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SEDIMENT METAL-MAGNETIC PROPERTIES IN URBAN CATCHMENTS.

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P.R. BECKWITH.

ABSTRACT

This research project examines the application of mineral magnetic techniques to the characterisation of particulates and their sources in the urban highway environment and in stormwater runoff.

A review of previous investigations into sources, levels and pathways of metals through the urban highway environment is presented. The principles upon which the mineral magnetic techniques are based and those parameters employed in this study are described. Previous environmental applications are reviewed.

A representative sampling scheme was established in a small well-defined sub-catchment. Copper, Fe, Pb and Zn concentrations in highway associated sediments increased with proximity to the road centre and seasonal maxima occurred in summer. Heavy metal loadings were dominated by the sediment loadings. Strong linear relationships between the metals, Cu, Fe, Pb and Zn, and magnetic mineral concentration related parameters, χ and IRM_{300mT}, were observed. Mineral magnetic characterisation achieved complete discrimination between highway associated sediments and roof sediments allowing the derivation of equations defining the sediment groupings. Variations in metal-magnetic properties of sediments with particle size were investigated. Primary source materials and particulates were analysed. Metallic and magnetic mineral parameters indicated that atmospheric and vehicle derived particulates were probably the dominant origins of source particulates.

The variation of particulate associated heavy metals in stormwater runoff at the sub-catchment is discussed. Mineral magnetic parameters characterised the majority of stormwater particulates with the roof sediment grouping. The implications of these investigations is discussed.

The study was expanded to encompass the parent catchment. The characterisation of source sediments from land use and road types other than that represented by the sub-catchment was carried out. Stormwater particulates collected at the main catchment outfall were found to be generally characterised with soil and roof sediment groupings.

The further application and use of mineral magnetic parameters in similar research is discussed.

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SEDIMENT METAL-MAGNETIC PROPERTIES IN URBAN CATCHMENTS

CHAPTER 1 INTRODUCTION.

1.1 Heavy Metals in the Environment.

The last twenty five years have seen mounting concern over the increased levels and incidence of heavy metals in the environment, and the possible implications to human health resulting from long term exposure to these metals. This has been particularly evident in relation to lead (Bryce-Smith and Stephens, 1980; Duggan, 1980; Royal Commission on Environmental Pollution, 1983; DHSS, 1980). The widespread dissemination of Pb throughout the environment has been well documented as a result of its use in petrol and paints (DoE, 1974; 1978; Roberts et al, 1974; Smith, 1976; Millar and Cooney, 1982; Brunekreef et al, 1983; Royal Commission on Environmental Pollution, 1983) as well as the inputs from industry (DoE, 1974; Roberts et al, 1974; Muskett et al, 1979; Page and Chang, 1979; Harrison and Williams, 1983; Royal Commission on Environmental Pollution, 1983). The detrimental effects of exposure to Pb have also been documented with regard to both aquatic organisms (Davies et al, 1976; Royal Commission on Environmental Pollution, 1983) and higher animals (Royal Commission on Environmental Pollution, 1983).The exposure to increasing levels of Pb, particularly in an urban environment, have caused considerable concern in relation to studies that have suggested that Pb can be neurotoxic, with young children being highly susceptible. The development of the central nervous system in particular was cited as being affected, resulting in mental retardation, decreased intelligence, hyperactivity, behavioural and psychological disorders (Roberts et al, 1974; Needleman, 1980; Bryce-Smith and Stephens, 1980).

While the emphasis has been placed on Pb, other metals entering the urban environment are also known to be potentially harmful. There is some evidence that exposure to Cd can cause hypertensive cardiovascular diseases, Cd-induced bone disease or osteomalacia and pulmonary disorders (Lewis et al, 1972; Lauwerys, 1979; Yasumura et al, 1980).

Copper and Zn can also be toxic to humans however it is unlikely that such exposure would occur except within an occupational context. These metals are essential for normal growth of plants and animals, however if present in excessive amounts they are known to have phytotoxic effects, inhibiting plant growth (DoE, 1987). A large volume of literature concerned with the occurrence, levels and toxicology of metals in the environment already exists but the question of their total environmental impact is far from being resolved.

The environment is a dynamic system and is often envisaged as a series of compartments or reservoirs, in which heavy metals move from a source or sources eventually entering a specific environmental compartment acting as a sink where they become fixed. In order to assess the total impact of heavy metals on the environment it is important to identify their levels in the principal sources, sinks and major reservoirs. Additionally, the factors controlling the supply, interaction and fixation of heavy metals within the environment must be investigated.

1.2 Heavy Metals in Urban Catchments.

The increased awareness of the health effects of heavy metals has brought about the recognition of areas of accumulation of heavy metals in man's immediate environment. One of the highly publicised areas of metal accumulation has been roadside dusts, particularly in connection with the campaign to reduce Pb in petrol. The importance of settled dusts in the routing of pollutants through the urban enviroment is not fully understood, although they are now widely recognised as a major intermediate source of heavy metals. The mobilisation of settled dusts in stormwater runoff and the possible solubilisation of the associated metals by rainfall-runoff can bring about discharges of highly polluted water. Studies in the USA, UK and Sweden have shown that there are frequent and prolonged periods when urban runoff discharges exceed toxic water standards (Ellis, 1986). In urban hydrological research there is a distinct need to identify the accumulation and movement of priority pollutants, such as heavy metals, from specific sources and to assess their relative contributions to outfall loadings (Delleur and Torno, 1983; Harrop, 1984a). The number of potential sources and their interactions within a non-industrialised urban catchment are indicated in Figure 1.1.

