were generated through computations based on average soil parameters could not match the variability of the monitored data. Conversely, as the area of the catchment increased, the effects of local variation would have been averaged out, producing runoff data that was closer to the prediction of the model.

The similar performance of the model for simazine and isoproturon when applied to both catchments suggests that the estimated parameters for the North Weald catchment (soil half-life and soil organic-matter content) were in the correct range. Further, it suggests that the ability of the model to predict the mean isoproturon concentration in storm event runoff to within one order of magnitude, was transferable and the results add further credibility to the robustness and usefulness of the model for assessing the risk to receiving waters near sites of application.

8.2.5 Modelling of diuron transport in the urbanised catchment using SoilFug

An attempt was made to use the SoilFug model to simulate the event mean concentrations of diuron in the runoff events subsequent to the application to roadside kerbstones in the urbanised catchment on 5/5/92 by the Road and Highway Department of Epping Forest Council. As described by Di Guardo *et al* (1994a), the operation of the model initially involves the defining of the physical volume and composition of the four soil phases—water, air, organic matter and mineral matter, and then allowing the pesticide to partition amongst the phases according to their respective fugacity capacities. Subsequent to the kerbstone diuron application, three storm events occurred in which residues from the application were considered to have been transported. These were the events on JD150, JD226 and JD276. The JD150 event was essentially made up of runoff from the hard-surface area of the urbanised catchment (14ha), whereas for events JD226 and JD276, the flow was composed of runoff from the entire 310ha of the North Weald catchment. Therefore, with respect to the requirements of the model, two soil environments were defined; the first for event JD150 and the second for events JD226 and JD276.

To use the SoilFug model to simulate the behaviour of a pesticide applied to a hard surface, the soil compartment had to be appropriately defined. Along with physico-chemical and application data, Table 8-14 shows the data used to emulate the hard surface environment for the JD150 event. A value of 1cm was chosen to represent the depth of the soil which was further defined as possessing a high volume fraction of air to mimic the direct exposure of the hard surface to the atmosphere. Since the composition of the hard-surface component of the urbanised catchment was essentially inorganic, a value of 0.1% was assigned to the organic matter content of the emulated soil environment. During the JD150 event, storm runoff was only generated from the hard-surface impervious areas of the urbanised catchment as the remaining areas of the urbanised catchment and agricultural sub-catchment had significant soil moisture deficits that consumed the vast majority of rainfall. Therefore, although the actual combined area of the urbanised and agricultural sub-catchment was 310ha, the modelled catchment area for this event was defined as being 14ha. In place of the half-life value based on soil-biodegradation, a value was chosen to represent the degradation of diuron through photolysis. The chosen value of 50 days was based on the probable photolysis rate (see Section 8.1) and also because it gave reasonable results from the model.

Table 8-14 also shows the soil properties used for the simulation of the storm events of Julian Days 226 and 276. In both cases runoff was generated from the entire 310ha of the North Weald catchment. Since the majority of the catchment that generated runoff was soil-based, the defined soil properties were similar to those used to model the fate of chlorotoluron etc. applied to the agricultural sub-catchment. However, the soil organic matter content was left at 0.1% to represent the minimal retention of the hard-surfaced area fraction of the urbanised catchment.

Since the model soil parameters for event JD150 were different to those used for events JD226 and JD 276, the model was run twice in a sequential manner. Initially with the soil properties set to emulate the hard-surface component of the urbanised catchment for event JD150 and then with the properties set to represent the entire North Weald catchment. During this procedure, the diuron remaining in the emulated soil environment after the simulation of event JD150 was entered as a pesticide application into the model for the second simulation for events JD226 and JD276. Table 8-15 shows the rainfall and runoff data used and also the period between diuron applications and the occurrence of the storm events.

Table 8-14 Physico-chemical, fate, catchment and application details for the Roads and Highway Departments application of diuron to the urbanised catchment.

Chemical Properties

Molecular weight: 233.1
Aqueous solubility: 36.4 gm^{-3}
Vapour pressure: $1.1x10^{-6}$ Pa
Log Kow: 2.85

Soil Properties event JD150

Soil half-life: 50 days
Catchment area: 14 ha
Soil temperature: 12 °C
Soil depth: 0.01 m
Diffusive depth of soil: 0.01 m
Volume fraction of air: 0.998
Volume fraction of water: 0.001
Mass fraction of organic carbon: 0.001

Application data event JD150

Area treated: 0.31 ha
Treatment rate: 2.5 kg/ha
Period before first event: 24 days

Soil Properties event JD226 & JD276

Soil half-life: 50 days
Catchment area: 310 ha
Soil temperature: 12 °C
Soil depth: 0.5 m
Diffusive depth of soil: 0.25 m
Volume fraction of air: 0.09
Volume fraction of water: 0.41
Mass fraction of organic carbon: 0.001

Application data event JD226 & JD276

Area treated: 0.31 ha
Treatment rate: 1.04 kg/ha
Period before first event: 76 days

Table 8-15 Rainfall and runoff volumes for the storm events for the Roads and Highway Departments application of diuron to the urbanised catchment.

Event (Julian day)	Period from application (days)	Rainfall (mm)	Runoff (mm)
150	24	25.5	19
226	100	23.5	3
276	150	17.5	12

Table 8-16 shows the event mean diuron concentrations predicted by SoilFug compared with the measured event mean concentrations for each storm event. The fit between the measured and modelled data for events JD150 and JD276 was very good. Unfortunately the runoff at Site D for event JD226 was not sampled due to sampler malfunction. However, the predicted mean concentration for the event appeared to be reasonable considering that the bulk of the diuron was probably removed during the first post-application event on JD150 (see Section 7.6.5).

Although the results of the modelling exercise appear favourable, they should be viewed with caution since to some extent the model parameters were adjusted to produce an output that was comparable with the measured data. Also, a level of uncertainty was associated with the approach of defining a soil compartment to emulate the behaviour of a pesticide applied to a hard-surface substrate. Further research would be required to confirm the estimated parameters used to represent pesticide degradation and retention on hard surfaces. This would involve field experiments to determine the rate of photolysis for pesticides applied to hard surfaces and also an experimental procedure to elucidate the extent and nature of pesticide retention on hard-surface substrates.

Table 8-16 Comparison of measured and modelled diuron event mean concentration data for the Roads and Highway Departments application of diuron to the urbanised catchment.

Event (Julian day)	Measured emc (µg/l)	Modelled emc (µg/l)
150	142.00	134.00
226	ns	0.14
276	0.11	0.09

ns: not sampled

The SoilFug model requires the inclusion of the average temperature of the soil environment which is fixed during the time period over which the modelled storm events occur. Whilst the soil temperature is unlikely to vary widely over a period of weeks or months, that of a hard surface would be likely to vary considerably, reaching considerably elevated temperatures when exposed to direct sunlight. Thus, in practice, the temperature of a hard surface environment may vary considerably on a daily basis which may have a significant effect on the level of pesticide volatilisation. Therefore, this effect would need to be evaluated, and if significant, accounted for during the simulation exercise. The simulation of the diuron application to the urbanised catchment revealed that the results from the model were particularly dependent upon a detailed knowledge of the surface hydrology of the modelled catchment and the response characteristics of the soil and impervious areas. From this the soil-property input parameter could be adjusted accordingly. Overall, the use of the model to simulate the fate of pesticides applied to hard surface substrates appeared to be feasible but to acquire the same level of confidence associated with the modelling of soil catchments, the model would need to be applied to a number of different pesticide runoff data-sets to fully assess its strengths and weaknesses.

8.2.6 Review of SoilFug performance

The overall performance of the SoilFug model in simulating the event mean concentrations of chlorotoluron, simazine and isoproturon in runoff from the North Weald agricultural sub-catchment was found to be very good. Essentially all predictions were within an order of magnitude and some were within a factor of 1.5. It was found that the level of accuracy between measured and modelled data generally appeared to decrease as the period of time between pesticide application and runoff events increased. This has been attributed to systematic errors produced by the model resulting from assumptions made with regard to the behaviour and fate of pesticide applied to the real environment, in order to simplify the design and operation of the model.

In every case the model had a tendency to over-predict the event mean concentrations with respect to the measured data and in some instances, particularly for chlorotoluron, the extent of the over-prediction increased with time. Walker (1987) and Beck *et al* (1995) reported that for a number of pesticides, the soil partition coefficient appeared to increase with time due to the sorbed pesticide molecule moving from a loosely-bound state to a strongly-bound state. As the period between pesticide application and storm event increased, the fraction of pesticide available for transport in the soil water would have decreased. This effect may have been most pronounced in the case of chlorotoluron since it had the highest organic carbon partition coefficient (K_{oc}) and therefore the greatest tendency to associate with the solid phase of the soil matrix.

Di Guardo *et al* (1994a and 1994b) observed a similar behaviour of the model when it was applied to runoff data from the Rosemaund catchment and made a number of suggestions to account for the model's tendency to over-predict the mean runoff concentration. It was noted that the model made no allowance for the amount of pesticide that may have been lost prior to the occurrence of the first event. This could occur through drift during application or from evaporation from the surface of the soil immediately after application when the pesticide had not yet achieved equilibrium with the soil matrix.

The input value used in the model to represent soil organic matter content was an average value representing the defined soil depth. Hence, it would not have taken into account the higher level of pesticide sorption to the top layer of the soil which would have been the first horizon of the soil profile to come into contact with the applied pesticide and also the horizon with the highest level of organic matter. Therefore the use of an average value would have led to an underestimate of the sorption in the top layer resulting in an over-prediction of mean pesticide concentration in the event runoff.

In summary, the results of the simulation of the pesticide runoff data measured at the North Weald agricultural sub-catchment shows that the SoilFug model was reasonably accurate in providing predictions within one order of magnitude of the measured data. However, the three pesticides modelled at North Weald were relatively water soluble and it is estimated that the results of the modelling exercise would not have been so favourable if the modelled pesticides had been more hydrophobic. In this situation, the pesticides would have been predominantly carried in the particulate phase of the event runoff which would not have been predicted by the model since it does not simulate soil erosion. However, provided the model is used with caution and its limitations are accounted for, it appears that it can be used with reasonable confidence to assess the fate of certain pesticides applied to small clay soil catchments and their removal in storm event runoff.

The SoilFug model was used to attempt to simulate the event mean concentrations of a pesticide in event runoff subsequent to application to hard-surface substrates in the urbanised catchment. Unfortunately only one application, that of diuron to roadside kerbstones in the urbanised catchment on 5/5/92 by the Road and Highway Department of Epping Forest Council, fully represented this type of application and so limited a wider evaluation. The results of the exercise indicated that the use of the model to simulate the fate of pesticides applied to hard-surface substrates was a possibility. However, to achieve the confidence necessary for routine simulations, the model needs to be fully evaluated with a number of different pesticide runoff data-sets which reflect the different scenarios. This would enable the strengths and weaknesses of the model to be fully identified for hard surface applications.

8.2.7 Statistical modelling of chlorotoluron transport in runoff from the agricultural sub-catchment using multiple linear regression analysis

Statistical modelling of the simazine and isoproturon runoff data from the agricultural sub-catchment and diuron from the urbanised catchment was not pursued since it was considered that too few storm-events were available to produce significant predictive equations. Multiple linear regression analysis was applied to the hydrological and chlorotoluron runoff data listed in Table 8-17 to identify predictive equations for the chlorotoluron event mean concentration, the peak concentration and percentage chlorotoluron loss with respect to application. The aim of the regression procedure was to fit the experimental data to the model:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + \ldots\ldots\ b_nX_n$$

where Y is the response variable (e.g. peak concentration), X_1, X_2, X_3 and X_n are the prediction variables (e.g. rainfall intensity), and b_0, b_1, b_2, b_3 and b_n are the regression coefficients (Mead *et al*, 1993). In theory the regression procedure could have produced a model incorporating all twelve prediction variables identified in Table 8-17 (columns 2 to 13). However, the aim was to keep the model as simple as possible, keeping the number of variables below six or seven, whilst retaining sufficient confidence in its ability to account for greater than 90% of the response variable prediction accuracy. Using Minitab® for Windows™ (Release 12.1), *stepwise multiple linear regression* and *best subsets multiple linear regression* were used to identify a subset of predictor hydrological variables for the construction of predictive equations that accounted for >90% response variable prediction accuracy. Once the subset of predictor variables was identified, it was examined using *ordinary multiple linear regression* to produce the regression model which, in turn, was subjected to analysis of variance to determine the overall fit of the model and its associated confidence level. The analysis of variance assessed the overall level of the regression model fit, by using an F-test to test the null hypothesis that all regression coefficients, except the constant term b_0, were zero.

Prior to the regression procedure, the response and predictor variables were tested for normal distribution and where necessary were log-transformed to reduce the leverage of extreme values. Each regression model was graphically and statistically evaluated. The predicted response variables were correlated with the corresponding measured variables and the 'Pearson product moment' correlation coefficient (r) calculated to measure the degree of linear association between two sets of variables.

Table 8-17 Hydrological and chlorotoluron runoff data from the eleven storm events sampled at site A during the course of the monitoring programme

JD	RI	RV	LAG	PF	TR	BFV	DRV	WB	ED	C	ADP	Ctfa	Cemc	Cpk	Closs
122	3.5	9.5	260	35.5	0.76	0.25	0.51	5.45	18	0.023	60.5	186	0.37	0.79	4×10^{-4}
227	6.5	23.5	480	97.7	2.81	0.49	2.32	9.9	33	0.034	19.7	290	1.09	1.47	0.003
276	4	17.5	200	434	6.87	1.86	5.01	29	14	0.244	50.2	340	1.28	1.62	0.02
294	9.5	49.5	231	1148	27.73	4.63	23.1	47	38.5	0.272	214.4	358	0.63	0.73	0.022
314	3	12	145	350	4.43	1.71	2.71	22.6	14	0.262	164.2	378	1.15	2.23	0.005
320	5	7.5	77	326	2.66	1.31	1.34	18	7	0.147	80.8	384	0.79	1.00	0.001
6	2	7.5	142	407	6.79	3.62	3.16	42	13	0.458	18.5	436	0.65	0.66	0.003
91	5	17.5	103	440	7.85	3.38	4.5	25.7	17	0.198	15.8	521	0.33	0.26	5E-04
95	2	8	260	240	4.84	2.55	2.28	29	18.5	0.27	31.5	525	0.36	0.24	7E-04
99	3.5	30.5	354	525	14.28	6.63	7.64	25	28	0.289	90.2	529	0.18	0.35	0.002
115	2.5	9.5	220	225	4.468	na	na	47	na	0.2023	na	545	0.3	0.31	1E-03

JD: Julian day on which event occurred
RI: Peak rainfall intensity during event (mm/hr)
RV: Volume of rainfall during duration of event (mm)
LAG: Period between rainfall centroid and peak hydrograph flow (min)
PF: Peak hydrograph flow (l/s)
TR: Total volume of runoff during of event (mm)
BFV; Volume of baseflow during event (mm)
DRV: Volume of direct runoff during event (mm)
WB: Event water balance (%)
ED: Event duration (hrs)
C: Runoff coefficient
ADP: Antecedent dry period (hrs)
na: no data available
Ctfa: Period between application and storm event (days)
Cemc: Chlorotoluron event mean concentration (µg/l)
Cpk: Peak event chlorotoluron concentration (µg/l)
Closs: Chlorotoluron loss w.r.t. application (%)

8.2.7.1 Multiple linear regression analysis for the prediction of chlorotoluron event mean concentration

Table 8-18 shows the results of the stepwise multiple linear regression for the prediction of chlorotoluron event mean concentration carried out on the storm event data shown in Table 8-17.

The stepwise regression procedure removes and adds variables for the purpose of identifying a useful subset of the prediction variables. In the first step, an F-test value for each prediction variable already in the model is calculated ('F-test' tests the null hypothesis that the regression coefficient of the prediction variable X_n is zero). If the F-test value for any prediction variable is less than the value specified in the 'F to remove' text box under *Options* in Minitab, the prediction variable with the lowest F-test value is removed and the output from the resulting model is displayed. In the following step, the F-test value for each prediction variable not in the current model is calculated. If any F-test value is greater than the value specified in the 'F to enter' text box, the predictor with the highest F-test value is entered and the output from the resulting model is displayed. These steps are repeated until no prediction variables meet the criteria for addition or removal. Because the storm events were driven by the occurrence of rainfall and the presence of pesticide residues in event runoff was a finite phenomenon, the prediction variables, RI, RV and Ctfas were designated in the stepwise regression procedure, as a set of prediction variables that could not be removed from the model, even when their F-test values were less than the stated 'F to enter' value.

As shown in Table 8-18, at each step, Minitab produced the prediction variable coefficient and t-value for each prediction variable in the model (the square root of the F-statistic is a t-value). Also produced was a value for the coefficient of determination (R-sq) which represented the proportion of variability in the response variable (in this case LogCemc) accounted for by the predictor variable. A value for S was also output which was an estimate of s, the estimated standard deviation about the regression line. From the results of the stepwise regression it appeared that the prediction variables Ctfa, LogRI, LogRV, LogDRV, WB, LogED, LogADP, LogPF and C were progressively important in accounting for the variability of the response variable LogCemc. Further, from Table 8-18 it appeared the best subset of six prediction variables for the determination of the response variable LogCemc consisted of Ctfa, LogRI, LogRV, LogDRV, WB and LogED. Whilst using the stepwise regression procedure, it was noticed that it did not always produce the most accurate results. When a chosen set of prediction variables was analysed by simple multiple linear regression (see below for description), it was occasionally found that a manual substitution, addition or even subtraction of prediction variables from the subset of prediction variables, given by the stepwise procedure, would sometimes produce better results. Therefore as a cross validation of the results of the stepwise regression, the full list of the prediction variables produced from the stepwise regression was further analysed using *best subsets multiple linear regression,* from which, the results are shown in Tables 8-19 and 8-20. The regression of the best subsets generates a series of regression models using the maximum R-Sq value criterion. This is achieved by first examining all *n* prediction variable multiple regression models and then selecting the two models (or a specified number) giving the largest R-Sq values.