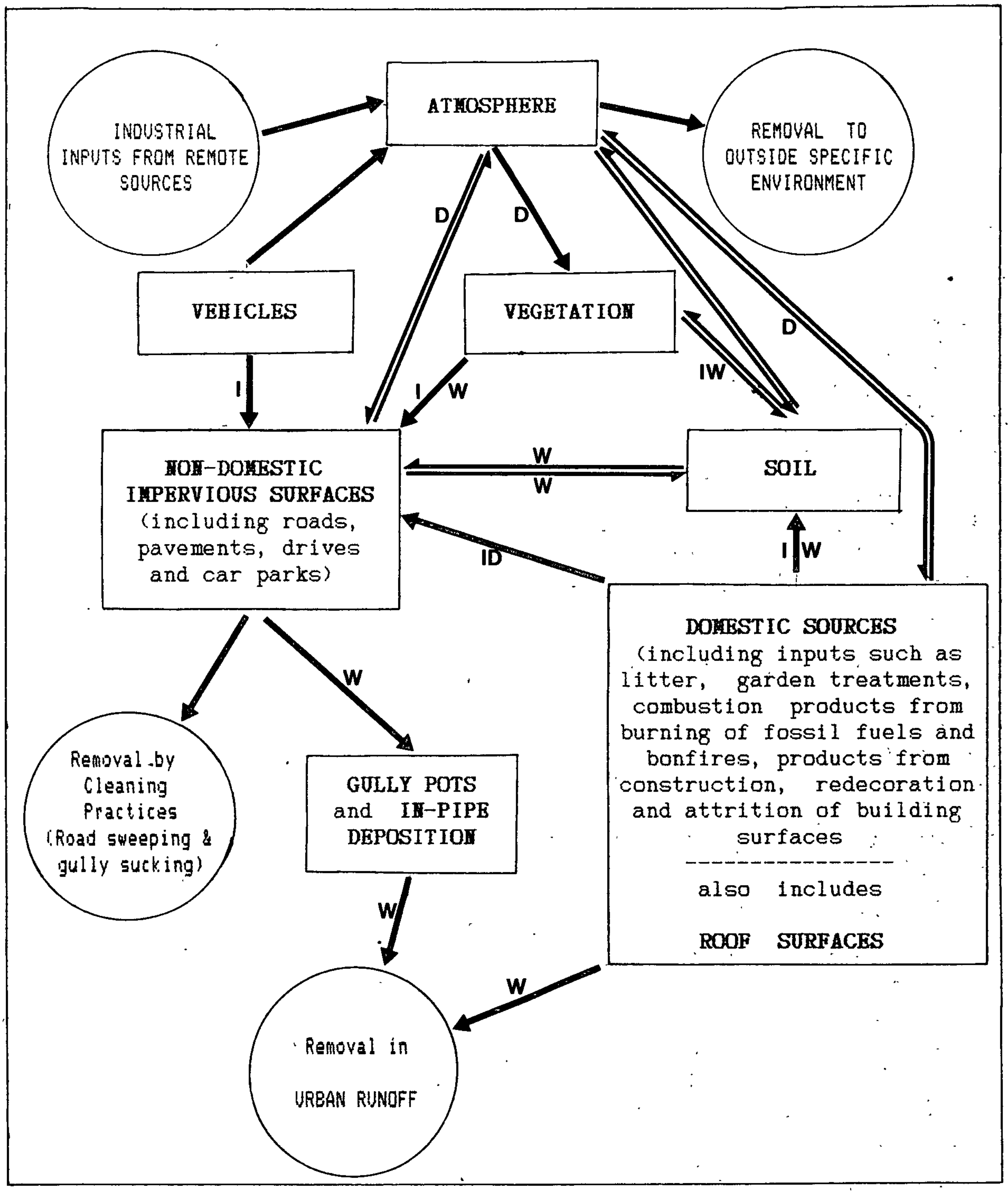
1.3 Research Context

There have been relatively few previous studies using tracer techniques, apart from dilution gauging and the use of non-degradable chlorinated benzoic acids in sanitary sewers, to evaluate times of concentration (Beckwith et al, 1986a). Graded sand marked with a fluorescent dye has also been suggested as a tracer technique (Roberts, 1985). The use of particle size and surface texture has also been used in attempts to characterise the sources of urban drainage sediments (Roberts et al, 1988).

Mineral magnetic parameters have been applied in a variety of aquatic environments to characterise source particulates (Dearing et al, 1981, Oldfield and Scoullos 1984) and to determine sediment contributions, routing and sequencing during storm runoff (Arkell et al, 1983; Oldfield et al, 1979; Walling et al, 1979). Revitt et al (1981) have indicated the potential of utilising these techniques to characterise particulates and their sources in urban highway and stormwater runoff.

1.4 Aims and Objectives of the Research Project.

The present research is intended to aid the understanding of the routing of heavy metals through a highway within a residential catchment, where concern is centred upon motor vehicles as potential major sources of heavy metals. The transport of metals within this system has been investigated using mineral magnetic parameters and this is considered a novel, yet logical and systematic, approach offering certain methodological and analytical advantages.



Abbreviations

I	Immediate Deposition	- Particles settling directly from immediate source by gravitation.
D	Wet and Dry Deposition	
W	Washoff	

Figure 1.1 Flow Diagram Showing Metal Distribution and Transport Routes in a Non-Industrialised Urban Environment.

The main aims of this research are as follows;

a) to identify and classify source materials and sediments occurring within an urban highway catchment.

b) to assess the concentrations and loadings of heavy metals in the source materials and sediments as an aid in typing or 'finger-printing' the dominant sources within the catchment.

c) to utilise the identified sediment characteristics as a means of tracing the pathways of source sediments and their associated heavy metals into and through the subsurface drainage system.

d) to investigate the occurrence, and identify the order of, the sequencing of pollutant loadings originating from source sediments in relation to storm events through variations in the mineral magnetic characterisation of stormwater suspended sediments. Subsequently, if sequencing is identified, an objective is to assess the relative importance of source sediments to the total loadings found at the outfall of the major catchment.

e) to model the inputs, cycling and outputs of heavy metals in an urban catchment by applying a mass balance approach. This will be achieved by considering both the concentrations and loadings of heavy metals found in the research catchment together with the evidence of mineral magnetic characterisations of sediments in various environmental compartments.

1.5 Outline of Thesis.

The thesis commences with a review of previous work centred on the pollution of the urban environment by the heavy metals, Cd, Cu, Fe, Pb, Mn and Zn (Chapter 2). The sources of these metals are described and attempts are made to quantify their input and their effects on the environment. The cycling of the metals through the urban highway environment, including the critical pathways and processes, are also discussed. Finally, the Chapter deals with the processes by which metals are removed from the urban highway environment.

The research project involves the use of a range of novel mineral magnetic techniques to trace urban source sediments. Chapter 3 outlines the principles upon which these techniques are based, followed by a description of the actual parameters employed and a review of previous environmental applications.

The characteristics of the experimental catchments and details of the sampling and analytical methodology utilised in this research programme are then described in Chapter 4.

The research results are discussed in Chapters 5 to 9 with the first of these presenting an investigation into the temporal and spatial distribution of heavy metals in source sediments within a small well-defined and non-industrialised urban catchment. This provides information relating to the types of source sediments and their characteristics in terms of heavy metals and mineral magnetic parameters. The initial results of this investigation have been presented in the co-authored paper 'Identification of Pollution Sources in Urban Drainage Systems Using Magnetic Methods' (Beckwith et al, 1984a).

Statistical analysis of source sediment properties provides equations which define specific source sediment groupings and these are subsequently used to characterise unknown samples. Chapter 6 further develops the understanding of source sediment behaviour within the small sub-catchment by investigating metal and mineral magnetic parameters in relation to particle size. The data resulting from the investigations discussed in Chapter 6 has been partly described in two co-authored publications entitled 'The Behaviour of Sediment Associated Heavy Metals within an Urban Surface Runoff Drainage System' (Beckwith et al, 1984b) and 'Particle Size Distributions of Cu, Pb, and Zn Across a Road Surface' (Beckwith et al, 1985).

The source materials and particulates including atmospheric particulates, soil particulates, surface constructional materials, automobile derived particulates and litter which contribute to the source sediments found within the sub-catchment are considered in Chapter 7. The characteristics of these materials and particulates are assessed and their relative contribution to the metal levels and magnetic mineral properties of surface sediments within the sub-catchment are discussed. The preliminary findings of the investigations reported in Chapters 5 and 7 are reported in a co-authored paper 'Heavy Metal and Magnetic Relationships for Urban Source Sediments' (Beckwith et al, 1986a).

Chapter 8 considers the relative importance of different source sediments to stormwater runoff particulates collected at the outfall to the Chilwell Gardens sub-catchment. The characteristics of the stormwater particulates are related to the source sediments using the equations derived by statistical analysis in Chapters 5 and 6. The estimated total input of particulate associated metals to the small catchment prior to storm events and the resulting output of particulate associated metals is discussed.

Chapter 9 describes the expansion of the research project to encompass the parent South Oxhey catchment. The analysis of source sediments not present in the small sub-catchment but existing in the main catchment is described and the data obtained is combined with that derived from the study of sediments in the sub-catchment to statistically derive equations which relate the source sediment type to stormwater particulates. The tracing of metals through the urban surface water drainage system and the dominant sources likely to effect the water quality of urban stormwater runoff are discussed. The results of the investigations reported in Chapters 5, 6 and 9 were used as part of the data base for the co-authored paper 'The Contribution of Highway Surfaces to Urban Stormwater Sediments and Metal Loadings' (Ellis et al, 1987).

The final Chapter summarises the main conclusions and discusses these with a view to future work and the application of mineral magnetic techniques as tracer and reconnaissance methods in urban environmental research.

CHAPTER 2 A REVIEW OF SOURCES AND PATHWAYS OF HEAVY METALS IN THE URBAN ENVIRONMENT.

Within the following section the sources and pathways of heavy metals in the urban environment are discussed. Where concentrations or loadings are cited as found occurring within the urban environment these have been restricted to those found within Europe as this has been taken to be more relevant and comparable to the present study. Research carried out in parts of the world other than Europe has not been ignored and such research is cited here with regard to principles, processes and reactions observed in the fate of heavy metals in the urban environment.

2.1 Sources of Heavy Metals in the Urban Environment.

Heavy metals in the urban environment are derived from a variety of sources of both natural and anthropogenic origin. A comparison of global emission rates for natural and anthropogenic sources is presented in Table 2.1. The dominance of anthropogenic sources over natural sources is apparent from inspection of this data.

Table 2.1 Worldwide Emissions of Trace Metals from Natural and Anthropogenic Sources for 1975 (From Nriagu, 1979).

	Cd	Cu	Pb	Zn
Natural	0.83	18.5	24.5	43.5
Anthropogenic	7.3	56	449	314

(All values $*10^6$ kg)

With the exception of copper, Table 2.1 illustrates that anthropogenic sources dominate by an order of magnitude. In the urban environment, where proximity to major anthropogenic sources will inevitably increase this dominance, the natural sources of these four metals are generally insignificant.

The high density of potential emission sources in urban areas inevitably results in high heavy metal concentrations in air, soils and vegetation in comparison to concentrations in similar phases found in rural areas. An exacerbation of heavy metal pollution in urban areas is therefore to be expected (Table 2.2). It should be stressed that direct comparisons should only be carried out between those given by the same workers as methods of analysis often differ.

The major sources of heavy metals in the urban environment can be broadly classified as;

industrial/commercial
domestic
vehicular

These are general classifications, but the interaction between source inputs as well as the similarity of the derivation of metals in more than one group, means that there will be some overlap between these categories. An example of this overlap is provided by the attrition of construction materials used in buildings which are included in both the industrial/commercial and domestic sector. A major difference however, will be the significance of the particular sectoral contribution to the total input in each category.

2.1.1 Industrial/Commercial Sources.

Industrial sources of heavy metals vary with respect to both qualitative and quantitative pollutant inputs. Table 2.3 gives an indication of the range of heavy metals employed in various major industries.

Not all the industrially associated metals, as indicated by Table 2.3, will be observed in the total surrounding urban environment. Metals emitted in industrial liquid effluents can have a detrimental effect on receiving waters but will have little if any effect on the urban highway environment. Metal rich particulates released from smoke stacks present a more widespread pollution problem potentially raising the overall metal burden of a large area downwind of a stack and increasing ambient atmospheric metal levels.

Table 2.2 Heavy Metal Concentrations in Urban and Rural Samples.

	Cd	Cu	Fe	Pb	Zn	Sample	Ref
<u>AIR</u> (ng m^{-3})							
	0.1-2.6			75-181	27-202	Rural	1
	0.3-5.1			1110-5840	74-251	Urban	1
				92-140		Rural	2
				134-309		Urban	2
				23-130		Rural	3
				180-380		Urban	3
				418		Rural	4a
				426-470		Urban	4a
				230		Rural	4b
				251-264		Urban	4b
<u>SOILS</u> (μg g^{-1})							
		5.1		0.4	4.6	Rural	5
		51.9		5.3	16.0	Urban	5
		6.5	6100	24	36	Rural	6
		46.0	9700	116	244	Urban	6
	0.1-1.1	3.4-305.0		24-749	30-384	Rural	7
	0.1-4.1	4.1-925.0		22-1900	18-1170	Urban	7
<u>VEGETATION</u> (μg g^{-1})							
		9.0		1.0	30.3	Rural	5
		10.9		3.5	44.6	Urban	5

<u>References</u>

1 Harrison and Williams, 1979.
2 De Jonghe and Adams, 1980.
3 McInnes, 1986.
4 Jensen and Laxen, 1987
  a) 1985 mean values
  b) 1986 mean values
5 Purves and Mackenzie, 1969.
6 Andersen et al, 1978.
7 Gibson and Farmer, 1983.

Table 2.3 Major Industries Employing Selected Heavy Metals.

	Cd	Cu	Fe	Pb	Mn	Zn
Pulp, paper mills, paperboard, building paper board mills		*		*		*
Textile manufacture and printing	*	*				
Organic chemicals, petrochemicals	*		*	*		*
Plastics	*					
Alkalis, chlorine, inorganic chemicals	*		*	*		*
Fertilizer	*	*	*	*	*	*
Paint			*	*	*	
Petroleum Refining	*	*	*	*		*
Basic Steel Works, Foundaries	*	*	*	*		*
Basic Nonferrous Metal Works, Foundaries	*	*		*		*
Electroplating	*	*	*	*		*
Motor Vehicles, Aircraft Plating, Finishing	*	*				
Battery Manufacture	*		*	*		
Electronics, including television tube Manufacture		*		*		
Steam Generation Power Plants						*

(From Dean et al (1972) and Patterson (1979)).

To provide an indirect quantification of the input of heavy metals into the environment from industrial sources, calculations of total emissions have been made by several authors. Table 2.4 presents a comprehensive list of estimated emissions for Europe (Pacyna, 1984) and the UK (Pacyna, 1984; Hutton and Symon, 1986). The difficulties in estimating total emissions can be seen by the difference in the estimates for the UK. Comparison of the figures in individual categories is not possible as the categories vary with author. The overall difference seen may reflect the changes in production rates between 1979, the data base used by Pacyna (1984) and those of 1980 to 1983, as used by Hutton and Symon (1986).

From Table 2.4 it can be seen that the major industrial source of Cd, Cu and Zn is primary non-ferrous metal production, while for Mn the major source is iron and steel production. The most important source of Pb is gasoline combustion with approximately 60% of total Pb source emissions being derived from automobiles. Although industrial emissions of Pb are, in overall terms, relatively minor on a local scale it has been demonstrated that these sources can cause serious increases in ambient

Table 2.4 European and United Kingdom Emissions of Trace Elements from Various Sources in 1979

	Percent of Total European Metal Emissions				
	Cd	Cu	Mn	Pb	Zn
Conventional thermal power plants	3.8	8.8	7.4	0.9	1.7
Industrial, commercial and residential combustion of fuels	5.8	13	10.1	1.3	2.3
Wood combustion	0.9	9.6		0.5	5.8
Gasoline combustion	1.1		0.7	60.4	
Mining	<0.1	1.2	2.0	0.9	0.6
Nonferrous metal production	81.3	54.2		22.8	69.1
Iron steel ferro alloys manufacturing	2.2	10.9	79.0	11.9	12.9
Refuse incineration	3.2	1.7	0.8	0.7	7.4
Phosphate fertilizer production	1	0.5		<0.1	0.3
Cement production	0.6			0.6	
Total European (t year^{-1})	2700	15500	13600	123000	80000
Total United Kingdom (t year^{-1})	99	580		10098	3488
*Total United Kingdom** (t year^{-1})	*14.1*			*7590*	

* Estimate for unspecified year

From Pacyna (1984) and Hutton and Symon (1986) (Indicated by italics).

airborne Pb levels (Harrison and Laxen, 1980). Smelting and sintering of non-ferrous metals has also been shown to result in an enrichment of Cd and Zn (Page and Chang, 1979; Harrison and Williams, 1983; Scokart et al, 1983) and Cu (Scokart et al, 1983) as well as Pb in the local environment.

Fugitive emissions of large particulates have been identified as a major source of elevated atmospheric metal levels in the immediate vicinity of metal smelting operations and are also responsible for the high rate of metal fallout in the local area (Roberts et al, 1974; Muskett et al, 1979; Harrison and Williams, 1983; Schwitzgebel et al, 1983; Davis and Clayton, 1986a).

The emission of fine particulates from smelting operations can result in elevated levels of metal concentrations over a significant area surrounding the smelting plant. The high temperatures used in smelting processes result in the surface enrichment of trace metals on the emitted fine particulates (Van Craen et al, 1983). The influence of smelters on the enhancement of concentrations of heavy metals found in the surrounding area is dependent on the size of the discharges from the chimney stacks (Roberts et al, 1974), the height of the stack, and ultimately on the size of the secondary metal works. The metal concentrations in air, soils and vegetation have been shown to increase, sometimes quite dramatically, with decreasing distance from smelting operations (Burkitt et al, 1972; Roberts et al, 1974; Linzon et al, 1976; Muskett et al, 1979; Page and Chang, 1979; Scokart et al, 1983; Løbersli and Steinnes, 1988). The effects, although termed "localised", may extend to areas greater than a distance of four kilometres from the source. (Griffiths and Wadsworth, 1980; Zwozdziak and Zwozdziak, 1982).