Table 8-18 Results of stepwise multiple linear regression for prediction of chlorotoluron event mean concentration (Log Cemc), showing regression coefficients and corresponding T-values for each variable, at each step

Step	1	2	3	4	5	6	7
Constant	0.2668	1.3821	4.9422	6.2821	6.545	2.7439	-8.6072
Ctfa	-0.00097	-0.00214	-0.00389	-0.00463	-0.00481	-0.00585	-0.00918
T-Value	-0.98	-1.95	-4.42	-8.24	-10.75	-10.16	0
LogRI	0.4	0.44	0.14	0.57	0.48	0.14	-2.5
T-Value	0.53	0.67	0.33	2.05	2.17	0.67	0
LogRV	-0.31	-1.19	-3.49	-5.92	-5.69	-5.1	-2.39
T-Value	-0.57	-1.71	-4.05	-6.27	-7.66	-9.4	0
LogDRV		0.71	3.23	4.69	4.67	3.17	-1.63
T-Value		1.72	3.76	6.79	8.73	3.95	0
WB			-0.05	-0.0744	-0.0735	-0.0741	-0.0492
T-Value			-3.07	-6.02	-7.67	-12.48	0
LogED				1.13	0.97	1.95	4.4
T-Value				3.02	3.16	3.79	0
LogADP					-0.122	-0.314	-0.971
T-Value					-1.73	-3.04	0
LogPF						1.46	6.23
T-Value						2.05	0
C							-4
T-Value							0
S	0.289	0.251	0.153	0.0881	0.0682	0.0423	1.11E+15
R-Sq(%)	28.48	55.02	86.59	96.68	98.67	99.75	100

Minitab provides output information on these models and then examines all *n+1* prediction variable regression models. Two models (or a specified number) with the largest R-Sq values are selected and information on these models is produced. This process continues until either the regression model contains all the prediction variables or a set limit of variables. At each stage Minitab also outputs R-Sq(adj) which is R-Sq adjusted for degrees of freedom. If a prediction variable is added to an equation, R-Sq will get larger even if the added variable is of no real significance. Therefore to compensate for this, Minitab also outputs R-Sq (adj), which is an approximately unbiased estimate of the population R-Sq that is a more reliable indicator of the goodness of fit of the regression model.

The results of the subsets regression procedure are shown as two Tables (Tables 8-18 and 8-19) rather than one because the procedure was limited to analysing a maximum of ten prediction variables. Therefore, the procedure was repeated twice, initially incorporating the prediction variable WB and secondly incorporating prediction variable C.

Table 8-19 Best subsets multiple linear regression analysis to identify prediction variables for chlorotoluron event mean concentration, incorporating WB [Regression includes LogRI, LogRV and Ctfa—not shown; 'x' denotes selected variable; the best subset of prediction variables with R-Sq >90% is shown with shaded bar]

R-Sq(%)	R-Sq(Adj)(%)	s	LogDRV	WB	LogED	LogADP	LogPF
86.6	69.8	0.15349	X	X			
60.1	10.1	0.26487				X	X
56.6	2.4	0.27607	X		X		
96.7	90	0.08813	X	X	X		
96.1	88.3	0.095547	X	X			X
92.1	76.2	0.13628	X	X		X	
98.7	94	0.068236	X	X	X	X	
97.4	88.3	0.095616	X	X	X		X
96.1	82.5	0.11701	X	X		X	X
99.7	97.7	0.042253	X	X	X	X	X

In the first case, the result of the best subsets regression analysis (Table 8-19) agrees with that of the stepwise regression analysis, in that the best subset of six prediction variables included Ctfa, LogRI, LogRV, LogDRV, WB and LogED. Further, the goodness of fit of the regression model was confirmed with an R-Sq(Adj) value of 90.

Table 8-20 Best subsets multiple linear regression analysis to identify prediction variables for chlorotoluron event mean concentration, incorporating C [Regression includes LogRI, LogRV and Ctfa—not shown, 'x' denotes selected variable]

R-Sq(%)	Adj.R-Sq (%)	s	LogDRV	C	LogED	LogADP	LogPF
60.6	11.4	0.26304	X	X			
60.1	10.1	0.26487				X	X
56.6	2.4	0.27607	X		X		
71.1	13.3	0.2601		X		X	X
63.4	0	0.29262	X	X	X		
62.1	0	0.29784	X	X			X
76.0	0	0.29038		X	X	X	X
72.1	0	0.31322	X	X		X	X
67.0	0	0.34063	X	X	X	X	
99.1	91.6	0.081151	X	X	X	X	X

Table 8-21 shows the results of ordinary multiple linear regression carried out on the subset of prediction variables, identified from the stepwise and best subset regression analysis, to produce a model to predict event mean chlorotoluron concentrations (Cemc). The equation produced from the ordinary multiple linear regression was:

$$\text{LogCemc} = 6.28 + 0.570\ \text{LogRI} - 5.92\ \text{LogRV} - 0.00463\ \text{Ctfa} + 1.13\ \text{LogED} + 4.69\ \text{LogDRV} - 0.0744\ \text{WB}$$

The estimated standard deviation (s) of the fitted regression line was 0.08813, and the R-Sq and R-Sq(adj) values were 96.7% and 90.0% respectively. The analysis of variance carried out to assess the level of overall goodness of fit gave an F value of 14.57 which was significant at p=0.025 or the 97.5% confidence level (the F-test is a test of the null hypothesis; all regression coefficients, excepting b_0, are zero). For each prediction variable, Table 8-21 shows the respective regression coefficient, the t-statistic value and the p-value. The t-test statistic tests the null hypothesis that each prediction variable coefficient is zero and the p-values determine whether there is significant evidence that the prediction variable coefficients are not zero. The coefficient of every prediction variable except LogRI was significant at, at least, the 95% confidence level. The confidence level for LogRI was 86.8%.

The regression coefficients with the most positive influences upon the variability of Log Cemc were those describing LogDRV and LogED which suggests that the chlorotoluron event mean concentrations were dependent upon the volume of direct runoff for a given storm event and also the duration of the event. These findings agree with the work of Squillace and Thurman (1992) and Southwick *et al* (1989) who found that average pesticide runoff concentration increased as the unit area runoff volume increased and that the amount of pesticide lost during an event was related to the event duration. The relative insignificance of the 'time from application' regression coefficient may reflect the long half-life of chlorotoluron which would have meant that to some extent the amount of chlorotoluron available during the monitoring period was relatively constant. The large negative coefficient for LogRV (-5.92) was unexpected and implies that the event mean concentration is inversely proportional to rainfall volume, which would be the opposite of reported pesticide behaviour. On a physical level, this value is unexplainable but may be an effect of the model collinearity further discussed in Section 8.2.7.4.

Table 8-21 Statistical results of ordinary multiple linear regression analysis to produce a model to predict event mean chlorotoluron concentration (Cemc)

Prediction variable	Regression Coefficient	t-value	p-value
Constant	6.2821	7.4	0.005
LogRI	0.5704	2.05	0.132
LogRV	-5.9201	-6.27	0.008
Ctfa	-0.00463	-8.24	0.004
LogED	1.1324	3.02	0.057
LogDRV	4.687	6.79	0.007
WB	-0.07438	-6.02	0.009

To further examine the goodness of fit of the model, the regression residuals were investigated. The residual is the difference between the measured value and the value predicted using the model. To decide if any of the residuals were unusually large they were assessed relative to their underlying variability. This was done by plotting the standardised residuals against the order of events (Figure 8-10). Each residual value was standardised by dividing by the residual standard deviation. Using the properties of the standardised normal distribution it would be expected that 95% of residuals would be inside the range of +/-2 if the model was adequately explaining the variation of the response variable, Log Cemc (Mead *et al*, 1993). None of the data points were outside the +/-2 range (Figure 8-10) and therefore it can be concluded that the model provides a good level fit for at least 95% of the residuals.

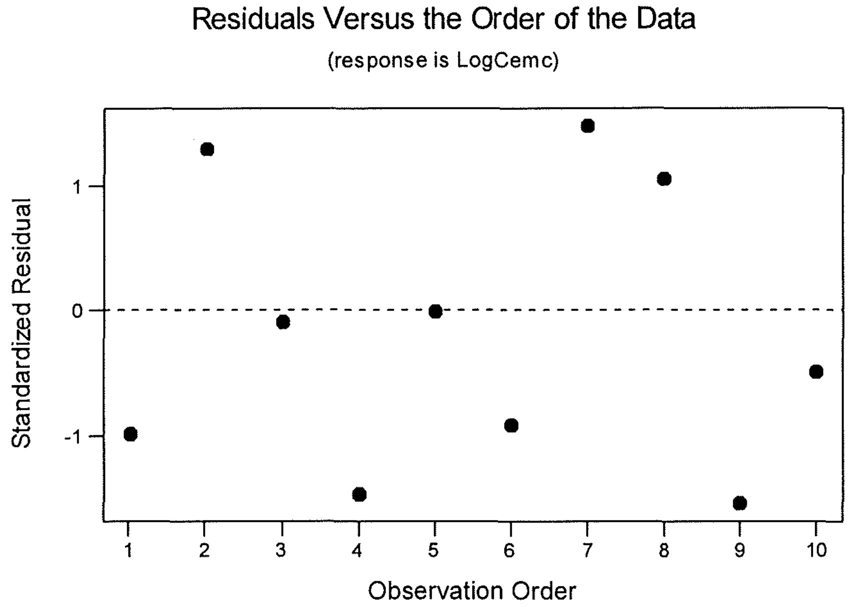

Figure 8-10 Plot of standardised residuals against storm-event order for the prediction of chlorotoluron event mean concentration

Further, if the model was adequate, then the standardised residuals should appear as a random sample from a normal distribution. Any systematic trend could indicate that the model does not adequately explain the variation in the response variable. The random nature of the residual data points confirms the adequacy of the model (Figure 8-10).

A graphical and statistical evaluation was carried out to assess the predictive ability of the regression model. This entailed correlation of the predicted response variables with the corresponding measured variables and calculation of the Pearson product moment correlation coefficient (r) to measure the degree of linear association between two sets of variables. Figure 8-11 shows an excellent fit for the correlation of predicted and measured chlorotoluron event mean concentrations with a Pearson product moment correlation (r) of 0.983, and a confidence level > 99.99%.

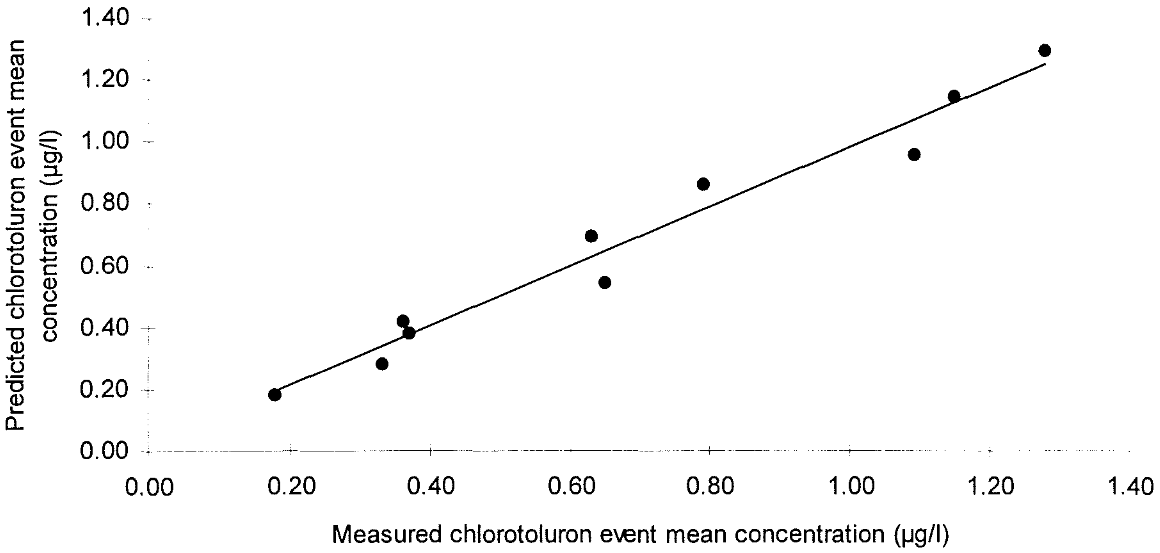

Figure 8-11 Comparison of predicted chlorotoluron event mean concentration with measured chlorotoluron event mean concentration ***[Pearson Correlation (r)= 0.983, confidence level > 99.99%]***

8.2.7.2 Multiple linear regression for prediction of peak event chlorotoluron concentration

Table 8-22 shows the results of the stepwise multiple linear regression carried out on the storm event data listed in Table 8-17 for the prediction of peak event chlorotoluron concentration (LogCpk). For the same reasons as previously described, the prediction variables, RI, RV and Ctfa, were designated in the stepwise regression procedure as a set of variables that could not be removed from the model. The results of the stepwise regression showed that the prediction variables LogRI, LogRV, Ctfa, LogED, LogPF, WB, LogADP, LogLAG and LogDRV appeared to be progressively important in accounting for the variability of the response variable LogCpk. Also from Table 8-22, it appeared that the best subset of prediction variables for the determination of the response variable LogCpk at greater than 90% accuracy consisted of LogRI, LogRV, Ctfa, LogED, LogPF, WB and LogADP, which had an R-Sq value of 99.9%. The full list of the prediction variables produced from the stepwise regression was further analysed using *best subsets multiple linear regression* and the results are shown in Tables 8-23 and 8-24. The results of the subsets regression procedure are shown as two Tables rather than one because the procedure was limited to analysing a maximum of ten prediction variables. Therefore, the procedure was repeated twice, initially incorporating the prediction variable WB and secondly incorporating prediction variable C.

Table 8-22 Results of stepwise multiple linear regression for prediction of peak event chlorotoluron concentration, showing regression coefficients and corresponding T-values for each variable, at each step

Step	1	2	3	4	5	6	7
Constant	0.6642	1.5413	1.0781	-2.5274	-4.1263	-4.0236	-4.771
LogRI	-0.029	-0.689	-0.613	-0.773	-1.184	-1.266	-1.31
T-Value	-0.04	-0.89	-0.73	-1.23	-15.97	-19.07	0
LogRV	0.04	1.22	0.76	-1.54	-2.58	-2.6	-2.42
T-Value	0.07	1.44	0.64	-1.09	-15.21	-22.79	0
Ctfa	-0.00209	-0.00266	-0.00317	-0.00546	-0.0081	-0.00824	-0.00835
T-Value	-2.05	-2.81	-2.39	-3.72	-34.56	-47.31	0
LogED		-1.31	-0.91	1.65	3	3.16	3.27
T-Value		-1.7	-0.85	1.13	16.39	20.9	0
LogPF			0.26	2.38	3.98	4.04	4.28
T-Value			0.6	2.23	25.48	37.03	0
WB				-0.0444	-0.0726	-0.0743	-0.0731
T-Value				-2.09	-24.47	-34.01	0
LogADP					-0.479	-0.489	-0.52
T-Value					-15.6	-22.95	0
LogLAG						-0.114	-0.086
T-Value						-1.86	0
LogDRV							0
T-Value							0
S	0.296	0.258	0.276	0.204	0.0225	0.0151	1.11E+15
R-Sq(%)	47.76	66.92	69.62	87.61	99.9	99.98	100

As shown in Table 8-23, the results of the best subsets regression analysis agreed with those of the stepwise regression analysis, in that the best subset of prediction variables having an R-Sq value of >90% was made up of the prediction variables Ctfa, LogRI, LogRV, LogED, LogPF, WB and LogADP. The overall goodness of fit of the regression model was also confirmed with an R-Sq(Adj) value of 99.5%.