Fossil fuel combustion by both domestic and industrial consumers is another major source of heavy metals (Bertine and Goldberg, 1971; Nriagu, 1979; Pacyna, 1984). Table 2.4 shows that, particularly for Cd and Cu, fossil fuel combustion is a major source which is second only in size to primary non-ferrous metal production. The contribution of fossil fuel combustion is accentuated when emissions from conventional power plants are also considered (Table 2.4). The operational temperatures of flue gases in coal fired power stations are equal to or greater than those found in smelting operations with similar surface enhancement of metals on emitted particulates (Natusch et al, 1974; Linton et al, 1976; Keyser et al, 1978).

Incineration of refuse, although not comparable to primary metal production or fossil fuel combustion as a source of heavy metals (Table 2.4), does contribute significant amounts of metals, particularly Zn, to the atmosphere (Greenberg et al, 1978a; 1978b; Kowalczyak et al, 1978). The higher stack temperatures found in incinerators compared to power plant stacks results in a greater metal enrichment of emitted particulates (Greenberg et al, 1978a).

The environmental impact of metals released from fossil fuel combustion in power stations and from incineration of refuse is similar to that of metals released from smelting operations. Increases in the concentrations of metals in soil have been found with decreasing distance from power stations (Klein and Russell, 1973; Ritter and Rinefierd, 1983). Evidence of enhancement of Cd and Pb in surface dusts as a result of fugitive emissions from an incinerator has also been observed (Hutton and Wadge, 1987).

Other industrial sources found to cause considerable localised heavy metal pollution include printing presses (Jensen and Laxen, 1985), scrap yards (Little and Heard, 1983; Blake et al, 1987) and car breakers (Blake et al, 1987). The main route of metal release was found to be the entrainment of fugitive dusts by persons and vehicles visiting the premises.

2.1.2 Domestic Sources.

The use of heavy metals in the construction of materials found in the domestic sector gives rise to a wide variety of potential sources of heavy metal pollution. Additionally, the use of fossil fuels for heating provides a source from which the mobilisation of metals is similar to that found in power plants, although on a much smaller scale.

Recent research has indicated that constructional and decorating materials, particularly paints, are a major source of Pb and are undoubtedly a cause for considerable concern (Jordan and Hogan, 1975; Solomon and Hartford, 1976; Ter Haar and Aronow, 1974; Millar, 1978; Inskip and Atterbury, 1983; Inskip, 1984; Rundle and Duggan, 1986; Duggan et al, 1986). From a study carried out at a London school, Millar and Cooney (1982) concluded that lead based paint presented a greater and more immediate threat to the health of children than airborne Pb from a nearby major highway. Paint in poor condition was found to significantly increase levels of Pb in playground dust at schools (Beeching and Lovell, 1985). Sturges and Harrison (1985) found that Pb from paint made up to 19% of the total Pb in street dusts and 15% of the total Pb in house dusts.

The Pb levels found in soil surrounding houses have been shown to increase with the age of housing (Jordan and Hogan, 1975; Davies, 1978; Thornton et al, 1985; Davies et al, 1987) (Table 2.5) and the condition of paintwork (Jordan and Hogan, 1975; Solomon and Hartford, 1976; Davies, 1978; Ter Haar, 1979). Blood Pb levels have been shown to be similarly affected (Reeves et al, 1982; Quinn, 1983).

Table 2.5 Heavy Metal Concentrations ($\mu g\ g^{-1}$) in Garden Soils Related to Age of the Garden and of House.

Type and Age		Cd	Cu	Pb	Zn	Ref
a) Gardens						
Rural	- Mature	0.5,3.1	18,75	182,509	30,663	1
	- Young	0.4	15	10	21	1
	- New	0.3	5.3,7.5	10,13	3.8,6.4	1
	- Allotments	0.3,0.9	15,28	10,13	64,71	1
Urban	- Mature	0.4-1.0	13-64	106-680	181-744	1
	- Young	1.9	75	380	240	1
	- Allotments	0.4,0.5	3.5,5.7	14,18	6.4,11	1
b) Houses						
Urban	pre 1950			342		2
	post 1950			176		2
Unknown	pre 1885			180-3500*		3
	post 1955			50-1500*		3

* Values read from Figure in reference.

References
1 Davies, 1978
2 Davies et al, 1987
3 Thornton et al, 1985

Lead from paints, concrete and plaster may be directly removed to the soil or paved surfaces in the form of paint flakes or solid chippings. Maintenance practices, such as the sanding down of paint surfaces, result in the removal and effective dispersal of Pb (Inskip and Atterbury, 1983; Inskip, 1984; Rundle and Duggan, 1986; Duggan et al, 1986; Warren 1987). Re-decoration has been found to increase the Pb concentration in household dusts (Davies et al, 1987) and in school playground dusts (Rundle and Duggan, 1986; Warren, 1987). Both attrition and maintenance practices can therefore contribute to the heavy metal burden of both immediate external and internal residential environments.

Lead is not the only heavy metal derived from external domestic surfaces. Zinc, as well as Pb, is also widely used as a weatherproofing material. In many countries copper is a popular material for roofing and for facade covering. In older buildings the use of Pb to "point" stonework, as on St. Pauls Cathedral, London, has resulted in areas of Pb being directly exposed to weathering (Schwar and Ball, 1983). Metals enter the environment from these sources as particulates released through attrition processes and also in the dissolved form in runoff due to leaching of metal coverings, particularly by rainfall of low pH (Jorgensen and Willems, 1987). High Zn deposition rates found at a Belgian site were attributed to corrosion of roofing materials near to the sampling site (Navarre et al, 1980). Malmqvist (1978) attributes differences in Cu and Zn contents of fallout/precipitation and stormwater to corrosion of building materials and states that this contribution is of greater importance than that of combined wet and dry deposition.

Household waste may contribute metals, although the majority of the waste is removed by statutory undertakers. Metal objects, such as tins, batteries and foil wrappings, will make a direct contribution. The majority of household waste consists of paper and plastics from packaging of consumable products. Cadmium is a common constituent of pigments and of stabilizers used in the plastic industry and as a consequence of uptake by trees occurs in paper and cardboard (Lagerwerff and Specht, 1970a). The breakdown and weathering of waste from domestic sources in the urban environment is another potential source of metal pollution.

Other domestic sources of heavy metals include garden treatments such as herbicides, fungicides and fertilizers which are known to contain significant levels of heavy metals (McGrath, 1964; Carrol, 1969; Lee and Keeney, 1975; Davies, 1978; Dickinson and Lepp, 1984; Magalhoes, 1985).

Domestic sources of heavy metals are rarely significant on a large scale, although their effect in terms of localised pollution, particularly in residential areas, can be of importance.

2.1.3 Vehicular Sources.

The use of Pb additives in petrol and consequently the large quantities emitted from vehicle exhausts (Table 2.4), has inevitably concentrated attention on the automobile as a major pollution source. Heavy metals which enter the urban environment from vehicular sources may have their derivation in;

exhaust emissions
attrition of vehicular materials
leakages and spills
direct inputs from bodywork fracture and corrosion
poor maintenance practices as well as direct dumping

Exhaust emissions, however, remain the dominant form of vehicular pollution. Tetra alkyl Pb compounds, in the form of ethyl and methyl derivatives are added to petrol as anti-knock agents. Small amounts of these compounds are lost by fuel evaporation and by passing through the engine unchanged. As a result relatively low levels are found in the atmosphere (Harrison, 1976; Harrison and Perry, 1977; Harrison and Radojevic, 1985). The majority of emitted Pb is exhausted as particulate inorganic compounds (Laxen and Harrison, 1977), mixed with iron (in the form of rust), base metals, soot, carbonaceous material and tars (Habibi, 1973). The majority of particulates are emitted in two size ranges; less than 1 μm and between 5 μm-50 μm (Habibi, 1973). The proportion of relatively small (<1 μm) to relatively large (5 μm-50 μm) particles in the emissions is highly dependent upon driving mode and speed (Ter Haar et al, 1972). A large amount of Pb is retained in the engine, the oil and the exhaust system during normal conditions. However, Pb particles from the exhaust system are re-entrained during high speed and high load conditions (Habibi, 1973; Ter Haar et al, 1972). Under cruise conditions, therefore, the smaller particulates predominate. However, in urban driving cycles the percentage of larger particulates contributing to total Pb emissions increases (Habibi, 1973;

Little and Wiffen, 1977). Larger particulates are subject to gravitational settling and turbulent deposition (Habibi, 1973), which leads to the increased Pb levels found within the immediate vicinity of highways. The smaller particles may remain airborne in the form of an aerosol for extended periods and these predominate away from the highway (Daines et al, 1970). The pattern of deposition of heavy metals in relation to the highway is dealt with in more detail in Section 2.4.2.