Table 8-23 Best subsets multiple linear regression to identify prediction variables for peak chlorotoluron event concentration (LogCpk), incorporating WB [Regression includes LogRI, LogRV and Ctfa—not shown; the best subset of prediction variables with R-Sq >90% is shown with shaded bar]

N° variables	R-Sq(%)	R-Sq.Adj (%)	s	LogDRV	WB	LogED	LogADP	LogPF
2	92.8	83.7	0.13485	X	X			
2	82.3	60.3	0.21073		X			X
2	69.7	31.9	0.27593	X				X
3	93.0	79.1	0.15276	X	X	X		
3	93.0	78.9	0.15364	X	X			X
3	92.8	78.5	0.15496	X	X		X	
4	99.9	99.5	0.022533		X	X	X	X
4	95.3	78.8	0.15394	X	X	X		X
4	93.2	69.6	0.18433	X	X	X	X	
5	100	99.7	0.019423	X	X	X	X	X

Table 8-24 Best subsets multiple linear regression to identify prediction variables for peak chlorotoluron event concentration, incorporating C [Regression includes LogRI, LogRV and Ctfa—not shown]

N° variables	R-Sq	Adj.R-Sq	s	LogDRV	C	LogED	LogADP	LogPF
2	69.8	32	0.27554		X			X
2	69.7	31.9	0.27593	X				X
2	69.6	31.7	0.27634			X		X
3	72.8	18.3	0.30204	X			X	X
3	71.9	15.7	0.30698		X		X	X
3	71.2	13.5	0.31093		X	X		X
4	76	0	0.34733	X	X		X	X
4	74.4	0	0.35905	X		X	X	X
4	72.5	0	0.37161		X	X	X	X
5	99	91.3	0.098779	X	X	X	X	X

Table 8-25 shows the results of ordinary multiple linear regression carried out on the subset of prediction variables, which was identified from both the stepwise and best subset regression analysis. The resulting model to predict peak event chlorotoluron concentrations (Cpk) can be expressed by the equation:

$$\mathrm{LogCpk} = -4.13 - 0.00810\,\mathrm{Ctfa} - 1.18\,\mathrm{LogRI} - 2.58\,\mathrm{LogRV} - 0.0726\,\mathrm{WB} + 3.98\,\mathrm{LogPF} + 3.00\,\mathrm{LogED} - 0.479\mathrm{LogADP}$$

The estimated standard deviation (S) of the fitted regression line was 0.02253 and the R-Sq and R-Sq(adj) values were 99.9% and 99.5%, respectively. The analysis of variance carried out to assess the level of overall goodness of fit gave an F value of 282.64 which was significant at p=0.004 or the 99.6% confidence level.

Table 8-25 Results of ordinary multiple linear regression to identify prediction variables for peak chlorotoluron event concentration

Predictor	Regression coefficient	t-value	p-value
Constant	-4.1263	-17.61	0.003
Ctfa	-0.0081	-34.56	0.001
LogRI	-1.18447	-15.97	0.004
LogRV	-2.5759	-15.21	0.004
WB	-0.07259	-24.47	0.002
LogPF	3.9825	25.48	0.002
LogED	2.9978	16.39	0.004
LogADP	-0.47875	-15.6	0.004

For each prediction variable, Table 8-25 shows the respective regression coefficient, the t-statistic value and the p-value. The coefficient of every prediction variable was significant at, at least a 99.6% confidence level. The regression coefficients with the most positive influence upon the variability of Log Cpk were those associated with LogPF and LogED, which suggests that the chlorotoluron peak event concentration was highly dependent upon the peak flow rate of the direct runoff for a given storm event and also the duration of the event. These findings concur with the work of Squillace and Thurman (1992) who found that peak pesticide runoff concentrations increased as the unit area runoff volume increased. In such situations they found that streamflow could consist of a relatively large percentage of overland runoff in which dissolved pesticides were less prone to re-adsorption than if transported through the soil profile. In a flood study of the Granta catchment, Gomme *et al* (1991) reported that the peak concentrations of a number of pesticides (isoproturon, simazine, chlorotoluron and propyzamide) correlated closely with peak flow rate. Again the relative insignificance of the 'time from application' regression coefficient may reflect the long half-life of chlorotoluron which would have meant that to some extent the amount of chlorotoluron available during the monitoring period was relatively constant. The negative coefficients for LogRV (-2.5759) and LogRI (-1.18) were unexpected and imply that the event mean concentration is inversely proportional to rainfall volume and intensity. As previously suggested for the model relating to chlorotoluron event mean concentration prediction, this is the opposite of reported pesticide behaviour and similarly may be an effect of the model collinearity further discussed in Section 8.2.7.4.

As initially described in Section 8.2.7.1, the goodness of fit of the model was further examined by plotting the standardised regression residuals against the order of events and observing if any of the residuals were outside the range of +/-2 and if the occurrence of the data points was in any way systematic (Figure 8-12). If this were the case then it may have suggested that the model was not adequately explaining the variation of the response variable, Log Cpk. None of the data points lie outside the +/-2 range (Figure 8-12) and therefore it can be concluded that the model provides a good level fit for at least 95% of the residuals. In addition, the random occurrence of the residual data points confirms the adequacy of the model.

To assess the predictive power of the regression model a graphical and statistical evaluation was carried out, as before. Figure 8-13 shows an excellent fit for the correlation of predicted and measured peak event chlorotoluron concentrations with a Pearson product moment correlation (r) of 0.999, and a confidence level of 99.95%.

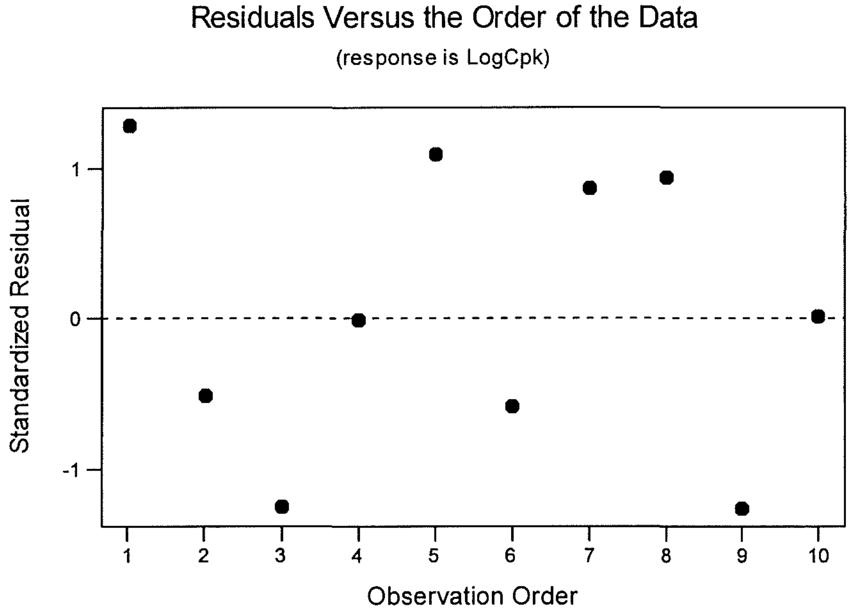

Figure 8-12 **Plot of standardised residuals against storm event orders for the prediction of peak event chlorotoluron**

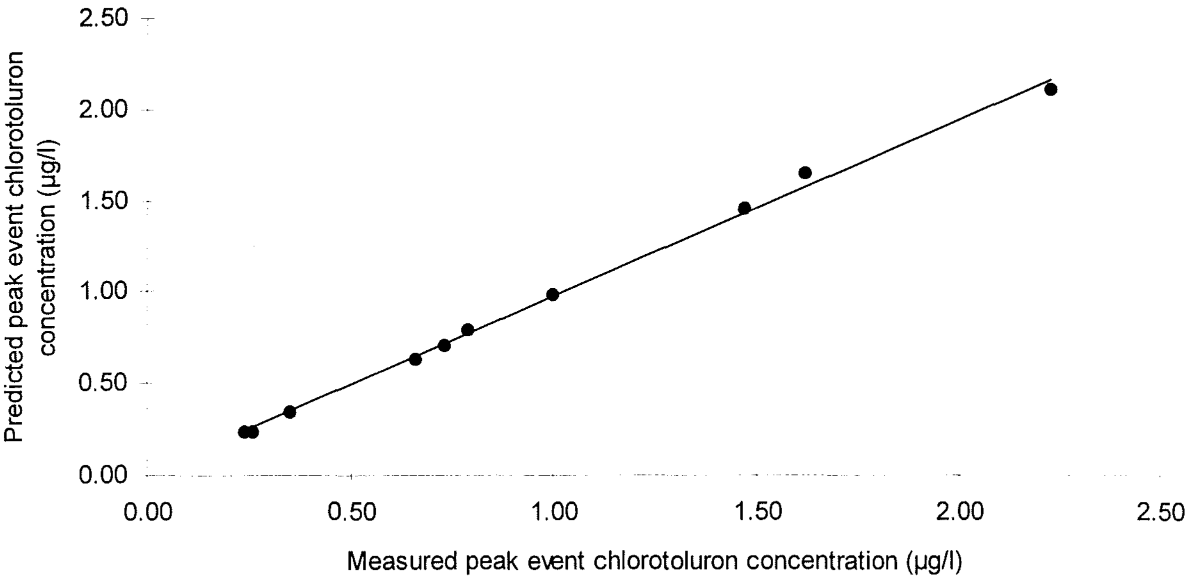

Figure 8-13 **Comparison of predicted peak event chlorotoluron concentration with measured peak event chlorotoluron concentration** ***[Pearson Correlation (r)= 0.999, Confidence level > 99.95%]***

8.2.7.3 *Multiple linear regression for prediction of chlorotoluron loss with respect to application*

Table 8-26 shows the results of the stepwise multiple linear regression carried out on the storm event data shown in Table 8-17 for the prediction of chlorotoluron loss with respect to application (LogCloss). Again, the prediction variables RI, RV and Ctfa were designated in the stepwise regression procedure, as a set of prediction variables that could not be removed from the model. The results of the stepwise regression showed that the prediction variables LogRI, LogRV, Ctfa, LogPF, LogLAG, LogADP, C, WB and LogDRV appeared to be progressively important in accounting for the variability of the response variable LogCloss. The best subset of prediction variables for the determination of the response variable LogCloss at greater than 90% accuracy included LogRI, LogRV, Ctfa, LogPF, and LogLag which had an R-Sq value of 92.12% (Table 8-26; step 3). The full list of the prediction variables produced from the stepwise regression was further analysed using *best subsets multiple linear regression.* The results of the subsets regression procedure are shown as two Tables (Tables 8-27 and 8-28) rather than one because of its limitation to analysing a maximum of ten prediction variables.

Table 8-26 Results of stepwise multiple linear regression for prediction of chlorotoluron loss with respect to application

Step	1	2	3	4	5	6	7
Constant	-3.522	-4.687	-8.199	-7.804	-8.521	-9.112	1.065
LogRI	-0.82	-1.6	-0.42	-0.59	-2.78	-2.15	-0.49
T-Value	-0.52	-1.96	-0.43	-0.57	-2.1	-1.27	0
LogRV	1.67	1.11	-0.49	-0.34	-0.08	-0.3	-4.32
T-Value	1.49	1.9	-0.46	-0.31	-0.1	-0.32	0
Ctfa	0.0015	-0.0056	-0.0055	-0.0062	-0.0081	-0.0082	-0.0074
T-Value	-0.7	-3.93	-4.53	-4.25	-5.69	-5.1	0
LogPF		1.6	2.18	2.33	3.83	3.88	0.78
T-Value		4.28	4.67	4.6	4.58	4.12	0
LogLAG			1.39	1.33	1.42	1.59	0.88
T-Value			1.71	1.59	2.38	2.26	0
LogADP				-0.25	-0.53	-0.54	-0.1
T-Value				-0.9	-2.16	-1.96	0
C					-4.3	-2.6	0.3
T-Value					-1.98	-0.78	0
WB						-0.015	-0.066
T-Value						-0.77	0
LogDRV							5
T-Value							0
S	0.6	0.305	0.259	0.265	0.189	0.212	1.11E+15
R-Sq	36.39	86.36	92.12	93.78	97.91	98.68	100

As shown in Table 8-27, the results of the stepwise regression analysis were superseded by those of the best subsets regression analysis. The step 3 prediction variable subset from the stepwise procedure with an R-Sq value of 92.12% for five prediction variables was replaced by a subset of five prediction variables with an R-Sq value of 98.4%. These prediction variables were Ctfa, LogRI, LogRV, WB and LogDRV. The overall goodness of fit of this regression model was also confirmed with an R-Sq(Adj) value of 96.3%. Table 8-29 shows the results of ordinary multiple linear regression carried out on the subset of prediction variables, which was identified from the best subset regression analysis, to produce a model to predict chlorotoluron loss with respect to application (Closs).

Table 8-27 Best subsets multiple linear regression to identify prediction variables for chlorotoluron loss with respect to application, incorporating WB [Regression includes LogRI, LogRV and Ctfa—not shown]

No variables	R-Sq	Adj.R-Sq	s	LogPF	LogLag	LogADP	WB	LogDRV
2	98.4	96.3	0.11791				X	X
2	92.1	82.3	0.25883	X	X			
2	88.5	74.2	0.31208	X		X		
3	99.7	99.1	0.058789		X		X	X
3	98.7	96.1	0.12166	X			X	X
3	98.5	95.4	0.13207			X	X	X
4	99.8	99.2	0.054219	X	X		X	X
4	99.7	98.6	0.071718		X	X	X	X
4	98.7	94.3	0.14704	X		X	X	X
5	100.0	99.9	0.016566	X	X	X	X	X

Table 8-28 Best subsets multiple linear regression to identify prediction variables for chlorotoluron loss with respect to application, incorporating C [Regression includes LogRI, LogRV and Ctfa—not shown]

No variables	R-Sq	Adj.R-Sq	s	LogPF	LogLag	LogADP	C	LogDRV
2	92.1	82.3	0.25883	X	X			
2	88.5	74.2	0.31208	X		X		
2	87.7	72.3	0.32374	X				X
3	93.8	81.4	0.26544	X	X	X		
3	93.0	79.0	0.28174	X	X		X	
3	92.1	76.4	0.29886	X	X			X
4	97.9	90.6	0.18871	X	X	X	X	
4	95.2	78.6	0.28447	X	X	X		X
4	93.6	71.2	0.32966	X	X		X	X
5	98.1	82.8	0.25508	X	X	X	X	X

The model produced from the ordinary multiple linear regression was:

LogCloss = 4.81 - 1.12 LogRI - 4.21 LogRV - 0.00741 Ctfa - 0.0702 WB + 5.66 LogDRV

The estimated standard deviation (S) of the fitted regression line was 0.1179 and the R-Sq and R-Sq(adj) values were 98.4% and 96.35% respectively. The analysis of variance carried out to assess the level of overall goodness of fit gave an F value of 48.12 which was significant at p=0.001 or the 99.9% confidence level. For each prediction variable, Table 8-29 shows the respective regression coefficient, the t-statistic value and the p-value. The coefficient of every prediction variable was significant to, at least, a 97.6% confidence level. The regression coefficient with the most positive influence upon the variability of LogCloss was that associated with LogDRV which suggests that during the course of a storm event the loss of chlorotoluron with respect to application was principally dependent upon the volume of direct surface runoff for a given storm event. This deduction agrees with the work of Gomme *et al* (1991) who found that pesticide loss or flux in runoff varied in accordance with average flow rate or runoff volume. Again the relative insignificance of the 'time from application' regression coefficient may reflect the long half-life of chlorotoluron which would have meant that to some extent, the amount of chlorotoluron available during the monitoring period was relatively constant. Again the negative coefficient for LogRV (-4.2) may, as mentioned previously, be an effect of the model collinearity which is further discussed in Section 8.2.7.4.

Table 8-29 Results of ordinary multiple linear regression to identify prediction variables variables for chlorotoluron loss with respect to application

Predictor	Regression coefficient	T	P
Constant	4.8146	4.97	0.008
LogRI	-1.1246	-3.54	0.024
LogRV	-4.2131	-6.36	0.003
Ctfa	-0.00741	-10.94	0
WB	-0.0702	-5.61	0.005
LogDRV	5.6618	8.58	0.001

As initially described in Section 8.2.7.1, the goodness of fit of the model was further examined by plotting the standardised regression residuals against the order of events (Figure 8-14). None of the data points lie outside the +/-2 range of the standardised normal distribution and therefore it can be concluded that the model provides a good level fit for at least 95% of the residuals. Also, the occurrence of the residual data points appears random with no indication of a systematic trend, which supports the adequacy of the model.

The fit of the regression model was assessed as previously described. Figure 8-15 shows an excellent fit for the correlation of predicted and measured chlorotoluron losses with respect to application with a Pearson product moment correlation (r) of 0.998 and which was significant at the 99.9% confidence level. The distribution of the data points illustrates the positive skew distribution of the chlorotoluron application loss data obtained from the monitored storm events. The majority of the data occurred in the 0 - 0.005% range with two values in the 0.02 - 0.025% range.

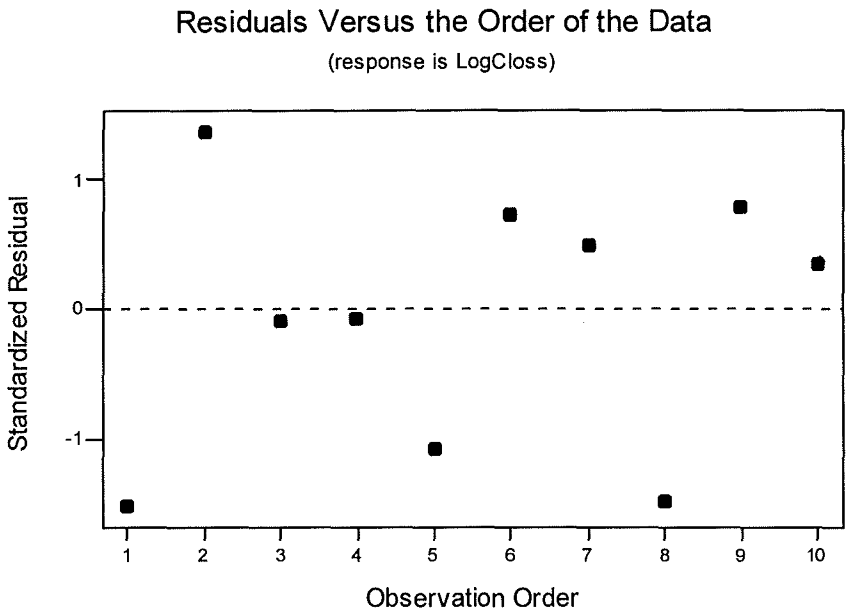

Figure 8-14 **Standardised residuals plotted against storm-event order for the prediction of chlorotoluron loss with respect to application**

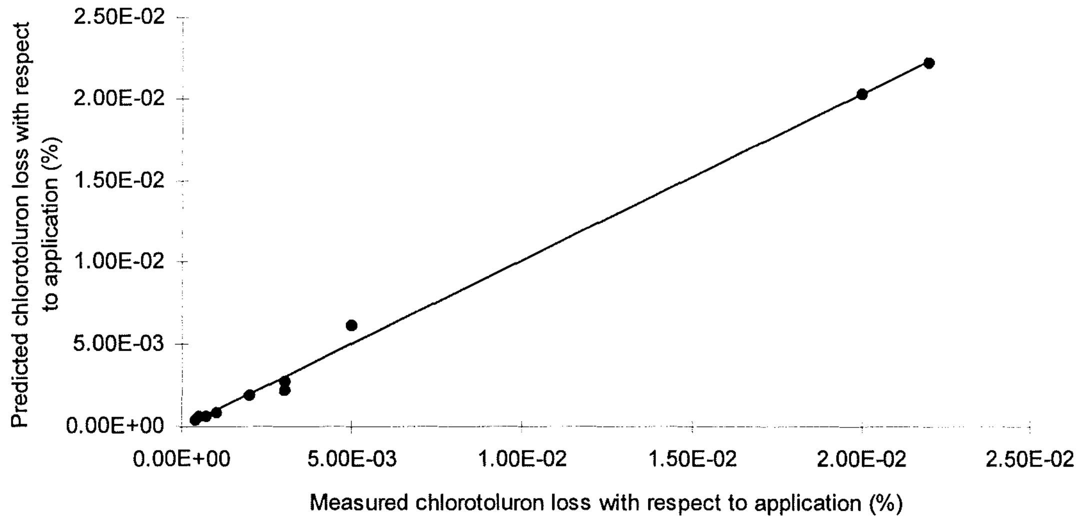

Figure 8-15 Comparison of predicted chlorotoluron loss (Closs) with respect to application with measured loss (%), ***[Pearson Correlation (r) = 0.998, confidence level > 99.9%]***

8.2.7.4 Discussion of statistical modelling results and comparison of fugacity and statistical modelling approaches

The predictive equations produced by the multiple linear regression procedures described in Sections 8.2.7.1, 8.2.7.2 and 8.2.7.3 are shown in Table 8-30. In each case, predictive equations were produced with >90% responses in variable prediction accuracy. The predictive equation for LogCemc incorporates six variables, the equation for LogCpk incorporates seven variables and the equation for LogCloss incorporates five variables.

Table 8-30 Multiple linear regression equations for the prediction of chlorotoluron event mean concentration, peak event chlorotoluron concentration and chlorotoluron application loss with respect to application

Predictive model	R-Sq.Adj (%)
LogCemc = 6.28 - 0.00463Ctfa + 4.69LogDRV - 5.92 LogRV - 0.0744 WB + 1.13 LogED + 0.570 LogRI	90.00
LogCpk = - 4.13 - 0.00810Ctfa + 3.98LogPF - 0.0726WB + 3.00LogED - 1.18LogRI - 0.479LogADP - 2.58LogRV	99.50
LogCloss = 4.81 - 0.00741Ctfa + 5.66LogDRV - 4.21LogRV - 0.0702WB - 1.12LogRI	96.35

The number of prediction variables used in each equation probably reflects the underlying complexity and transience of the specific response variable in question. For example, it is reasonable to consider that the complexity of the processes and inherent transient nature associated with the occurrence of peak concentrations occurring over a relatively short time period would require more explanatory prediction than the amount of chlorotoluron lost over a storm-event lasting many hours. For each of the predictive equations shown in Table 8-30, the regression coefficients and associated predictive variables with the greatest positive influence on the dependent variables appear to be reactive rather than proactive prediction variables. For example, in principle, for the prediction of LogCemc and LogCloss, LogDRV should be equivalent and as equally important as LogRV since Log DRV is in practice dependent on LogRV. This is assuming other factors such as soil moisture deficit and evapotranspiration, are taken into account. Likewise, in the prediction of LogCpk, LogPF should in practise be equivalent to and as important as LogRI. However, in each case the proactive variables appear to have a negative influence upon the dependent variable.

One conclusion that can be drawn from this behaviour is that although the predictive equations appear to simulate the measured data from which, in part, they were derived, they are inherently statistically unstable. This idea is further borne out by the variance inflation factors[1] (not shown) for each regression coefficient, which were generally greater than ten, which implies that the associated predictive variable has a high level of collinearity with other independent variables; i.e. a given independent variable has a significant level of its variance explained by other variables. Given the high levels of collinearity present within each of these models, it is possible that they may not be stable or accurate if used to simulate the dependent variables other than those used to derive the models. Therefore for an unequivocal evaluation they would need to be tested on a separate chlorotoluron data-set obtained from the North Weald agricultural sub-catchment. To improve the stability of the three models it is considered that other, less related, independent variables such as soil moisture deficit and soil hydraulic conductivity would need to be entered into the regression procedure.

Since only one application of chlorotoluron was made during the course of the monitoring programme, the three predictive models were not able to be used for the simulation of an independent chlorotoluron data-set obtained from the sub-catchment. However, if a further chlorotoluron runoff data-set had been available, it is considered likely that the amount of chlorotoluron applied to the agricultural sub-catchment would have been as significant as the elapsed period between application and storm-event occurrence, in predicting mean and peak chlorotoluron concentration as well as the loss during an event with respect to application if the storm events occurred relatively soon after application. A similar relationship was reported by Wauchope and Leonard (1980), who in the derivation of an empirical formula for the prediction of maximum pesticide concentrations in agricultural runoff from a number of catchments, found that pesticide concentrations in individual runoff events could be predicted to within one order of magnitude if the pesticide formulation, application rate and the period elapsed between application and event were known. Prior to making a prediction, the pesticides were grouped into four broad classes according to their ‘availability’ for loss in runoff. ‘Availability’ was defined as the ratio between application rate (kg/ha) and runoff concentration (μg/l), if runoff occurred immediately after application. They found that no further parameters (e.g. rainfall volume) could be added to the formula to improve its prediction accuracy, without making it site specific. In

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[1] The variance inflation factor (VIF) is a measure of how much the variance of an estimated regression coefficient increases if the predictors are correlated (multicollinear).

contrast, it is very probable that the predictive equations derived in this study for chlorotoluron movement from the agricultural sub-catchment would be site specific. If used to predict the behaviour of chlorotoluron from another agricultural catchment, it is considered that reasonable results would only be obtained if the catchment had similar characteristics to the North Weald agricultural sub-catchment, i.e. similar size, slope, field drainage and field management.

Through correlations with measured pesticide runoff data, the three models described in Sections 8.2.7.1, 8.2.7.2 and 8.2.7.3 have demonstrated the possibility of simulating the measured chlorotoluron values for the North Weald agricultural sub-catchment. However, the use of the predictive equations to genuinely forecast chlorotoluron runoff data from the agricultural sub-catchment would be limited by the requirement of the fore-knowledge of the hydrological variables relating to a given storm event. Despite this, the multiple linear regression analysis model approach could be useful in the development of a screening tool in which each required hydrological variable was replaced by an equivalent probability distribution obtained from flood event analysis of the temporal hydrological regime of the agricultural sub-catchment at North Weald. A similar approach for stochastic rainfall distribution estimation was used by Haith (1987) and Mills and Leonard (1984), in conjunction with deterministic hydrology and pesticide runoff models. Therefore, through the combination of a stochastically-estimated hydrology data-set with the defined predictive models, an array of probability or return-period-ranked chlorotoluron runoff data could be produced for a given storm event occurring at a designated period of time after the chlorotoluron application.

Comparison of the two approaches suggests that the SoilFug model was significantly more useful and widely applicable than statistical modelling for the prediction of the fate of pesticides applied to the North Weald agricultural sub-catchment. Although the predictive equations derived for the simulation of chlorotoluron concentration and loss produced accurate results with respect to measured data, the multiple linear regression analysis approach was likely to be site specific and possibly unstable. It did not lend itself to the prediction of pesticide runoff fate for pesticides with half-lives considerably shorter than chlorotoluron.

8.3 Reducing the impacts of pesticide use on receiving water quality

The following subsections discuss a number of techniques and approaches aimed at reducing the impact of pesticides on receiving waters following their application to agricultural and urban land. Applications to the different land surface types are considered separately using a common approach based on the various stages involved from the amount of pesticide applied to the eventual contamination of surface waters. The techniques and rationale available to reduce the amount of pesticide initially applied [1&2][2] are considered first of all, followed by procedures available to reduce off-site losses of applied pesticides [3]. This is followed by an examination of the use of vegetative buffer zones for the interception and treatment of contaminated runoff before it enters the receiving water-body [4]. Finally, where applicable, consideration is given to the effectiveness of natural and constructed wetlands to clean up contaminated surface waters [5].

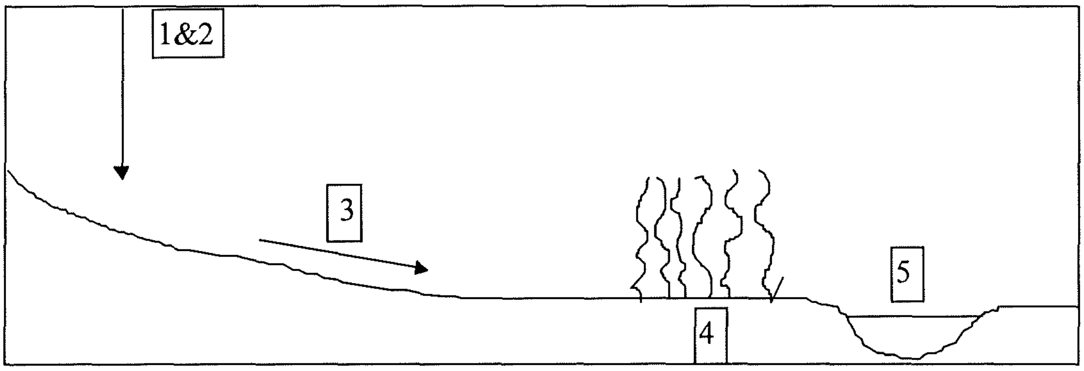

Figure 8-16 Conceptualised diagram of approaches aimed at reducing the impact of pesticides applied to agricultural and urban land, on receiving waters. [1&2] reductions in amount applied; [3] procedures for reducing off-site losses; [4] the use of vegetative buffer zones for intercepting and treating contaminated runoff; and [5] use of reedbeds to treat surface waters once contaminated.

8.3.1 Within the agricultural environment

The measures identified in Figure 8-16 [1-5] for the minimisation the use of pesticides, the adoption of practices to minimise their off-site loss and the control of their consequent adverse

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[2] [ ]: numbers in parenthesis refer to the different stages represented diagrammatically in Figure 8-16

effects on the environment fall within the principles of Integrated Pest Management. This has been defined as the production of food without endangering the environment (Kaaya, 1994). The principles of Integrated Pest Management were conceived in the early 1980s, and since this time an abundance of interpretations have evolved to reflect the perceptions, politics and economics of its advocates (Grant, 1994). Generally, the range of interpretations lie between the views of the organic farming lobby which are closest to the original principles of Integrated Pest Management (Pedigo, 1995) and those of the agro-chemical and biotechnology industries. The latter advocate the use of crops which have been genetically modified to be herbicide resistant as well as the use of non-selective herbicides, such as glyphosate, which are reported to be less susceptible to off-site loss in storm-event runoff (Bradshaw *et al*, 1997; Garnet, 1995; Horsch, 1993).

The use of genetically modified crops in combination with non-selective herbicides has attracted a great deal of concerned debate from both the public and the scientific communities (Kapteijns, 1993). Overall the public are concerned with the health risks and ethics associated with the consumption and production of genetically modified crops (Frewer *et al*, 1998; Boulter, 1997). The scientific community has raised concerns about the regulation and introduction of genetically modified crops and the possible release and indiscriminate hybridisation of the herbicide-tolerance genes into agriculture and the natural ecosystem (Marshall, 1998; Rissler and Mellon, 1996; Radosevich, 1993). Concerns have also been reported regarding the safety of genetically modified crops where the insertion of foreign genes into host crops has led to the unexpected production of toxic metabolites and allergic reactions (Inose and Murata, 1995; Nordlee *et al*, 1996).

A number of workers have reported the ongoing world-wide occurrence of herbicide-resistant weeds. Heap (1997) has reported that an average of nine new cases of herbicide weed tolerance occur annually and that 61 weed species have evolved resistance to the triazine herbicides. Powles *et al* (1998) have reported that after fifteen years of successful use in Australia, the herbicide glyphosate has failed to control widespread populations of the ryegrass weed. This report has serious implications for the use of crops genetically engineered to be resistant to non-selective herbicides such as glyphosate; clearly in this case the biotechnology involved would be out-of-date. A possible scenario exists in which the agrochemical and biotechnology industries would need to operate in a state of constant 'catch-up' as weeds evolve to become as equally resistant as the genetically modified crops with which they compete, making their control with non-selective herbicides ineffectual.

Perrin (1997) suggests that the use of biotechnology will not solve the problems associated with sustainable global food supply and proposes that various non-chemical approaches, combined with minimal pesticide use, need to become more available and affordable through appropriate commercialisation and government policy directives. Priority should be given to those that are compatible with ecology-based integrated pest management. Falconer (1998) has described the potential role of environmental policy instruments for achieving pesticide-use reduction and the use of market mechanisms to achieve policy objectives, especially through the introduction of financial incentives for producers to switch to Integrated Pest Management practices involving the application of less pesticide. Legg *et al* (1997) suggest that a 'clean technology' approach to modern agriculture is urgently needed and that both field management and biological approaches (such as the use of natural semiochemicals which influence insect behaviour) offer the means of reducing pesticide use. Also proposed is the use of computer-based decision support systems to improve the precision with which pesticides are applied. Mitchell *et al* (1996) describe the use of a geographic information system incorporating hydrological, soil erosion and pesticide-runoff models to predict the surface movement of herbicides in response to rainfall events as influenced by slope, soil, field management practices and time of herbicide application. This approach showed that the areas of greatest herbicide-runoff risk could be located within a catchment and the effect of alternative management practices evaluated to reduce the overall risk of off-site pesticide transport.

The types of field-crop management practices covered by the principles of Integrated Pest Management are numerous and include the use of natural pesticides (botanicals), the use of sacrificial crops, the use of semiochemicals, the use of conservation tillage, the use of buffer zones and the planting of riparian cover adjacent to streams bordering agricultural fields. Grant (1994) reports that research on pesticide products produced from natural plants has demonstrated a number of desirable properties within the context of Integrated Pest Management. Examples of such properties include mode of action, selective activity, short persistence and low mammalian toxicity. The study of chemical ecology, particularly involving pheromones and other semiochemicals that influence insect behaviour, will allow the development of ecological methods of pest control as alternatives to the exclusive and intensive use of pesticides (Pickett *et al*, 1997). These approaches should be used with other Integrated Pest Management strategies to maximise their effectiveness. For example, sacrificial crops should be planted alongside the main crops, and pests stimulated to colonise the sacrificial crop through the use of pheromones. Pest populations should be monitored to allow their effective treatment with botanical pesticides.

A number of workers have reported reduced pesticide loss in overland surface runoff from agricultural land, through the practice of conservation-tillage field-management techniques (e.g. Levanon *et al*, 1994). Essentially, this practice involves the use of the minimum or no post-harvest tillage when crop residues are left undisturbed in the soil. This has the effect of increasing natural soil drainage through the development of natural soil macropores combined with an increase in soil organic matter in the top layer of the soil (Levanon *et al*, 1993). The increase in top-soil organic matter reduces the probability of pesticide loss in overland surface runoff due to higher rates of biochemical degradation and shorter periods of soil persistence. In addition, pesticides tend to be less mobile due to their higher association with the increased levels of soil organic matter. The associated increased rates of rainfall infiltration reduce the probability and volume of overland surface runoff and therefore reduce the overall pesticide load lost. However, there are reports that when overland runoff does occur, the reduced volume may lead to higher pesticide concentration and also that the higher rates of infiltration may result in increased pesticide movement through the unsaturated zone into groundwater (Malone *et al*, 1996).

From a survey of the literature reporting the results of conservation tillage on pesticide loss in overland runoff, Baker *et al* (1995) report that field-management systems based on conservation tillage reduce herbicide loss in overland runoff by an average of 60% compared to mouldboard ploughing, with a range of 98 to 100%. However, for soils where water infiltration was limited due to high clay content, conservation tillage may not increase infiltration or reduce herbicide loss in overland flow. Jones *et al* (1995) have reported on the results of experiments carried out at Brimstone Farm to develop field-management strategies for the reduction of pesticide in storm runoff via macropore flow through the profile of high clay content soils. The studies conducted examined the effect of drainage restrictions, application rates, soil sealants and pesticide sorption properties. It was found that incorporation of pesticides into the surface soil had no effect on pesticide loss. Drainage restrictions reduced losses of moderately to strongly sorbed pesticides relative to control experiments. Pesticide losses were lower with reduced application rate and promising results were found for the use of soil sealants but further work was required before definite conclusions could be drawn regarding their effectiveness.