The quantification of the amount of Pb produced from vehicular sources is difficult, although an estimation can be made. In the UK in 1985, cars and taxis accounted for 229380 million vehicle kilometres (CSO, 1988). Assuming an average of 30 miles to the gallon (approximately 10.62 km l^{-1}) this would mean that 21598.87 million litres of petrol were used by cars and taxis. This will be an over-estimate as taxis use diesel fuel and there is also a small percentage of diesel cars in the UK. However, this will be more than compensated for by the 1.4 million motor cycles, mopeds and scooters as well as the petrol driven commercial traffic not taken into account by this calculation.

Using the pre-1986 level for Pb in petrol of 0.4g l^{-1}, the amount of Pb which entered the engines of cars in 1982 can be calculated to be 8639.5 tonnes. Since 75% of this Pb is released in the exhaust (Chamberlain et al, 1979) the eventual emission of Pb from vehicular sources would be 6479.6 tonnes. This value compares favourably with that of 7275 tonnes Pb in vehicle emissions quoted in the Royal Commission on Environmental Pollution Ninth Report (1983) and that of 6720 tonnes given by McInnes (1986). The latter was based on petrol deliveries for the period of January to March 1985 and 70% of the Pb in the petrol being emitted in the exhaust from motor vehicles. The Royal Commission report suggests that 10% of this output is deposited within 100m of the roadside, which is similar to the data presented by Huntzicker et al (1975). However. Huntzicker et al (1975), pointed out that this is an under-estimate given that large particle size emissions probably occur on uphill sections and areas where vehicles undergo heavy loads (Habibi, 1973). The 10% estimate was based on data derived from sampling on a unidirectional highway with a slight decline. An upper limit can be calculated using figures given by Ter Haar et al (1972) which state that over the lifetime of a car, 40% of the Pb burned is emitted as coarse particulates. The range of Pb deposition to the roadside environment as estimated by these calculations is therefore a minimum of 679 tonnes (10% of the estimate of Pb emissions made in this study) to a maximum of 2910 tonnes (40% of the Royal Commission emission figure).

From January 1986 the Pb content of petrol was reduced to 0.15 g l^{-1}. McInnes (1986) estimates that the Pb emissions from motor vehicles for January to March 1986 amounted to 640 tonnes, giving an approximate annual emission of 2560 tonnes. In 1986 cars and taxis accounted for 242430 million vehicle kilometres (CSO, 1988). Using a Pb concentration of 0.15 g l^{-1} and carrying out a similar calculation as before the estimated Pb emission from vehicular traffic is 2568 tonnes. This figure is extremely close to that of McInnes (1986). The equivalent range for Pb deposition to the roadside environment after reduction of the Pb content of petrol to 0.15 g l^{-1} from 4 g l^{-1} is estimated to have been 257 to 1027 tonnes. While this does represent a significant reduction in the mass of Pb deposited to the roadside there is still a substantial amount of Pb deposited which will be subjected to the environmental processes described previously.

The concentrations of metals in new and used automobile and roadway products (Table 2.6) suggest that attrition of road surfaces and vehicle components also contribute other heavy metals in addition to Pb and these metals are present in the road surfaces and vehicle components in greater concentrations than that of Pb in gasoline. The actual weight of metal input into the highway environment is not dominated by the concentration but by the weight of the product that is used, i.e. Pb from particulates in exhaust emissions is much greater than that from brakes as the weight of gasoline used in a typical journey is very much greater than the weight of brake linings that is used and abraded in the same journey.

Zinc is derived from a number of vehicle components, including galvanised exhaust sytems, plating and more significantly, tyres.

Table 2.6 Metals Levels ($\mu g\ g^{-1}$) in Automobile and Roadway Products

	Cd	Cu	Pb	Zn
Gasoline		4	663	10
Motor Oil (Unused)	(0.2-0.26*)	3	9	1060(642*)
Motor Oil (Used)		36$^{\times}$	13600$^{\times}$	3570$^{\times}$
Transmission Fluid			8	244
Antifreeze		76	6	14
Undercoating		5	7	108
Brake Fluid		5	7	15
Brake Linings		30600	1050	124
Rubber	(20-90*)	182	1110	3570(7300^{+})
Asphalt		51	102	164
Concrete		99	450	417
Deicing Salt			8.7°	6°

From Shaheen (1975) except * Lagerwerff and Specht (1970)
$^{\circ}$ Hedley and Lockley (1978)
$^{+}$ Christensen and Guinn (1979)
$^{\times}$ Wilber and Hunter (1980)

Christensen and Guinn (1979) have estimated the deposition rate per vehicle kilometre of Zn from tyres using the equation:

$$\text{Zn deposition} = (\pi * TD * TW * WR * D * Z * N)$$

where TD = Tyre diameter
TW = Tyre width
WR = Wear rate (1cm/32000km)
D = Tyre density (1.07g cm^{3})
Z = Zn concentration (0.0073 g g^{-1})
N = Number of tyres on vehicle (4)

Using the data for US tyres, Christensen and Guinn calculated that the deposition rate of Zn from tyres was 3 mg Zn per vehicle kilometre. British tyres, however, are generally smaller than US tyres and a deposition rate of 324 mg of particulates per vehicle kilometre including 2.4 mg Zn per vehicle kilometre has been calculated using the tyre dimensions of a standard British saloon car (14 cm width and 55 cm diameter). Dannis (1974) and Pierson and Brachaczek (1974) estimated the average tyre wear in the United States of America to be 90 and 93 mg vehicle km^{-1}, respectively, while Brunner (1975) estimated the production of tyre wear products in West Germany to be 120 mg vehicle km^{-1}.

Using the extremes of these deposition rates, the number of vehicle kilometres driven used previously to calculate the mass of Pb deposition and the data in Table 2.6 it was calculated that the total Zn deposited in 1985 by cars and taxis would have been between 73.7 and 550.5 tonnes. This value does not include commercial traffic which accounted for 47780 million vehicle kilometres in 1985. The deposition of Zn from commercial vehicles was calculated using the tyre dimension values of Christensen and Guinn (1979) and assuming a tyre number of 6 to be an average for all commercial traffic. The resulting figure for deposition of Zn from wear of tyres fitted to commercial vehicles would have been 215 tonnes in 1985. The estimated deposition of Zn based on the concentration of Zn in tyres given by Shaheen (1975) and the wear rate given by Dannis (1974) would be 15.4 tonnes. The total input of Zn to the highway environment from tyres in Britain in 1985 would therefore have been approximately 89-766 tonnes. Tyres also contain quantities of other metals (Table 2.6) and using the same procedure the input of Cd, Cu and Pb was calculated. The total mass of particulates and metals estimated to result from tyre wear is presented in Table 2.7.

Table 2.7 Estimated Inputs (Tonnes)to the Highway Environment from the Vehicle Associated Sources for 1985.

	Cd	Cu	Pb	Zn	Particulates
Vehicle Exhaust			679-2910		679-2910
Tyre Wear	0.5-8.6	5-17	28-106	89-766	24985-95102
Brake Wear		69-95	2-3	0.3-0.4	2262-2516
Highway Surface Wear		33	103	120	507614

Pierson and Brachaczek (1974) stated that the majority of tyre wear products were in the form of non-suspendable particles which were deposited near the road. This conclusion was substantiated by Cadle and Williams, (1978) who found that particulates resulting from tyre wear range in size from less than 0.01 μm to greater than 30 μm, with the larger particulates dominating the total mass. They also found that the majority of tyre debris settled within 5 m of the pavement edge of the highway studied. Tyre wear therefore results in a significant input of particulates and metals directly to the immediate roadside environment.