The previous measures considered for the reduction of the impact of pesticide use on agricultural land upon receiving waters have focused on practices to reduce pesticide use and minimise the probability of loss in surface runoff. For situations where runoff does occur, buffers zones may be used to intercept and treat the contaminated runoff. Buffer zones can be considered as areas of land approximately 5 to 100 metres wide located between the runoff source areas and the receiving waters. The buffer zone reduces the direct connection between the potential pollution source and the receiving water body by providing a biochemical and physical barrier to the movement of contaminated runoff directly into receiving waters (Muscutt *et al*, 1993). Baker *et al* (1995) reviewed the use of buffer zones and found that their efficiency for reducing herbicide runoff losses was related to the trapping of sediment-sorbed herbicides and that the removal of dissolved herbicides was associated with the sorption of herbicides onto organic matter and vegetation. The review concluded that the efficiency of herbicide removal from runoff depended on soil type, soil water content, runoff volume, buffer width and buffer vegetation. The range of removal efficiencies was between 9 and 91% with an average of 48%. Patty *et al* (1997) have reported on the effectiveness of using ryegrass buffer zones to remove pesticides, applied to winter wheat, from overland surface runoff. Buffer zones of 6, 12 and 18 metre widths located at the footslope of field plots ($250m^2$) reduced the volume of overland runoff by 43 to 99%. Lindane losses reduced by 72 to 100% and isoproturon losses by approximately 99%. The use of rainfall simulators showed that the buffer zones remained significantly effective during conditions of intense overland runoff.

From the experiments discussed above it can be concluded that the use of vegetative buffer zones can significantly reduce the adverse effects of pesticide transport, via overland surface runoff, on receiving water quality. However, as well as transport in overland runoff, pesticides can also enter receiving waters through movement in sub-surface interflow after initial infiltration through the soil surface (Harris *et al*, 1994). Nair *et al* (1993) have suggested that riparian buffer zones planted with deep-rooted poplar trees (*Poplus* sp.) next to streams have the potential for retarding pesticide movement in subsurface interflow through plant uptake and enhanced biodegradation (Figure 8-17).

Schnoor *et al* 1995 have reviewed the use of phytoremediation of organic contaminants in soils and sediments. Plants and trees are believed to remediate organic pollutants via three mechanisms:

- The direct uptake of contaminants and subsequent accumulation of non-phytotoxic metabolites into plant tissue.
- The release of exudates and enzymes that stimulate microbial activity and biodegradation in the rhizosphere, where typical microbial communities include bacteria, actinomycetes and fungi.
- The enhancement of mineralisation in the rhizosphere which is attributed to symbiotic mycorrhizal fungi and abundant microbial populations, which are supported by oxygen supplied by plant roots that in turn promote aerobic biodegradation in the rhizosphere.

The use of hybrid poplars planted as riparian zone buffer strips, along the banks of small streams, for the interception and treatment of pesticides in sub-surface agricultural runoff have been described (Nair *et al*, 1993). No performance data was given for the reduction of subsurface-runoff pesticide concentrations but it was reported that 10-20% of the applied atrazine was taken up by the trees. With reference to pesticide loss in runoff from agricultural land in the UK, Harris *et al* (1994) reported that approximately 30% of cereals are grown on clay soils that are normally underdrained to improve crop productivity.

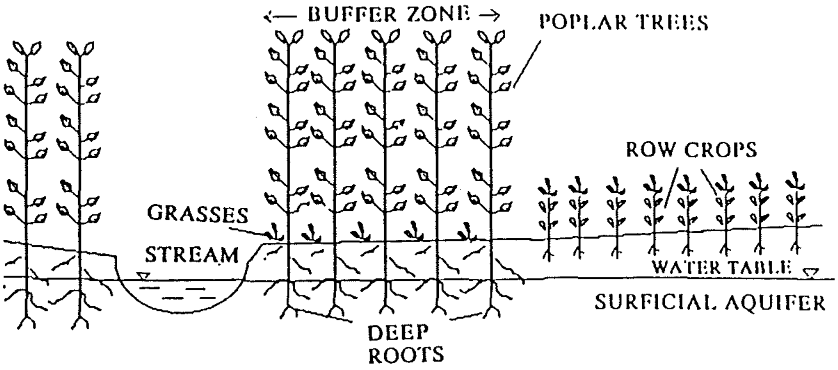

Figure 8-17 The use of riparian popular tree buffer zones to intercept and treat sub-surface interflow contaminated with pesticides

Muscutt *et al* (1993) suggested that in such situations the effectiveness of riparian buffer zones would be compromised since they would be by-passed by the sub-surface drainage systems. To circumvent this situation, Petersen *et al* (1992) suggested the creation of 'horseshoe wetlands' at subsurface drain outlets (Figure 8-18). These are described as semi-circular excavations within a more extensive buffer strip at each drain outlet with dimensions of approximately 10m x 8m and planted with aquatic macrophytes such as reeds. A number of authors have described the effective treatment of organic compound-contaminated runoff through the use of natural and constructed wetlands (Ellis *et al*, 1994; Revitt *et al*, 1997; Cobban *et al*, 1998). Stoeckel *et al* (1997) report that riparian wetlands could be useful for the treatment of herbicides from non-point sources such as agricultural runoff. Alvord *et al* (1996) studied the use of constructed wetlands for the treatment of atrazine and found that load reductions of 26 to 64% were achievable depending on the runoff residence time within the wetland.

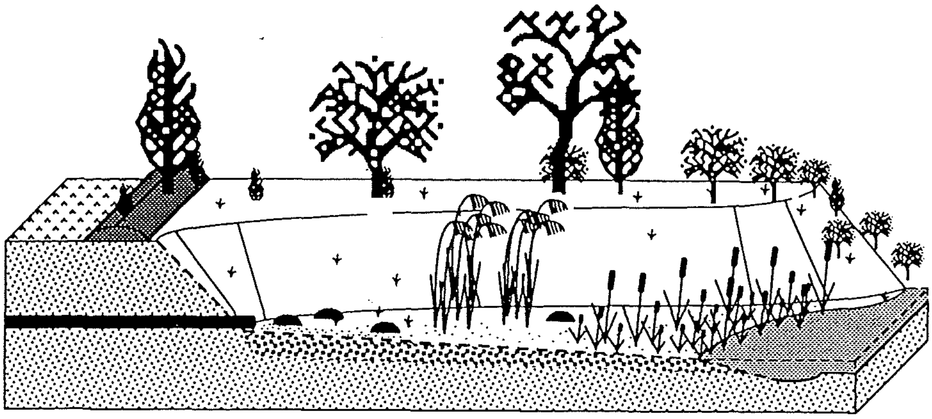

Figure 8-18 Diagram of riparian wetland horseshoe to receive sub-surface runoff from a tile drain system and act as a zone for pesticide and nutrient retention (from Petersen *et al* (1992))

The phytoremediation mechanisms associated with macrophytic reedbed plantations are very similar to those reported by Schnoor *et al* (1995) described above, with the additional advantage that macrophytes can grow in soil environments where their rhizospheres are submerged in water with air being supplied to the root system through the plant stem. This localised diffusion of oxygen in the vicinity of the rhizosphere allows the simultaneous activity of both aerobic and anaerobic microbial populations.

It is not known to what extent reductions in pesticide runoff brought about through the use of Integrated Pest Management practices are additive. However, it is considered that the use of conservation tillage and buffer zones along with other practices in a systems approach, would produce greater reductions in pesticide runoff than would be expected with a single practice, thus minimising the risk to receiving waters.

The practices available for reducing the impact of pesticide runoff, from agricultural land, on receiving water can be classified as either biotechnologically- or ecologically-based approaches to Integrated Pest Management. The use of genetically modified crops combined with non-selective herbicides has raised a number of concerns among the public and scientific communities with respect to health risks, ethics, regulation, release of the herbicide-tolerance gene into the environment and the evolution of herbicide-resistant weeds. It has been suggested that the use of biotechnology to provide global food supplies is unsustainable and that ecologically-based Integrated Pest Management is urgently required. It is considered that this should be facilitated through the use of environmental policy instruments and consequent financial incentives for producers to adopt ecologically-based Integrated Pest Management strategies involving the use of less pesticide.

Practices that are covered by Integrated Pest Management include the use of naturally derived pesticides in conjunction with sacrificial crops and semiochemicals; measures for reducing the probability of pesticide runoff occurring such as conservation tillage; and measures for intercepting and treating contaminated overland and subsurface runoff including the use of riparian buffer zones planted with grass, trees and reedbeds as appropriate. Finally it is suggested that the combined use of these measures in a systems approach would provide greater protection for receiving waters than would be expected with a single practice and that the design of an effective system may be best achieved through the use of decision support techniques involving geographical information systems that take account of soil topography, soil hydrology and field management practices.

8.3.2 Within the urban environment

Before considering the measures available to reduce the impact of non-agricultural pesticide use on receiving surface waters, it is worth reviewing their wide usage pattern. As described in Section 2.4.2, from a survey of herbicide use in non-agricultural situations in England and Wales (DoE, 1991) the range of significant user groups included: power and industry, local transport, forestry, water companies, and the golf and leisure industries. The main reasons given for the use of pesticides in non-agricultural situations were those of safety and aesthetics. For example with respect to safety, the establishment of weeds on paved hard-surfaces could produce raised edges and unevenness and with respect to aesthetics. The public expect paved areas such as shopping centres to be free from unsightly weeds. From the DoE survey it was estimated that the greatest usage with respect to substrates were applications to hard surfaces. The monitoring programme at

North Weald and other work (Court *et al*, 1995; Davies *et al*, 1995; Heather and Carter, 1996) indicates that compared to applications made to grassed-amenity areas and gravelled areas, pesticide applications made to hard-surface substrates are most likely to produce an adverse effect on receiving water quality. Therefore, with respect to reducing impacts upon receiving surface waters through the non-agricultural use of pesticide, the measures and practices considered will focus on situations where applications are made to hard surfaces.

Apart from the work described in this thesis, very little research has been carried out on the environmental fate of pesticides applied within the non-agricultural environment (Racke, 1993). This reflects the fact that compared with the use of pesticides on agricultural land, the awareness and acknowledgement that pesticide loss from use on non-agricultural land leads to a significant water-quality problem is relatively recent (Clay and Stevens, 1991; White and Pinkstone, 1993). The incorporation of the EC Drinking Water Directive (80/778/EEC) into the Water Supply (Water Quality) Regulations 1989 and the results of associated monitoring programmes showed the widespread presence of pesticides in surface waters (see Section 2.5.1). These included simazine and atrazine in situations where their level of agricultural use was negligible and their presence was thought to be due to their relatively minor use on roads, railways and amenity hard-surfaces for the total control of weeds (White and Pinkstone, 1995). In response the Advisory Committee on Pesticides banned the non-agricultural use of simazine and triazine from September 1993. Subsequently, driven by concerns regarding the protection of the aquatic environment and the quality of drinking water resources, a number of programmes were set up by the water supply companies, the Environment Agency, the Department of the Environment and the agrochemical companies. The purpose of these programmes was to educate non-agricultural pesticide users as to the consequences to drinking water resources of the over-use and misuse of pesticides on hard surfaces (DoE, 1994). Users were encouraged to review the necessity of weed-control practices through the adoption of an integrated approach to weed management (Garnett, 1995). This focused on the reappraisal of weed control objectives and emphasised that herbicide use should be viewed as the last available option once the use of alternative measures had been considered. A blanket pesticide application regardless of the level of weed infestation should be avoided. Users were encouraged to re-evaluate the need for weed control on a case-by-case basis and on a strategic basis to assess how much weed growth was acceptable. Where possible the replacement of the use of residual (long acting) herbicides such as diuron by less persistent contact herbicides such as glyphosate and imazapyr was encouraged.

Such approaches to integrated urban weed management were extensively reviewed and examined by Davis and Dudley (1989) in an investigation commissioned by Norwich City Council on the use of pesticides by local authorities. With respect to hard-surface pesticide applications, the investigation reviewed practices used for the maintenance of paths, kerbs and channels, and highways and, where practical, gave recommendations for replacing pesticide use with alternative practices. The report concluded that in some instances the use of manual weeding was a viable option considering that weeds do not emerge from every road and footpath. The biggest problem would probably exist on the least-used thoroughfares and, in most cases, pedestrian trampling would control emerging weeds on footpaths and pavements. For the control of kerbside weeds it was reiterated that the operation of roadsweepers was very effective at preventing the emergence of weeds. It was also suggested that optimum landscape design could minimise weed problems at source and that good structural maintenance could prevent the ingress of weeds. For situations where the manual weeding of hard surfaces was impractical, the use of flame and infra-red weed control technologies were viewed as viable alternatives to the use of pesticides. Clay and Stevens (1991) and Greenfield (1993) reported that flame techniques incorporating propane burners were effective alternative techniques to herbicide use, especially as replacements for contact herbicides which have to be applied to emergent weeds.

Little research has been conducted on measures to reduce the impact of hard-surface pesticide use on receiving water quality. This reflects the relatively recent awareness that pesticide losses from hard-surface applications can be detrimental to receiving water quality. However, research on the occurrence, effects and measures to mitigate highway and urban runoff have received attention from a number of workers (Perry and McIntyre, 1986; Ellis, 1989; Livingstone *et al*, 1989). These studies reported that highway and urban runoff was characterised by elevated levels of faecal coliforms, nutrients, heavy metals, hydrocarbons and polyaromatic hydrocarbons. Other than the work carried out at North Weald (Ellis *et al*, 1997) there have been very few reports of the contamination of urban runoff with pesticides as a result of their direct use on urban hard surfaces. In many cases the measures applicable for the control and treatment of highway and urban runoff contaminated with heavy metals and polyaromatic hydrocarbons may be equally applicable to runoff contaminated with pesticides and therefore it is useful to review these practices. Smisson (1991) describes a highway-and urban-runoff management approach termed 'source control' which aims to address the problem of contaminated runoff where it begins. The successful operation of a source control system relies firstly on uncontaminated runoff being allowed to either recharge groundwater or to discharge to a local watercourse and secondly that all contaminated runoff should be collected by the foul sewer system and treated at the local treatment works. For the control and infiltration of uncontaminated runoff to groundwater a number of techniques were suggested including drainpipe discharge to grassed areas, permeable pavements, local soakaways and swales (grass ditches with shallow side slopes).

However, without the use of engineered flow control devices it is probable that in storm-events of given magnitudes, the contaminated runoff would overload the foul drainage system and the treatment works. Alternatively, a number of workers have shown that rather than divert contaminated runoff into the foul sewer system, runoff contaminated with heavy metals, hydrocarbons, polyaromatic hydrocarbons and faecal coliforms can be efficiently treated by being passed through natural wetlands, and more effectively, through constructed wetlands planted with reeds (Cutbill, 1993; Ellis *et al*, 1994; Revitt *et al*, 1997; Shutes *et al*, 1997). The treatment mechanisms described in Section 8.3.1, including reed uptake and contaminant mineralisation by the enhanced microbial population associated with the root rhizosphere of reed species (such as *Typha latifolia* and *Phragmites australis*) have been attributed to the successful treatment of highway and urban runoff contaminated with metal and micro-organic pollutants (Cooper *et al*, 1996). Although there are no literature reports of the successful treatment of pesticide-contaminated highway and urban runoff, a number of workers have reported on the treatment of micro-organic pollutants through the use of natural and constructed wetlands. Jones *et al* (1994) reported the efficient removal of polyaromatic hydrocarbons from urban and highway runoff by passage through the natural reedbeds surrounding the Welsh Harp reservoir in North London. Experimental pilot reedbeds have been evaluated for their efficiency in reducing glycol based de-icing agents in runoff from Heathrow airport. Using systems planted with *Typha latifolia* and *Phragmites australis*, results from initial dosing trials showed load reductions of approximately 50% and 19% for ethylene and diethylene glycol respectively (Revitt and Llewellyn, 1996). Finally, Cobban *et al* (1998) described the use of a natural wetland at the Imperial Chemical Company, Billingham (NE England) to reduce the concentrations of chlorophenols in effluent wastewater by more than 95%. Of the chlorophenols, one was pentachlorophenol which is an active ingredient used in a number of herbicide products.

In summary, in the non-agricultural environment, pesticides are mainly used for reasons of safety and aesthetics and the majority of applications are herbicides to hard surfaces such as road kerbstones and paved areas. The few reports of herbicide transport after non-agricultural use, including the monitoring at North Weald, have shown that pesticide applications to hard surfaces are most likely to have a detrimental effect on receiving water quality. In the UK, the awareness that hard-surface pesticide applications may have an effect on receiving water quality, became more apparent with the enhanced monitoring of water resources associated with the privatisation of the water industry in the late 1980s. As a result the most common receiving water contaminants, simazine and atrazine, were withdrawn from non-agricultural use and the government, the Environment Agency and the water and agrochemical industries encouraged non-agricultural users to review their use of pesticides and to adopt integrated weed management programmes. Users were encouraged to reassess the need for absolute weed control and to view herbicide use as the last available control option and, if herbicides were used, to replace the use of residual herbicides (long persistence) with contact herbicide (short persistence), where practical. A number of alternatives to pesticides for treating weeds on hard surfaces were suggested including manual weeding, pedestrian trampling, the use of roadsweepers, and flame and infra-red weed control technologies.