Copper is used in brake linings to add mechanical strength and aid dissipation of heat. Malmqvist (1983) gives an estimate of brake emissions of 8 mg of particulates per kilometre, 6.5 mg of which was airborne matter and 1.5 mg of which was sedimentary. Jacko and DuCharme (1973) found that approximately 3.7% of emitted particulates from braking operations was airborne, 81.9% was deposited on the road and 14.4% was retained in the braking equipment. The airborne particulates have an average diameter of 3 μm with 90% of the total mass being greater than 1 μm (Malmqvist, 1983). The size range of the particulates falls between the extremes of exhaust particulates and this would be reflected in the distribution of the particulates, probably being similar to that of exhaust particulates but not to the extremes of distribution. Using the previously quoted data of the number of vehicle kilometres travelled in Britain in 1985 and the data in Table 2.6 the total mass of metal and particulates resulting from the use of brakes in 1985 was estimated (Table 2.7).

Cu input to the highway environment is estimated as 69 to 95 tonnes. This is an order of magnitude smaller than Pb or Zn inputs from exhaust particulates and tyre wear, respectively. Cu is also used in the manufacture of engine bearings and brushes and erosion of these parts may release further Cu into the highway environment.

De-icing salt has been shown to significantly increase the heavy metal burden of the highway (Hedley and Lockley, 1975) and in addition the presence of salt may stimulate corrosion and therefore produce further metal pollutant input. In the case of Pb, Harrison and Laxen (1977) suggest that salt only accounts for 5% of the total highway input .

Leakages and spills of vehicular fluids can produce localised increases of heavy metals as they contain appreciable concentrations of metals (Table 2.6). Motor oil contains appreciable levels of Zn before use and after use motor oil contains considerably increased Pb levels (Table 2.6). Up to 10-33% of Pb in petrol which passes through the engine is retained in motor oil (Ter Haar et al, 1972; Huntzicker et al, 1975). The heavy metal input from leakages and spills is not evenly distributed as such inputs are greatest in areas where vehicles are parked regularly, particularly if vehicle maintenance is carried out. The overall effect of this is to cause 'hot spots' of heavy metal concentrations on the highway which may show up as anomolies in investigations of spatial variations of heavy metals.

Highway surfaces are also contributors to the heavy metal burden (Table 2.6) and this contribution will be directly related to the constituents and condition of the surface material, its wearing rate, as well as traffic density. Brunner (1975) estimated the wear of road surfaces by vehicles not using studded tyres in West Germany to be between 1 kg of solids per metre to 10 kg of solids per metre of highway. The smallest highway considered had a traffic density of 4500 vehicles per day. Göttle (1978) estimated wear of motorways and city streets to be on average 8-10 kg per metre of highway. An estimate of the metals and particulates resulting from wear of road surfaces was made by assuming all motorways and trunk roads to be concrete and having a wear rate of 8 kg m^{-1} and all other public roads to be asphalt and having a wear rate of 1 kg m^{-1}. The length of public roads in the UK is approximately 361406 km and the length of motorways and trunk roads is approximately 18276 km. The results are presented in Table 2.7.

Road marking paints may also make a minor contribution to the heavy metal concentrations on highway surfaces. Analysis of yellow road paint has shown it to have levels of Cu, Pb and Zn of 2.96, 7.03 and 1.4% respectively (Warren, 1987). Turner (1973) found that very little Pb was derived from yellow road markings and it is likely that unless the paint is in poor condition the contribution to the heavy metal loadings is extremely small.

Vehicles have been clearly shown to be a significant source of a variety of heavy metals in significant amounts and it would therefore be expected that environmental heavy metal concentrations would increase with traffic density. Table 2.8 which presents heavy metal levels in air for roadways carrying traffic of differing densities shows that Pb levels in air increase with increasing traffic density. It can also be noted that the effects of enclosure also increase the concentrations in air, the maximum levels occurring in road tunnels (Table 2.8).

Temporal variations have been observed in lead in air measurements made in the vicinity of roads. These have been shown to further indicate motor vehicles as a major source by correlating with traffic flow (Atkins, 1969; Laxen et al, 1985). Meteorological conditions have also been found to affect the concentrations, particularly with regard to seasonal variations (Atkins, 1969).

In a similar manner to Pb concentrations found in air, Pb deposition rates have been found to correlate positively with traffic density (Elias and Croxdale, 1980). It would be expected that a similar relationship would be found between metal concentrations in surfaces receiving deposited particulates. Lead concentrations in soils at a uniform distance from the road verge have been found to increase with increasing traffic density (Lagerwerff and Specht, 1970b; Motto et al, 1970; Schuck and Locke, 1970; Rameau, 1972; Rolfe and Jennett, 1973; Havre and Underdal, 1976; Smith, 1976; Ward et al, 1977; Wheeler and Rolfe, 1979; Yassaglou et al, 1987), as have Cd and Zn concentrations (Lagerwerff and Specht, 1970a; 1970b; Ward et al, 1977; Yassaglou et al, 1987) and Cu concentrations (Ward et al, 1977). The concentration of heavy metals in roadside vegetation has also been found to increase with increasing traffic density for Pb (Webb and Burley, 1962; Lagerwerff and Specht, 1970b; Rameau, 1972; Ward et al, 1977; Wheeler and Rolfe, 1979), Cd and Zn (Lagerwerff and Specht, 1970a; 1970b; Ward et al, 1977) and Cu (Ward et al, 1977).

From the information presented, vehicular sources can be seen to give rise to a large input of a variety of heavy metals, the effects of which are noticeable in the immediate vicinity of highways in air, soil and

Table 2.8 Heavy Metal Concentrations in Air (μg m^{-3}) at Highways of Varying Traffic Densities.

Cd	Cu	Pb	Zn	Traffic Flow (Vehicles hour^{-1})	References
		2.8-4.5(3.5)		1620[w*]	Bullock and Lewis, 1968 - High Street, Warwick
		8.3-19.1(13.8)		3000[w]	Bevan et al, 1974 - M4, Harlington, Middlesex
		3.2		1644	Harrison et al, 1974 - a) Wide open suburban street, London, SW7
		4.0		548	b) Narrow street, Central London, W1
		4.3		560	c) Narrow street, Central London, W1
		8.8		5089	d) Major arterial road (Talgarth Rd), London, W14
		32.2		1596	e) Heathrow Tunnel
		0.9-7.2(3.0)		1167[w]	Hickman et al, 1976 - a) Urban dual carriageway - Butts Rd, Coventry
		1.2-2.5(1.7)		833[w]	b) Suburban shopping area - Walsgrave Rd, Coventry
		1.7		833[w]	c) Major arterial Road - Foleshill Rd, Coventry
		1.0-2.1(1.5)		667[w]	d) Road in mainly residential area - Holyhead Rd, Coventry
		5.0-15.5		4000	Little and Wiffen, 1977 - M4, Heston, London.
		7.1-14.2		4000	Little and Wiffen, 1978 - M4, Heston, London.
		4.2		1250	De Jonghe and Adams, 1980 - average at road tunnel, Antwerp, Belgium
		2.1-2.6(2.4)		706	Hickman and Lunn, 1980 - a) 8m from road under bridge carrying motorway
		2.0-3.4(2.7)		706	b) 7m from kerbside of road at gap in bridge carrying motorway
		1.8-7.8(3.9)		252	c) 1m from kerbside of road under bridge carrying motorway
		0.6-5.5(1.4)		3500	Hickman and Lunn, 1981 - a) A406, Finchley Road, London
		1.8		5300[w]	b) A406, Finchley Road, London (Weekdays)
		1.0-3.3(1.9)		1460	Millar and Cooney, 1982 - Major road - Rochester Way, London.
		0.1-24.1(3.8)		2720	Colwill et al, 1983 - 60m from Heathrow Airport Tunnel
		20		-	Schwar and Ball, 1983 - a) Blackwall Tunnel, London
		2.2		1667	b) A40, Hillingdon, Middlesex.
		3.2		-	c) Westway, London, W10.
		1.2-1.8(1.6)		<1250	Caswell, 1985 - a) 3 London streets
		1.3-1.9(1.5)		1250-2500	b) 7 London streets
		0.8-3.9(1.9)		>2500	c) 5 London streets
(0.001)	(0.22)	0.4-0.8(0.6)	(0.73)	2920	Warren and Birch, 1987 - A13, Newham, London

[w] - Weekdays only
[w*] - Based on 11 hour measurement on a Friday
Mean values in parentheses

vegetation and increase with the traffic density.