Few reports exist on the treatment of pesticide-contaminated highway and urban runoff. Therefore the adoption of the present strategies for the treatment of highway and urban runoff contaminated with heavy metals and polyaromatic hydrocarbons is suggested. The use of 'source control' where uncontaminated runoff is allowed to infiltrate the groundwater or be discharged to a local watercourse whereas contaminated runoff is diverted to treatment works is suggested. As an alternative to treatment at sewage works it has been suggested that pesticide contaminated runoff could be efficiently treated through the use of natural and constructed wetlands which have been shown to successfully treat micro-organic pollutants including chlorophenols.

8.4 Conclusions and comments

The research in this thesis gives an insight into the fate of pesticides applied to agricultural and non-agricultural land and the subsequent impacts on receiving surface waters. The work was carried out at North Weald between Spring 1991 and Spring 1993 during which period concentrations present in an upper catchment watercourse were monitored during and between rainfall events, in conjunction with the continuous measurement of flow rate and rainfall. The receiving stream was monitored as it left the head of the catchment (Site A) which was predominantly made up of agricultural and wooded land. After leaving this area, the watercourse flowed through an urbanised area composed of residential developments, a railway line, a golf course and a small industrial estate. The stream was also monitored as it left this area (Site D).

The monitoring of runoff at the outlets of the agricultural sub-catchment and the whole catchment allowed the comparison of the temporal surface hydrology characteristics of the two land areas. Although an in-depth comparison was limited by the intermittent failure of the flow monitoring equipment at Site D, it was observed that the varying land use of the two areas led to differing surface runoff characteristics. For the same rainfall event, the extra surface runoff generated from the impervious areas associated with roofs, roads and paved areas of the urbanised area tended to give higher water balances with less seasonable variability compared to the runoff from the vegetated agricultural sub-catchment. The greatest variation produced by the differing land uses of the two areas was most apparent during the summer growing season. Typically, during this period the soil moisture deficit of the agricultural sub-catchment was sufficiently large to prevent the generation of significant surface runoff volumes. However, within the urbanised catchment, although the vegetated areas were similarly unproductive, the seasonally constant imperviousness of the hard-surfaced areas produced significant volumes of surface runoff regardless of the prevailing soil moisture deficit. Further, in the urbanised catchment, for a given rainfall event, the event duration and rainfall-runoff lag time were generally shorter compared to the same parameters for the agricultural sub-catchment. However, there were instances during the wettest part of the 1992/93 winter where Site A hydrographs peaked marginally before those of Site D. This was probably caused by the more rapid movement of overland runoff generated on the bare saturated soil of the arable portion of the agricultural sub-catchment, compared to the runoff from the urbanised area which may have been impeded by sur-charging in the storm sewer network.

8.4.1 Pesticide movement from the agricultural sub-catchment

The clay soil of the agricultural sub-catchment was particularly prone to the generation of surface runoff. The fine structure of the soil produced relatively low levels of hydraulic conductivity and therefore was susceptible to being waterlogged from late autumn to early spring. To improve the soil drainage all the arable fields of the agricultural sub-catchment were underdrained. At times of low soil moisture content, the fine structure of the clay soil also made the soil profile prone to cracking, which, combined with the underdrainage, provided preferential flow routes which by-passed the soil matrix thus allowing the rapid movement of surface water through the soil profile into drainage ditches and streams. Therefore with respect to pesticide loss in surface runoff, the clay-soil fields of the agricultural sub-catchment to some extent represented a potential worst case scenario.

The application details of the herbicides simazine, chlorotoluron and isoproturon were obtained through close liaison with farm managers. Each herbicide was applied following normal agricultural practice according to product label recommendations. The majority of the herbicide applications were made during October and November 1991 with a second isoproturon application during February 1993. Atrazine was detected both in baseflow and event runoff but no details were available regarding its application. It was considered that the detections were the result of applications to the M11 motorway which bordered the top of the agricultural sub-catchment.

Generally throughout the monitoring period, individual herbicides were detected in baseflow at concentrations of up to four times the EC Drinking Water Directive of 0.1µg/l. The level of exceedence decreased as the period between application and detection increased. With regard to the time between herbicide application and last detection, the durations of individual herbicide-exceedence periods in inter-event baseflow were in the approximate same order as the herbicide soil biochemical half-life values.

The monitoring of inter-event baseflow concentrations showed that herbicide residues were detectable at concentrations above the EC Drinking Water Directive limit for approximately 150 days after application. For simazine, the maximum concentration detected in baseflow was 0.30µg/l and residues were detected at concentrations above 0.1µg/l for 132 days after application; for isoproturon the respective values were 0.31µg/l and 154 days; and for chlorotoluron the respective values were 0.19µg/l and 148 days. Although no application details were available for atrazine, the maximum concentration detected in inter-event baseflow was 0.39µg/l.

With the onset of a storm event, the herbicide concentration determined in event runoff rapidly increased, and in some cases, rose to values thirty-two times that of inter-event baseflow concentrations and one-hundred times the EC Drinking Water Directive (EC-DWD) limit. The results of the storm event monitoring showed that surface runoff herbicide concentrations exceeded the EC-DWD limit in events occurring 320 to 550 days after their application, depending on the individual herbicide. It was observed that the magnitude of exceedence was generally related to the period of time that had lapsed between herbicide application and detection. In addition, the post application period during which exceedence occurred was related to individual herbicide soil half-life values. A review of all the herbicide data, for individual storm events, showed that the range of detected peak concentrations was 0.03µg/l to 10.0 µg/l with a median of 0.34µg/l; the range of event mean concentrations was 0.03µg/l to 4.25µg/l with a median of 0.22µg/l; and the range of losses with respect to application was 0.0004% to 0.204% with a median of 0.0046%.

The maximum peak herbicide concentration detected (10µg/l) and the maximum event mean concentration (4.25µg/l) were both for isoproturon. The total seasonal isoproturon loss ranged from 0.058 to 0.47% ($^{w}/_{w}$). It is worth noting that the ranges of concentrations and application loss data were generally higher than the equivalent data produced from a similar isoproturon runoff experiment at Rosemaund Farm (Williams *et al*, 1995). The difference is probably attributable to variations in soil composition, field management and soil topography.

For the November 1991 simazine application, the peak and maximum event mean concentrations in storm runoff were 0.6µg/l and 0.33µg/l respectively, which occurred 259 days after application during the event of 13/8/92. After this event, concentrations in event runoff decreased to a point of no detection in the storm event occurring 353 days after the application. Simazine residues were detected in runoff at Site A at concentrations above the EC-DWD for up to 347 days after the application. The peak atrazine concentration detected in event runoff was 0.21µg/l. The total simazine loss with respect to application, in monitored storm events, was 0.085% ($^{w}/_{w}$).

The pattern of occurrence of chlorotoluron residues in surface runoff subsequent to the October 1991 application was somewhat unusual compared to the other monitored herbicides. Generally the herbicide event mean concentration followed a downward trend after the first post-application monitored storm event. However, the chlorotoluron event mean concentration appeared to increase during the first few post application events before following the general downward trend. This pattern was particularly obvious if the event mean concentration based on direct runoff, rather than total runoff, was considered. The behaviour was attributed to the particularly dry weather that occurred after the chlorotoluron application, which probably enabled the chlorotoluron molecules to bind with soil-particle active sites that would normally have been occupied by more polar water molecules. With time, as the catchment became wetter during the autumn of 1992, the chlorotoluron molecules were displaced into the soil water and made available for movement in event runoff. Chlorotoluron was probably more susceptible to this effect than the other monitored herbicides because of its more polar character derived from its higher solubility and also its longer half-life value. These factors would have comparatively increased its affinity with the active polar sites of the soil particle substrate in which state the molecules would have been relatively stable.

For chlorotoluron, the maximum concentration of 2.23µg/l occurred 378 days after application during the event of 9/11/92. The maximum event mean concentration occurred on 13/8/92 which was 290 days after the application. The differing times of occurrence of these parameters resulted from the degree of overlap of concentration and hydrograph peaks for specific events which had a pronounced effect on the chlorotoluron load transported during an event. Chlorotoluron residues were detected in storm event runoff at concentrations above the EC-DWD limit for up to 545 days after the application. This was the longest persistence period of the monitored herbicides and was indicative of chlorotoluron's greater half-life value compared with simazine and isoproturon. The total chlorotoluron loss with respect to application, in monitored storm events, was 0.058% ($^{w}/_{w}$).

Isoproturon residues were detected in storm event runoff at concentrations above the EC-DWD limit for up to 321 days after the 1991 application. The highest exceedence occurred in the first storm event after the 1993 application when the EC-DWD limit was breached by a factor of one hundred. The fate of the isoproturon applications in October-November 1991 and February 1993 was heavily influenced by the contrasting rainfall patterns that occurred during the two harvest years. Compared to the average monthly rainfall totals for the catchment, the 91/92 season was drier than average and the 92/93 season was wetter than average. As a consequence, for the 1991 isoproturon application the first significant storm event to be monitored did not occur until after 177 days whereas the comparable period in 1993 was 57 days. The difference in temporal rainfall distribution and the subsequent timing of post application storm events, had a significant effect on seasonal isoproturon losses. For the 1991 application, the maximum concentration of isoproturon detected in event runoff was 1µg/l compared to 10µg/l for the 1993 application. As mentioned previously, the event mean concentration values were 0.34µg/l and 4.25µg/l respectively and the total seasonal losses with regard to application were 0.008% ($^{w}/_{w}$) and 0.477%($^{w}/_{w}$) respectively.

The timing of the Spring 1993 isoproturon application to the North Weald agricultural sub-catchment and subsequent storm events coincided very closely with a similar experiment carried out at Wytham Farm, Oxfordshire (Johnson *et al*, 1994). It was very probable that the runoff from each site was influenced by the same frontal weather system. The work at Wytham Farm was carried out on a field plot (0.18ha) and comparisons of the isoproturon loss data from the first post-application storm events showed close agreement once the specific parameters of each site and experiment were taken into account. Though only comparing one storm event, these results demonstrate that the use of field plots for pesticide fate studies, can be representative of catchment scale behaviour.

The in-depth analysis of the fate of simazine was to some extent precluded due to the relative paucity of concentration data, compared to that for isoproturon and chlorotoluron, resulting from the autumn of 1991 application of the herbicide. Correlation analysis of simazine data with the associated hydrological data suggested that the elapsed time period between herbicide application and storm event occurrence was the most significant factor for interpreting herbicide loss behaviour. Though no application details were available, it appeared that the same factor was applicable for interpreting the loss behaviour of atrazine.

Correlation analysis carried out on the isoproturon runoff data relating to the Autumn 1991 and Spring 1993 applications indicated that runoff concentrations were strongly dependent on the time period between application and storm event occurrence. Comparison of the decay constants relating to the exponential regression of these variables showed that the half-life values for the decrease of isoproturon runoff concentrations with time, were significantly different between the two data-sets (83 days for the Autumn 1991 application and 13 days for the Spring 1993 application). The first value related to a data-set sampled between 177 and 339 days after application whereas the second value related to a data-set sampled between 57 and 81 days after application. Therefore, as found by other workers, an explanation of the differing half-life values was through consideration of the ages of the two data sets and could also be attributed to the isoproturon soil-partition coefficient increasing with time as reversibly sorbed isoproturon molecules became irreversibly associated with soil sorption sites.

For chlorotoluron, correlation analysis of runoff data with associated hydrological data, similarly showed that runoff concentration was related to the time period elapsed between application and storm event occurrence and also that loss with respect to application was related to runoff volume. Using multiple linear regression analysis, statistical models based on hydrological and associated variables were produced for the simulation of chlorotoluron runoff behaviour. Models were derived for the simulation of peak storm event concentrations, event mean concentrations and event losses with respect to application and were found to give excellent results for the prediction of measured runoff data. However, further statistical evaluation of the models showed that they were inherently unstable and were probably highly site-specific and therefore would need to be tested on an independent chlorotoluron runoff data-set from North Weald and other clay-soil agricultural catchments in order to determine their general robustness and applicability.

The storm runoff data for simazine, chlorotoluron and isoproturon were used to evaluate the performance of the SoilFug fugacity model produced by Antonio Di Guardo while working at Milan University (Di Guardo *et al*, 1994). Overall the performance of the model for the simulation of event mean concentrations was very good and generally all simulations were between a factor 1.5 and an order of magnitude. In every case the model had a tendency to over-predict with respect to the measured runoff data. For chlorotoluron particularly, this tendency appeared to increase with time and was attributed to the soil-partition coefficient increasing with time. Generally, the over-prediction behaviour was associated with the assumptions and simplifications made by the model in order to reduce the amount of complexity required for its use.

8.4.2 Pesticide movement from the urbanised catchment

The interpretation of the pesticide movement from the urbanised catchment was more difficult to define than that for the agricultural sub-catchment. This was because storm runoff sampled at Site D was usually composed of runoff from both catchments and sources of simazine, atrazine, chlorotoluron and isoproturon were applied to both catchments. Diuron was the only herbicide specifically applied to the urbanised catchment. Compared to the agricultural sub-catchment, the urbanised catchment was characterised by more diverse land use including agricultural land, areas of residential development, grassed amenity areas, general paved areas, a railway line and an array of roads and pavements. Subsequently, it was found that the surface hydrology and pesticide loss characteristics were strongly influenced by the imperviousness of the varying types of herbicide application substrate within the urbanised catchment.

The application details of simazine, atrazine, chlorotoluron and diuron were obtained by close liaison with a number of herbicide users who applied the products according to label recommendations following normal codes of good practice. Up to October 1991 simazine was applied to the railway line by London Underground Ltd for total weed control. In 1992 its non-agricultural use was revoked and it was replaced with diuron. A mixture of atrazine and diuron was used for grass and weed control on grassed amenity areas and paths by the Epping Forest District Council Parks and Recreation Department. Chlorotoluron was applied to an area of arable land within the urbanised catchment, for protection of cereal crops. Diuron was applied to roadside kerbstones and pavements for total weed control by Epping Forest District Council Roads and Highways Department.

The monitoring of inter-event baseflow at Site D showed the common occurrence of simazine, atrazine, chlorotoluron, isoproturon and diuron at concentrations above the 0.1µg/l limit of the EC-DWD. The most common and greatest exceedences were for simazine and atrazine. Spot sampling of secondary watercourses and urban drainage systems suggested the source of these detections was the railway line. A laboratory rainfall-runoff experiment showed that the railway ballast readily leached significant concentrations of simazine and atrazine. The simazine was related to an application in September 1991 whereas the atrazine detection was related to an application several years previously which suggested that the half-life of a herbicide applied to railway line ballast was considerably longer than for soil applications. The highest detections of simazine and atrazine in baseflow were observed at the beginning of the monitoring programme. During the course of the programme the base flow concentrations of simazine and atrazine were observed to decrease possibly as a result of the 1992 revocation of the non-agricultural use of the triazine herbicides.

The detection of chlorotoluron in inter-event baseflow was difficult to fully interpret due to significant applications in both catchments. As the period between the single application in Autumn 1991 and sampling date increased, baseflow concentrations were observed to decrease reflecting the gradual removal of chlorotoluron through biochemical decay and off-site loss.

Detections of isoproturon were relatively few and the level of occurrence declined with the passage of the monitoring period. This behaviour was attributed to the absence of an application within the urbanised catchment combined with the relatively quick degradation of the application made within the agricultural sub-catchment.

Diuron, despite being applied four times within the urbanised catchment, during the course of the monitoring programme, was only detected in baseflow at Site D on two occasions at a maximum concentration of 0.32µg/l. It was considered that the relative absence of diuron could be generally explained by the hard surface nature of the application substrates which were directly drained into an engineered drainage system linked to the main watercourse. In such situations the herbicide would have been prevented from infiltrating the soil profile during event rainfall from where it would have interacted with sub-surface baseflow between storm events.

With the onset of a storm event, herbicide concentrations at Site D rapidly increased from the levels detected in baseflow during non-storm conditions. Most often the water samples from Site D were composed of runoff containing simazine and atrazine residues from the agricultural sub-catchment and the urbanised catchment, and therefore it was difficult to infer pesticide fate behaviour that was specific to the urbanised catchment. However, for a number of storm events, due to negligible runoff from the agricultural sub-catchment, the water sampled at Site D was almost exclusively composed of runoff containing triazine residues from within the urbanised catchment. Diuron was only applied to the urbanised catchment and therefore data interpretation was more straightforward. A review of all the herbicide data that was solely derived from applications within the urbanised catchment indicate a range of peak concentrations between 0.2µg/l and 238.42µg/l with a median of 0.7µg/l; a range of event mean concentrations between 0.01µg/l and 142µg/l with a median of 0.4µg/l, and a range of losses with respect to application between 0.01% and 45.1% with a median of 0.28%. For each parameter, the maximum range values were related to a diuron application made by the Roads and Highways Department to roadside kerbstones and pavements. Typical durations for the presence of diuron in event runoff at concentrations above the EC-DWD were between 80 and 150 days. Values for other the herbicides were more difficult to determine due to the existence of multiple sources from both catchments.

The fates of herbicides in relation to type of applied substrate in the urbanised catchment are shown in Table 8-31. For simazine and atrazine, the data shown in the Table relate to storm events monitored at Site D that were essentially composed of runoff containing residues from the urbanised catchment, and therefore solely indicative of the behaviour of a non-agricultural application. The Table shows herbicide loss, peak concentration and event mean concentration ranges with respect to the different types of substrate treated within the urbanised catchment. Although the herbicides had slightly different physico-chemical properties and the data-sets were not collected under standardised conditions, the nature of the application substrate appeared to have had a pronounced effect on the herbicide fate. Thus as the application substrate became more impervious and directly associated with an engineered drainage system, a greater fraction of applied herbicide was transported in event runoff and at higher concentrations. This behaviour was most apparent for the diuron application to the roadside kerbstones and pavements, which due to their minimal infiltration capacity and organic matter content (which would promote pesticide retention and microbial degradation), produced very significant runoff losses. In this environment it was considered that evaporation and photodegradation would be more significant as an in-situ loss mechanism. Generally, due to the lack of substrate retention, the data showed that as application substrates became more characteristic of a hard surface, the associated higher herbicide loss in storm event runoff entailed a more short lived herbicide presence in subsequent storm events.

The comparison of the isoproturon runoff data in the storm events following the Spring 1993 application to the agricultural sub-catchment, at Sites A and D, show an interesting phenomenon. The isoproturon load determined at Site A was found to be between three to seven times greater than that determined at Site D. This behaviour was considered to be the result of the significantly higher ionic strength of the runoff from the urbanised catchment at that time, as a result of major road de-icing operations, that would have 'salted out' the isoproturon from the agricultural runoff as it mixed with the runoff from the urbanised catchment.

Table 8-31 Herbicide fate related to application substrate type, showing range of loss with respect to application, range of peak concentration, and range of event mean concentration

Herbicide	Substrate	Loss (%) range	Peak concentration range (μg/l)	Event mean concentration range (μg/l)
Diuron	Railway line ballast	0.06 - 0.177	0.15 - 0.69	0.07 - 0.09
Simazine	Railway line ballast	0.04 - 0.84	0.47 - 2.23	0.26 - 1.08
Atrazine	Grassed amenity areas and paths	0.1 - 0.1.11	0.68 - 1.28	0.48 - 0.58
Diuron	Grassed amenity areas and paths	0.29 - 3.28	1.06 - 1.33	0.65 - 0.66
Diuron	Kerbstones and pavements	0.25 - 45.1	0.96 - 238.39	0.11 - 142

Although designed to simulate the movement of pesticides from agricultural catchments, an attempt was made to use the SoilFug model to simulate the behaviour of diuron applied to a hard surface. This was essentially achieved by adjusting the model soil property input parameters to emulate the behaviour of a hard surface environment. The result suggested that such an application was possible but that the exercise would need to be repeated for a number of different compounds and environmental scenarios before the model could be recommended for such applications with any degree of confidence.

8.4.3 Comparison of agricultural and non-agricultural pesticide loss to receiving surface waters

The key differences between the impact on receiving surface water of normal pesticide use in the agricultural sub-catchment and the urbanised catchment, are summarised in Table 8-32 and Figure 8-19. The Table shows the respective pesticide inputs and the subsequent differences in terms of the ranges and median values for application loss, peak concentration and event mean concentration for grouped pesticide runoff data from the agricultural sub-catchment and the urbanised catchment. The figure shows the upper end of the range values for the same parameters. It is worth noting that the pesticide input value for the urbanised catchment included 70kg of chlorotoluron applied to arable land, and that the consequent runoff data had no effect on the parameter ranges shown.

Table 8-32 Comparisons of pesticide fate parameters for the agricultural sub-catchment and urbanised catchment

Parameter	Agricultural sub-catchment	Urbanised catchment
Total pesticide input (kg)	187.829	73.501*
Event mean concentration (µg/l)	0.03 - 4.25 (median 0.22)	0.01 - 142 (median 0.4)
Peak concentration (µg/l)	0.03 - 10 (median 0.34)	0.2 - 238.42 (median 0.7)
Application loss (%)	0.0004 - 0.240 (median 0.0046)	0.01 - 45.1 (median 0.28)

* 70kg was applied to arable land which had no effect on the parameter ranges

Overall, the pesticide runoff data from the two catchments shows that although comparatively much higher amounts of herbicide were applied to the agricultural sub-catchment, the level of loss and magnitude of herbicide concentrations were significantly higher following relatively minor applications in the urbanised catchment.

It is considered that the underlying factor that differentiated between the fates of pesticides applied to the agricultural sub-catchment and the urbanised catchment, was the difference in the application substrate properties. Specifically, the surface hydrology and pesticide retention behaviour of hard urban surfaces, normally characterised by very low infiltration capacity and organic matter content, allowed applied pesticides to be transported, un-hindered, in storm event runoff to receiving surface waters. Further, the pesticide would have been removed rapidly from the application site in event runoff and transported to the receiving water via an engineered drainage system thus circumventing any opportunity for retention and amelioration by a soil matrix.

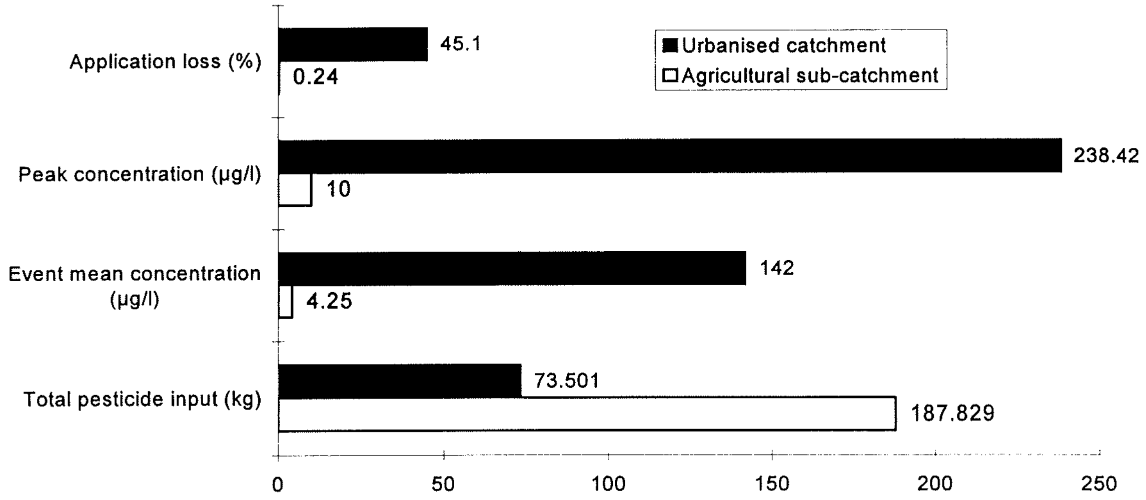

Figure 8-19 Comparison of summated pesticide fate parameters for the agricultural sub-catchment and urbanised catchment [Upper range values shown, see Table 8-32]

Overall it is concluded that although the non-agricultural use of pesticides only makes up approximately 3% of annual pesticide use, the described mechanisms result in surface waters in many lowland areas of the United Kingdom being contaminated with pesticide residues at concentrations which are often above the 0.1μg/l limit of the EC Drinking Water Directive. In addition, the pesticides derived from agricultural use also contribute to the exceedence of the recommended standard.

8.4.4 Comments on field work and laboratory procedures

A number of conclusions can be drawn regarding the manner in which the experimental work at North Weald was carried out and concerning issues which could have improved the operation of the experiment. With respect to the field experiment a number of problematic areas were identified. The collation of pesticide application data, particularly for the urbanised catchment, was difficult due to the fact that pesticides were applied to the catchment by a multitude of independent users who in some cases were not prepared to supply pesticide application details. This situation could have been improved if the details of significant pesticide applications made to the catchment had been archived to a central database which could also have served as an useful information resource for developing catchment management policy.

Field equipment failure was also identified as an area which could have been improved upon. The intermittent breakdown of the flow measuring equipment at Site D prevented a continuous comparison of the temporal hydrological characteristics of the agricultural sub-catchment and the urbanised catchment. The problems at Site D could have been solved by the installation of proven reliable equipment backed up by a second system, as was the situation at Site A. A number of important storm events were missed at both sites because of sampler trigger failure which was either rendered inoperable by accumulated vegetative debris or preferentially closed by floating debris or a natural disturbance. This situation could have been rectified either through the use of an electronic system or by having the sampler activation linked to real-time flow rate.

A number of manual samples were taken during non-storm conditions from secondary watercourses, in order to identify the locations of all possible pesticide residue sources within the North Weald catchment. Although the data from these samples was useful, it was considered that a more detailed representation of pesticide movement and allocation of specific source areas would have been achieved if key secondary watercourses had been equipped with flow measurement equipment and automatic samplers. Further, it would have been beneficial if the rain gauge, flow monitors and automatic samplers had been interactively linked via a telemetry system to a 'home-base' at the University. This facility would have allowed more control and more efficient use of site-resources; for example it would have provided real-time remote monitoring of rainfall and subsequent runoff and enabled the automatic samplers to have been remotely activated and deactivated and, if necessary, reprogrammed to optimise their efficient use for data collection. Such a system would also have allowed the reporting of equipment faults and thus enabled prompt servicing to be carried out, therefore minimising the risk of missing sample collection for an important storm event.

With regard to the laboratory procedures, it was considered that a larger pesticide runoff data-set could have been collated if the method of pesticide determination had been automated to some extent. It was often necessary, due to a laboratory backlog, for a number of field sample-sets to be sub-sampled because insufficient time was available to allow the determination of the entire sample-set. Suggestions for procedures by which laboratory throughput could have been improved include: (i) the use of immunoassay techniques to allow the rapid screening and subsequent allocation of sample HPLC determination; (ii) the use of an automated gradient HPLC system. In this case, considering the physico-chemical properties of the pesticides in the analysis suite ensured that only negligible fractions of pesticides were associated with the suspended sediment, an in-line extraction and HPLC system based on solid phase extraction could have been used. The envisaged automated system would initially filter the 1l sample to remove particulates, the filtrate would then be directed to a HPLC incorporating an automated sample preconcentration unit (ASPEC). Here, the analytes would be extracted as the 1l sample passed through an off-line solid phase extraction (SPE) column, where the post-extraction water was led to a waste outlet. Whilst off-line the extract would also be automatically cleaned-up through elution of the SPE column with specific solvents etc.. At this point the SPE column would be brought on-line and the eluted with HPLC mobile phase directly on the analytical column, thus achieving a very high concentration factor. To minimise run time, the separation would be achieved using a gradient solvent delivery system. This would save considerable time compared to the employed manual injection isocratic system which required a run time of approximately 80 minutes per sample. Detection would be similarly achieved using a photodiode array detector with the addition of software algorithms that would identify pre-defined conditions and allow certain samples to be further analysed and confirmed using LC-MS.

8.4.5 Recommendations for further work

The results of the work presented in this thesis and other experiments show that surface runoff, occurring after the normal use of pesticides in agricultural and non-agricultural situations, can lead to the contamination of receiving surface waters at concentrations above the EC Drinking Water Directive limit value for a single pesticide of 0.1μg/l. Therefore the following recommendations for further work are suggested.

8.4.5.1 Further work relating to the agricultural use of pesticides

The application of herbicides to clay soil for the protection of arable crops usually results in the contamination of receiving waters through a combination of overland runoff and/or sub-surface runoff moving through sub-soil macropores. Therefore to reduce the impact of normal pesticide use on receiving waters, it is suggested that further research is required on the range of practices incorporated within the paradigm of Integrated Pest Management. These practices include:

- Reduced pesticide input through the use of decision support systems to identify areas that do not require applications and also areas that have a high potential to contaminate receiving waters.

- The use of conservation tillage systems to minimise the generation of runoff and amount of subsequent amount of off-site pesticide loss.

- The use of integrated buffer zones incorporating (as considered appropriate) grassed buffer strips to intercept and treat contaminated overland runoff; riparian tree cover to intercept and treat contaminated sub-surface runoff; and the use of riparian reedbeds to further treat contaminated overland and sub-surface runoff, but mainly to intercept and treat the water from field drainage pipes, prior to discharge to receiving waters.

8.4.5.2 Further work relating to the non-agricultural use of pesticides

A significant portion of non-agricultural pesticide use is attributed to the treatment of weeds in public grassed-amenity, hard-surfaced areas and railway lines. The work reported in this thesis has shown that storm event runoff subsequent to such applications, particularly those to hard surfaces connected directly to receiving waters via engineered drainage systems, is highly likely to contaminate receiving waters at concentrations of up to four orders of magnitude above the EC Drinking Water Directive. Therefore, to reduce the impact of the normal use of pesticides on receiving waters within the urban environment, it is suggested that further research is required on a range of practices broadly encompassed by the term Integrated Urban Weed Management. Approaches and practices include:

- Redefining the need for total weed control within the urban environment, including informing and educating the public of the environmental impact that total weed control entails and reshaping perceptions regarding the level of weed growth that is acceptable.

- Reducing the level of use of pesticides through their utilisation as a last option in favour of alternative methods including manual weeding (where practical), mulching, use of flame and infra-red weed control technologies, control on busy thoroughfares by pedestrian trampling, control at the roadside by roadsweepers, and regular maintenance of engineered structures. In addition, urban design should be optimised to either minimise weed occurrence or make weed occurrence visually and structurally acceptable.

- The investigation of pesticide runoff characteristics from non-agricultural application substrates through the use of laboratory-based rainfall-runoff experiments, thus leading to the identification of those pesticides which are most susceptible to transport in urban and highway runoff and hence to producing subsequent contamination of receiving waters.

- The use of vegetated systems that buffer the impact of pesticide-contaminated urban and highway runoff upon receiving waters, such as the use of grass swales and natural or constructed wetlands.

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10. Appendix: Tabulated Pesticide Data (Automatic samples)

KEY: ND - below detection limit, NA - not available, Sim - simazine, Atra - atrazine, Ctu - chlorotoluron, Ipu - isoproturon, Diu - diuron

10.1 Site A Agricultural sub-catchment (rainfall event samples)

10.1.1 Event of 1/5/92 (JD 122)

CODE		CONC				
A122	TIME	SIM	ATRA	CTU	IPU	DIU
1	0455	0.11	0.21	0.06	0.07	ND
2	0555	0.11	0.11	0.79	1.00	ND
3	0655	0.14	0.14	0.56	0.59	ND
4	0755	0.29	0.14	0.41	0.56	ND
5	0855	0.27	0.13	0.28	0.39	ND
6	0955	0.26	0.11	0.27	0.27	ND
7	1055	0.16	0.10	0.22	0.32	ND
8	1155	0.22	0.11	0.20	0.28	ND
9	1255	0.27	0.10	0.19	0.26	ND
10	1355	0.21	0.09	0.15	0.21	ND
11	1455	0.24	0.09	0.13	0.20	ND
12	1555	0.19	0.08	0.11	0.20	ND
13	1855	0.14	0.07	0.07	0.13	ND
14	2155	0.16	0.07	0.08	0.14	ND
15	0055	0.28	0.06	0.10	0.20	ND

10.1.2 Event of 13/8/92 (JD226)

CODE		CONC				
A226	TIME	SIM	ATRA	CTU	IPU	DIU
1	2140	0.17	0.16	0.81	0.13	ND
5	0140	0.20	0.15	1.47	0.29	ND
19	0840	0.60	0.07	0.33	0.15	ND

10.1.3 Event of 2/10/92 (JD276)

CODE		CONC				
A276	TIME	SIM	ATRA	CTU	IPU	DIU
1	00:00	0.15	ND	1.29	0.13	ND
6	02:30	0.09	ND	1.62	0.18	ND
15	11:00	0.27	0.03	0.47	0.27	ND
18	20:00	0.33	0.09	0.63	0.19	ND

10.1.4 Event of 20/10/92 (JD 294)

		CONC				
A294	TIME	SIM	ATRA	CTU	IPU	DIU
1	0443	0.10	ND	0.41	ND	ND
8	0843	0.10	0.05	0.62	ND	ND
9	0943	0.11	0.06	0.73	ND	ND
16	1643	0.09	0.11	0.40	ND	ND

10.1.5 Event of 9/11/92 (JD 314)

CODE		CONC ug/l				
314 A	TIME	SIM	ATRA	CTU	IPU	DIU
1	1900	0.10	0.03	1.26	ND	ND
3	2000	0.07	0.03	2.23	0.08	ND
4	2030	0.13	0.03	1.39	ND	ND
5	2100	0.11	0.03	0.47	ND	ND
6	2130	0.06	0.03	0.44	ND	ND
7	2200	0.06	0.03	0.04	NA	NA
8	2300	0.07	ND	0.40	ND	ND
9	2400	0.07	NA	NA	NA	NA
10	100	0.07	NA	NA	NA	NA
19	1900	0.07	ND	0.14	ND	ND