2.2 Pathways of Heavy Metals in Urban Highway Environments.

The urban environment contains many sites where heavy metals will deposit and collect. These may be intermediate or short term sites such as plant surfaces, or long term sites such as soils, where metals may undergo chemical interaction and fixation. In addition there are important transport mechanisms such as urban runoff, by which metals are transported and may be eventually removed from the urban area.

Where an industrial source is present it will normally dominate the environment and it is more typical for a non-industrialised highway environment to be considered where sources, other than a single industry, and their effects may be evaluated. Figure 1.1.summarises the sinks, compartments and transport routes within a non-industrialised urban environment such as a residential catchment. It is important to identify each component of the environment and the levels of heavy metals contained therein so that health risks and total environmental impact can be identified and quantified.

2.2.1 Atmosphere.

The atmosphere is important with regard to heavy metal pollution as many inter-site transport processes occur through and within this section of the environment (Figure 1.1). In areas where a predominant atmospheric pollution source, such as a local industrial plant, is not present the background input of metals from remote industrial sources can still be significant.

In a small non-industrialised urban environment the local sources outlined in Figure 1.1 including vehicular and domestic emissions may far outweigh the input of remote heavy metal particulates which have been transported via the atmosphere from distant sources. Only by direct quantification of all sources involved can the balance between local and remote sources be ascertained with confidence.

Vehicular sources are capable of giving rise to elevated airborne concentrations of heavy metals, being dependent on traffic density and degree of enclosure of the highway (Table 2.8). It would be expected that heavy metal concentrations in air would decrease with distance from source, the metals becoming more dispersed. Table 2.9 presents heavy metal concentrations in air with distance from the highway. All the figures are not directly comparable as each road will vary as to traffic density, gradient and average vehicle speed however the trend for concentrations to decrease with distance can be seen to be documented on a variety of road types. There is a corresponding decrease in metal deposition with distance from the highway (Table 2.10). This would appear to indicate that the variation of airborne metal concentration and of metal deposition are linked and are dependent on the characteristics of the highway.

The airborne pollutants released from cars giving rise to the concentration and deposition gradients may be transformed, as both gaseous pollutants and pollutants associated with suspended particulates whilst in the atmospheric compartment. Although heavy metals rarely occur in a gaseous form in the urban environment, Pb in the form of tetraalkyl compounds (TAL) may be present due to evaporation from petrol. 1-6% of Pb in street air may exist as TAL compounds (Harrison et al, 1979; Harrison and Laxen, 1980) while levels of 3.5%-20.7% have been measured at the central reservation of a motorway and higher values of up to 59.4% have been measured at filling stations (Colwill and Hickman, 1973). It has been suggested that in the atmosphere these TAL compounds are liable to undergo photochemical reactions resulting in the degradation to a Pb containing aerosol (Huntzicker et al, 1975; Harrison and Laxen, 1978). Photochemical degradation of PbClBr, a predominant form of Pb in vehicle exhaust emissions, to Pb oxides and chlorine gas has been suggested (Pierrard,1969). Research has shown, however, that light is not essential for the transformation of PbClBr to Pb oxides, Pb carbonate and Pb oxycarbonate (Ter Haar and Bayard, 1971; Harrison and Biggins, 1979). An alternative method of degradation of emissions has been suggested to occur by coagulation of sub-optical particles of

Table 2.9 Heavy Metal Concentrations in Air ($\mu g\ m^{-3}$) at Varying Distances from the Highway.

Cd	Cu	Pb	Zn	Distance (m)	Ref
		8.3-19.1(13.8)		0	1
		4.5-11.9(6.9)		30	1
		2.7,3.7(3.2)		60	1
		2.0		90	1
		1.4,1.9(1.7)		120	1
		4.1		0	2
		3.0		20	2
		2.5		30	2
		1.2		50	2
		5.0-15.5		0	3
		2.4-6.2		5	3
		2.9		15	3
		1.9		30	3
		8.5-25.6		0	4
		3.4-17.4		2	4
		2.4-13.6		8	4
		4.5-9.6		18	4
		3.0-6.9		33	4
		2.87	1.65	3	5
		0.98	1.31	350	5
0.01		2.1		1	6
0.007		1.1		10	6
UD		0.8		30	6
UD		0.5		100	6
		2.2		25	7a
		0.86		95	7a
		0.66		183	7a
		0.93		26	7b
		0.58		96	7b
		0.42		300	7b
	42	255		1	8*
	6	55		10	8*
	3	8		125	8*
0.001	0.02	0.69	0.07	5	9
0.001	0.02	0.43	0.07	22	9

Mean values in parentheses UD - Under detection limits.
* - Values taken from diagram.

<u>References</u>

1 Bevan et al, 1974 - M4, Harlington, Middlesex.
2 Hickman, 1976 - A4 Cromwell Road, London
3 Little and Wiffen, 1977 - M4, Heston, London.
4 Little and Wiffen, 1978 - M4, Heston, London.
5 Mc Kee et al, 1980 - A38, Birmingham.
6 Muskett and Jones, 1980 - A40, Hillingdon, Middlesex.
7 Turner et al, 1980 a) M4, West Drayton, Middlesex.
b) A406, Neasden, London.
8 Johnston and Harrison, 1984 - M6, Lancaster.
9 Warren and Birch, 1987 - A13, Newham, London.

Table 2.10 Heavy Metal Deposition (mg m^{-2} day^{-1}) at Varying Distances from Highways.

Cd	Cu	Pb	Zn	Distance (m)	Ref
		14.22		CR	1
		7.79-13.44		0	1
		4.27		5	1
		7.05-14.2		CR	2
		5.2-13.44		2	2
		2.09-5.58		8	2
		1.0-2.82		18	2
		0.52-1.61		33	2
0.003		0.633		25	3a
0.0027		0.6		95	3a
0.0043		0.533		183	3a
0.0023		1.367		26	3b
0.0013		0.733		96	3b
0.0017		0.567		300	3b
		0.11-1.61(0.54)		6	4a
		<0.01-0.15(0.06)		20	4a
		0.02-0.07(0.04)		100	4a
0.0056	0.3226	1.065	0.7097	3	4b
0.0073	0.3548	1.016	0.6613	5	4b
0.0018	0.0968	0.226	0.2419	7	4b
0.0019	0.0726	0.124	0.1613	10	4b
0.0077	0.0323	0.0613	0.0677	19	4b
0.0014	0.0613	0.0355	0.071	37	4b
0.0053	0.0484	0.015	0.0452	57	4b
0.001	0.0597	0.0177	0.0758	104	4b
0.0043*	0.121*	0.217-2.643		3.8	5
0.0043*	0.017*	0.0829-0.2843		9.0	5
0.0043*	0.004*	0.0214-0.1586		15.0	5
0.0029*	0.026*	0.0371-0.1329		34.0	5
0.0021*	0.014*	0.0257-0.1329		63.0	5
0.0016*	0.014*	0.0171-0.0643		113.0	5
0.0008*	0.017*	0.0143-0.0371		223.0	5

* - Values taken from diagram in reference.

<u>References</u>

1 Little and Wiffen, 1977 - M4, Heston, London.
2 Little and Wiffen, 1978 - M4, Heston, London.
3 Turner et al, 1980 - a) M4, West Drayton, Middlesex.
b) A406, Neasden, London.
4 Lygren et al, 1984 - a) Deposition measured in dustfall.
b) Deposition calculated from concentration in snow 2 months after snowfall.
5 Johnston and Harrison, 1984 - M6, Lancaster.

primary vehicle exhaust with solution droplets of neutral and acid sulphates (Harrison and Biggins, 1979; Harrison and Laxen, 1980).