10.1.6 Event of 15/11/92 (JD 320)

CODE		CONC ug/l				
320 A	TIME	SIM	ATRA	CTU	IPU	DIU
1	03:16	ND	ND	0.21	ND	ND
2	03:46	ND	ND	1.00	ND	ND
3	04:16	ND	ND	0.33	ND	ND
4	04:46	ND	ND	0.19	ND	ND
5	05:16	ND	ND	0.09	ND	ND
6	05:46	ND	ND	ND	ND	ND
7	06:16	ND	ND	ND	ND	ND
8	07:16	ND	ND	ND	ND	ND
9	08:16	ND	ND	ND	ND	ND
10	09:16	ND	ND	ND	ND	ND
11	10:16	NA	NA	NA	NA	NA
12	11:16	NA	NA	NA	NA	NA
13	12:16	NA	NA	NA	NA	NA
14	13:16	NA	NA	NA	NA	NA
15	14:16	NA	NA	NA	NA	NA
16	15:16	NA	NA	NA	NA	NA
17	19:16	NA	NA	NA	NA	NA
18	00:16	NA	NA	NA	NA	NA
19	04:16	ND	ND	ND	ND	ND
20	08:16	NA	NA	NA	NA	NA

10.1.7 Event of 6/1/93 (JD 6)

CODE		CONC ug/l				
6//93A	TIME	SIM	ATRA	CTU	IPU	DIU
1	18:15	ND	ND	0.16	ND	ND
2	18:45	ND	ND	0.66	ND	ND
3	19:15	ND	ND	0.36	ND	ND
4	19:45	ND	ND	0.33	ND	ND
5	20:15	ND	ND	0.27	ND	ND
6	20:45	ND	ND	0.23	ND	ND
7	21:15	ND	ND	0.26	ND	ND
8	22:15	ND	ND	0.17	ND	ND
9	23:15	ND	ND	0.11	ND	ND
10	00:15	NA	NA	NA	ND	ND
11	01:15	NA	NA	NA	ND	ND
12	02:15	NA	NA	NA	ND	ND
13	03:15	NA	NA	NA	ND	ND
14	04:15	NA	NA	NA	ND	ND
15	05:15	NA	NA	NA	ND	ND
16	06:15	ND	ND	0.06	ND	ND
17	20:15	NA	NA	NA	NA	NA
18	00:15	NA	NA	NA	NA	NA
19	04:15	NA	NA	NA	NA	NA
20	08:15	NA	NA	NA	NA	NA

10.1.8 Event of 1/4/93 (JD 91)

CODE		CONC ug/l				
91 A	TIME	SIM	ATRA	CTU	IPU	DIU
1	1125	ND	ND	0.10	0.11	ND
2	1155	ND	ND	0.26	0.11	ND
3	1225	ND	ND	0.22	9.99	ND
4	1255	ND	ND	0.13	9.76	ND
5	1325	ND	ND	ND	9.83	ND
6	1355	ND	ND	ND	7.96	ND
7	1425	ND	ND	ND	7.43	ND
8	1525	ND	ND	ND	5.74	ND
9	1625	ND	ND	ND	4.07	ND
10	1725	ND	ND	ND	5.05	ND
11	1825	ND	ND	ND	4.16	ND
12	1925	ND	ND	ND	3.55	ND
13	2025	ND	ND	ND	2.88	ND
14	2125	ND	ND	ND	2.83	ND
15	2225	ND	ND	ND	2.55	ND
16	2325	ND	ND	ND	2.19	ND
17	325	ND	ND	ND	0.93	ND
18	725	ND	ND	ND	0.85	ND
19	1125	ND	ND	ND	0.57	ND
20		NA	NA	NA	NA	NA

10.1.9 Event of 5/4/93 (JD 95)

CODE		CONC ug/l				
95 A	TIME	SIM	ATRA	CTU	IPU	DIU
1	08;50	ND	ND	ND	ND	ND
2	09:20	ND	ND	ND	ND	ND
3	09:50	ND	ND	0.21	4.99	ND
4	10:20	ND	ND	0.22	5.78	ND
5	10:50	ND	ND	0.24	6.98	ND
6	11:20	ND	ND	0.22	8.58	ND
7	11:50	ND	ND	0.18	8.69	ND
8	12:50	ND	ND	0.16	8.79	ND
9	13:50	ND	ND	0.08	6.20	ND
10	14:50	ND	ND	0.08	3.75	ND
11	15:50	ND	ND	ND	3.09	ND
12	16:50	ND	ND	ND	2.40	ND
13	17:50	ND	ND	ND	1.60	ND
14	18:50	ND	ND	ND	1.37	ND
15	19:50	ND	ND	ND	1.23	ND
16	20:50	ND	ND	ND	0.98	ND
17	24:50	ND	ND	ND	0.49	ND
18	28:50	ND	ND	ND	0.49	ND
19	:	NA	NA	NA	NA	NA
20	:	NA	NA	NA	NA	NA

10.1.10 Event of 9/4/93 (JD 99)

CODE		CONC ug/l				
99 A	TIME	SIM	ATRA	CTU	IPU	DIU
1	14:15	ND	ND	ND	0.08	ND
2	14:45	ND	ND	0.20	0.30	ND
3	15:15	ND	ND	0.25	5.33	ND
4	15:45	ND	ND	0.22	5.66	ND
5	16:15	ND	ND	0.35	5.02	ND
6	16:45	ND	ND	0.22	3.67	ND
7	17:15	ND	ND	ND	8.67	ND
8	18:15	ND	ND	0.12	7.33	ND
9	19:15	ND	ND	0.28	7.97	ND
10	20:15	ND	ND	0.14	7.71	ND
11	21:15	ND	ND	0.10	4.46	ND
12	22:15	ND	ND	0.07	3.34	ND
13	23:15	NA	NA	NA	3.35	NA
14	00:15	ND	ND	0.13	3.43	ND
15	01:15	NA	NA	NA	2.80	NA
16	02:15	ND	ND	0.05	2.20	ND
17	06:15	ND	ND	ND	1.28	ND
18	10:15	ND	ND	ND	0.81	ND

10.1.11 Event of 25/4/92 (JD 115)

CODE		CONC ug/l				
115 A	TIME	SIM	ATRA	CTU	IPU	DIU
1	04:00	ND	ND	0.10	0.37	ND
2	04:30	ND	ND	0.28	0.44	ND
3	05:00	ND	ND	0.31	1.57	ND
4	05:30	ND	ND	0.28	2.69	ND
5	06:00	ND	ND	0.13	2.45	ND
6	06:30	ND	ND	0.10	1.82	ND
7	07:00	ND	ND	0.13	2.17	ND
8	08:00	ND	ND	0.09	1.76	ND
9	09:00	ND	ND	0.08	1.33	ND
10	10:00	NA	NA	NA	NA	NA
11	11:00	ND	ND	0.13	1.49	ND
12	12:00	ND	ND	0.06	1.59	ND
13	13:00	ND	ND	0.05	0.93	ND
14	14:00	NA	NA	NA	NA	NA
15	15:00	NA	NA	NA	NA	NA
16	16:00	NA	NA	NA	NA	NA
17	20:00	NA	NA	NA	NA	NA
18	00:00	NA	NA	NA	NA	NA
19	04:00	NA	NA	NA	NA	NA
20	08:00	NA	NA	NA	NA	NA

10.2 Site D Urbanised catchment (Rainfall event samples)

10.2.1 Event of 15/4/92 (JD 106)

CODE		CONC				
D106	TIME	SIM	ATRA	CTU	IPU	DIU
1	0225	0.38	0.51	0.22	0.22	1.06
2	0425	0.45	0.58	0.26	0.07	0.71
3	0525	0.33	0.46	0.20	0.05	0.67
4	0655	0.67	0.68	0.32	ND	0.83
5	0825	0.30	0.57	0.21	ND	0.69
6	0925	0.23	0.59	0.18	0.05	0.67
7	10:25	0.22	0.55	0.33	0.06	0.40
8	11:25	0.20	0.69	0.18	0.09	0.60
9	18:25	0.22	0.44	0.26	0.13	0.27

10.2.2 Event of 28/4/92 (JD 119)

CODE		CONC µg/l				
D119	TIME	SIM	ATRA	CTU	IPU	DIU
1	1232	0.08	0.26	0.25	0.24	1.33
2	1332	0.09	0.36	0.29	0.48	0.94
3	1432	0.15	0.49	0.26	0.41	0.76
4	1532	0.20	0.68	0.19	0.28	0.63
5	1632	0.23	0.53	0.17	0.21	0.63
6	1732	0.26	0.49	0.14	0.18	0.63
7	1832	0.47	0.47	0.20	0.31	0.62
8	1932	0.29	0.42	0.14	0.17	0.61
9	2032	0.25	0.50	0.12	0.11	0.60
10	2132	0.27	0.42	0.29	0.08	0.58
11	2232	0.25	0.41	0.14	0.09	0.52

10.2.3 Event of 1/5/92 (JD 122)

CODE		CONC				
D122	TIME	SIM	ATRA	CTU	IPU	DIU
1	0400	0.10	0.21	0.28	0.09	0.25
2	0500	0.05	0.10	0.40	0.25	0.10
3	0600	0.12	0.11	0.30	0.34	0.06
4	0700	0.20	0.16	0.20	0.28	0.08
5	0800	0.07	0.10	0.15	0.18	0.18
6	0900	0.10	0.09	0.11	0.14	0.06
7	10:00	0.14	0.18	0.08	0.13	ND
8	11:00	0.15	0.16	0.08	0.15	ND
9	12:00	0.17	0.15	0.08	0.17	0.05
10	13:00	0.16	0.11	0.10	0.19	0.07
11	14:00	0.14	0.10	0.06	0.08	0.08
12	15:00	0.19	0.23	0.43	0.08	0.08
13	18:00	0.18	0.13	0.05	0.08	0.05
14	20:00	0.14	0.13	0.07	0.06	0.13

10.2.4 Event of 29/5/92 (JD150)

CODE		CONC				
D150	TIME	SIM	ATRA	CTU	IPU	DIU
1	0841	2.23	1.14	3.36	0.64	226.75
2	0941	1.22	0.38	2.70	0.24	238.39
3	1041	0.85	0.69	4.51	0.41	177.56
4	1141	0.97	1.16	1.97	1.75	69.76
5	1241	0.93	1.28	1.66	3.27	47.93
6	1341	0.81	1.22	1.35	3.10	41.08
7	1441	1.08	1.18	1.10	2.64	40.98
8	1541	1.22	1.06	1.03	2.34	34.79
9	1641	1.64	0.66	0.82	0.80	63.42

10.2.5 Event of 2/10/92 (JD276)

		CONC				
A276	TIME	SIM	ATRA	CTU	IPU	DIU
1		0.09	0.84	0.91	0.50	0.96
4		0.24	0.37	0.37	0.28	0.07
12		0.43	0.07	0.84	0.07	0.09
15		0.53	0.05	0.61	0.12	0.07

10.2.6 Event of 20/10/92 (JD 294)

				CONC		
D294	TIME	SIM	ATRA	CTU	IPU	DIU
1	0334	0.29	0.14	0.55	ND	ND
3	0434	ND	0.15	0.79	ND	ND
19	1334	ND	ND	ND	ND	ND

10.2.7 Event of 9/11/92 (JD 314)

CODE				CONC ug/l		
314 D	TIME	SIM	ATRA	CTU	IPU	DIU
1	18:00	ND	ND	0.20	ND	0.39
2	18:30	ND	ND	0.10	ND	0.34
3	19:00	ND	ND	0.07	ND	0.13
4	19:30	0.05	ND	0.24	ND	0.06
5	20:00	ND	ND	0.34	ND	0.08
6	20:30	ND	ND	0.16	ND	0.08
7	21:00	ND	ND	0.11	ND	0.05
8	22:00	ND	ND	0.20	ND	ND
9	23:00	ND	ND	0.06	ND	0.05
10	00:00	ND	ND	0.07	ND	0.06
11	01:00	NA	NA	NA	NA	NA
12	02:00	ND	ND	0.06	ND	ND
13	03:00	ND	ND	0.07	ND	ND
14	04:00	ND	ND	0.09	ND	0.05
15	05:00	ND	ND	0.11	ND	0.06
16	06:00	NA	NA	NA	NA	NA
17	10:00	NA	NA	NA	NA	NA
18	14:00	0.07	ND	ND	ND	0.07
19	18:00	NA	NA	NA	NA	NA
20	22:00	NA	NA	NA	NA	NA

10.2.8 Event of 15/11/92 (JD 320)

CODE				CONC ug/l		
320 D	TIME	SIM	ATRA	CTU	IPU	DIU
1	02:30	ND	ND	0.27	0.10	0.24
2	03:00	ND	ND	0.17	0.04	0.69
3	03:30	0.06	ND	0.43	0.07	ND
4	04:00	NA	NA	NA	NA	NA
5	04:30	ND	ND	0.18	0.05	0.08
6	05:00	ND	ND	0.12	0.05	0.08
7	05:30	NA	NA	NA	NA	NA
8	06:30	ND	ND	ND	ND	ND
9	07:30	ND	ND	0.04	ND	ND
10	08:30	ND	ND	0.04	ND	0.06
11	09:30	ND	ND	0.04	ND	0.06
12	10:30	ND	ND	0.05	ND	ND
13	11:30	ND	ND	0.05	ND	ND
14	12:30	ND	ND	ND	ND	ND
15	13:30	ND	ND	ND	ND	0.06
16	14:30	ND	ND	0.09	ND	0.08
17	18:30	NA	NA	NA	NA	NA
18	22:30	NA	NA	NA	NA	NA
19	02:30	NA	NA	NA	NA	NA
20	06:30	NA	NA	NA	NA	NA

10.2.9 Event of 6/1/93 (JD 6)

CODE		**CONC ug/l**				
^6/93D	**TIME**	**SIM**	**ATRA**	**CTU**	**IPU**	**DIU**
1	**20:00**	ND	ND	**0.06**	ND	**0.17**
2	**20:30**	ND	ND	**0.05**	ND	**0.09**
3	**21:00**	ND	ND	**0.04**	ND	**0.10**
4	**21:30**	ND	ND	ND	ND	**0.11**
5	**22:00**	ND	ND	ND	ND	**0.06**
6	**22:30**	ND	ND	ND	ND	ND
7	**23:00**	ND	ND	ND	ND	ND
8	**00:00**	ND	ND	ND	ND	ND
9	**01:00**	ND	ND	**ND**	ND	ND
10	**02:00**	NA	NA	NA	NA	NA
11	**03:00**	ND	ND	ND	ND	ND
12	**04:00**	ND	ND	ND	ND	ND
13	**05:00**	ND	ND	ND	ND	ND
14	**06:00**	ND	ND	ND	ND	ND
15	**07:00**	ND	ND	ND	ND	ND
16	**08:00**	ND	ND	ND	ND	ND
17	**12:00**	ND	ND	ND	ND	ND
18	**16:00**	ND	ND	ND	ND	ND
19	**20:00**	NA	NA	NA	NA	NA
20	**00:00**	NA	NA	NA	NA	NA

10.2.10 Event of 1/4/93 (JD 91)

CODE		**CONC ug/l**				
91 D	**TIME**	**SIM**	**ATRA**	**CTU**	**IPU**	**DIU**
1	**17:00**	ND	**0.09**	ND	ND	**0.15**
2	**17:30**	NA	0.07	NA	NA	0.11
3	**18:00**	ND	**0.05**	ND	**0.12**	**0.07**
4	**18:30**	NA	0.05	NA	0.16	NA
5	**19:00**	ND	**0.05**	ND	**0.20**	ND
6	**19:30**	NA	0.6	NA	0.26	NA
7	**20:00**	ND	**0.10**	ND	**0.33**	ND
8	**21:00**	NA	0.15	NA	0.37	NA
9	**22:00**	ND	**0.19**	ND	**0.41**	ND
10	**23:00**	ND	**0.08**	ND	**0.41**	**0.05**
11	**00:00**	NA	0.09	NA	0.44	NA
12	**01:00**	ND	**0.10**	ND	**0.47**	**0.05**
13	**02:00**	NA	0.10	NA	0.46	NA
14	**03:00**	ND	**0.09**	ND	**0.46**	**0.05**
15	**04:00**	NA	NA	NA	NA	NA
16	**05:00**	NA	NA	NA	NA	NA
17	**09:00**	ND	**0.13**	ND	**0.33**	**0.07**
18	**13:00**	NA	NA	NA	NA	NA
19	**17:00**	NA	NA	NA	NA	NA
20	**21:00**	NA	NA	NA	NA	NA

10.2.11 Event of 25/4/92 (JD 115)

CODE		CONC ug/l				
115 D	TIME	SIM	ATRA	CTU	IPU	DIU
1	04:00	ND	ND	ND	0.14	0.10
2	04:30	ND	ND	ND	0.11	0.16
3	05:00	ND	0.07	ND	0.17	0.11
4	05:30	ND	ND	ND	0.25	0.10
5	06:00	ND	ND	ND	0.15	0.05
6	06:30	ND	ND	ND	0.16	0.05
7	07:00	ND	ND	ND	0.14	0.08
8	08:00	ND	ND	ND	0.25	0.05
9	09:00	ND	ND	ND	0.11	0.14
10	10:00	ND	ND	ND	0.21	0.18
11	11:00	ND	ND	ND	0.30	ND
12	12:00	ND	ND	ND	0.29	ND
13	13:00	ND	ND	ND	0.26	0.05
14	14:00	ND	ND	ND	0.12	ND
15	15:00	ND	ND	ND	0.18	ND
16	16:00	ND	ND	ND	0.22	ND
17	20:00	ND	ND	ND	0.18	ND
18	00:00	ND	ND	ND	0.03	ND
19	04:00	NA	NA	NA	NA	NA
20	08:00	NA	NA	NA	NA	NA