The degradation of atmospheric compounds is important in relation to the solubility of the toxic metals present. $PbBr_2$ and $PbCl_2$ are only sparingly soluble to the extent of 4 g l^{-1} and 1000 g l^{-1}, respectively. However, the reaction products PbO and $PbSO_4$ are even less soluble with values of 0.017 g l^{-1} and 0.04 g l^{-1}, respectively (Chamberlain et al, 1979).

In addition to direct emissions to the atmosphere, there will also be indirect inputs due to resuspension of particulate associated metals and soluble metals. Resuspension may be caused by natural air turbulence, turbulence caused by the passage of traffic or by inefficient street cleaning practices. The passage of traffic across any wet surface will result in resuspension of heavy metals, both soluble and insoluble, in the form of spray. Vehicular spray will be dependent on vehicle speed and intensity, rainfall duration and wind speed and direction (Jones and Tinker, 1984). A study of pollutant losses from the road surface has found that between 9.3 and 57.3% of the total suspended solids lost from the road surface during a rainfall event were removed as spray, assuming pollutant concentrations in spray and runoff were equal (Jones and Tinker, 1984). The high percentage losses were found for rainfall events during which the road surface was only partially wetted so that while spray occurred road runoff was minimal. Ratcliffe and Beeby (1984) have suggested that vehicle generated spray could be responsible for a considerable proportion of the seasonal variation in Pb content of roadside vegetation. Pope et al (1979) estimated that 42% of the Pb in soil adjacent to highways was transferred by spray processes from the road surface. The levels of Pb associated with spray decreased with distance from the highway (Pope et al, 1978).

2.2.2 Deposition of Heavy Metals.

The principal removal mechanisms for heavy metals from the atmosphere are wet and dry deposition. Dry deposition occurs by sedimentation, diffusion and inertial impaction. Wet deposition involves the incorporation of heavy metals in rainwater in the form of rainout or washout. Rainout is the formation of raindrops about particle nucleii and consequential deposition, whereas washout involves the scavenging of particles by rain drops during deposition. The relative importance of rainout as opposed to washout seems to be variable although in general rainout appears to be the dominant process (Mueller and Beilke, 1975). The removal efficiency of metals from the atmosphere depends on a variety of factors including;

a) the physical characteristics of the suspended material with which the metals are associated
b) the solubility of the metals
c) the meteorological conditions
d) the nature of the receiving surface
e) the height at which the metal emission occurs

This last factor is important in the consideration of industrial inputs where emissions are normally released from tall stacks in order that dispersion can occur before deposition. In a non-industrialised urban catchment industrial emissions of particulates from sources outside the catchment may contribute to the background deposition of metals in the catchment (Figure 1.1).

Physical characteristics such as particle size, mass and morphology can dictate the time duration for which a particle will remain suspended in the atmosphere. As described in Section 2.1.3 exhausted particles of larger size, particularly those greater than 5 μm, deposit after a short suspension time and this decreases with increasing particle size and mass. Submicron particulates may remain suspended for extended periods of time and only be removed by wet deposition processes. Tyre wear has been shown to result in particulates varying in size from 0.01 μm to large pieces of debris although the majority of tyre wear is in the form of non-suspendable particulates which are deposited near the road (Pierson and Brachaczek, 1974; Cadle and Williams, 1978). There is some disagreement as to whether the majority of brake particulates are sedimentary or airborne with between 19 and 82% of emitted particulates being predicted to be deposited directly onto the road (Jacko and

DuCharme, 1973; Malmqvist, 1983).

Meteorological conditions will effect both the distribution of particulates and the size of the input. Heavy metal concentrations will be elevated downwind of the source and this has been observed for industrial sources (Burkitt et al, 1972; Little and Martin, 1972; Janssens and Dams, 1975; Ronneau et al, 1978; Harrison and Williams, 1983; Davis and Clayton, 1985a; 1985b; Zauke et al, 1985; Davis and Clayton, 1986a; 1986b) and vehicular sources (Atkins, 1969; Chow, 1970; Bevan et al, 1974; Little and Wiffen, 1978). However it has been found in certain cases that the influence of the prevailing wind is negligible (Hickman, 1976; Hickman et al, 1976). In the case of low level sources such as vehicles, the presence of buildings and trees will give shelter and reduce the directional effects of the wind. The velocity of the wind will also affect the size of particles that remain suspended.

The relative importance of wet deposition as opposed to dry deposition is not certain although wet and dry deposition of the metals, Cd, Pb, Mn and Zn is of generally similar magnitude (Galloway et al, 1982) as is deposition of Cu and Fe (Jeffries and Snyder, 1975). In a highway environment deposition rates will be dominated by vehicle emissions, both direct and in the form of resuspended particulates. This is indicated by the decrease in deposition rates of heavy metals with distance from source i.e. the highway (Table 2.10). As a consequence of decreasing deposition rates with distance from the highway there is a pattern of decreasing metal levels on receiving surfaces such as soils and plants with distance from highways (Table 2.11 and 2.12).

The nature of the receiving surface will greatly affect whether particulates remain on the surface or are resuspended. Surface roughness will facilitate collection of deposited particulates and this has been observed with respect to leaf surfaces where rough leaves with surface hairs collect significantly more particulates than smooth waxy leaves (Little and Wiffen, 1977; Flanagan et al, 1980). Similar effects will occur with road and pavement surfaces where particulates resting on smooth surfaces will be prone to resuspension. Alternatively, the crevices and pits on rough surfaces will act as accumulation sites for

Table 2.11 Heavy Metal Concentrations (μg g^{-1}) in Soils at Varying Distances from Highways.

Cd	Cu	Fe	Pb	Mn	Zn	Distance (m)	References
			130			CR	Rameau, 1972 - E36 (Utrecht-Arnhem), Netherlands.
			365			0	
			40			40	
			27			130	
			2613, 3085			CR	Bevan et al, 1974 - Transect either side of M4, Harlington, Middlesex.
			2022, 1564			3.05	
			1600, 870			4.58	
			870, 653			6.1	
			80, 258			9.15	
			74, 93			15.25	
			628, 744			2	Farmer and Lyon, 1977 - 2 transects on Great Western Road, Glasgow.
			598, 380			10	
			296, 363			20	
			1621, 3740			0	Little and Wiffen, 1978 - Transect either side of M4, Heston, London.
			304, 594			5	
			210, 241			15	
			169, 313			30	
			167, 118			50	
			202			100	
			756		422	0	Wade et al, 1980 - Combined results for 3 major roads, Scotland.
			483		413	2	
			323		351	5	
			212		188	10	
			191		168	15	
			212		182	25	
			188		127	50	
			189		168	150	
			344, 647			0.5	Colwill et al, 1982 - Transect either side of M3 between Junctions 2 and 3, Surrey.
			256, 282			1.0	
			50, 165			2.0	
			59, 106			5.0	
			16	225	12	8	Albasel and Cottenie, 1985 - Available metal in soil, Brussels-Ostend Highway, Aalst, Belgium.
			3	27	5	20	
			55	178	55	1	Albasel and Cottenie, 1985 - Available metal in soil, Brussels-Ostend Highway, Drongen, Belgium.
			26	57	24.5	5	
10	5.1	820	1000	10	10	0.2	Sarosiek and Kwapulinski, 1987 - Wrockaw-Legnica Highway, Poland.
10	2.0	340	100	10	10	150	
			300, 400			0	Deroanne-Bauvin et al, 1987- Transect either side of Bruxelles-Namur Highway, Belgium.
			47, 107			10	
			32, 42			30	
6.0	345.8		1769.1		971.9	0	Warren and Birch, 1987 - Mean levels of 3 transects from A13, Newham Way, London.
3.0	179.2		956.5		534.4	6	
1.4	117.4		442.6		490.1	10	
0.8	78.4		347.2		341.5	20	
1.4	98.0		299.6		411.3	30	
0.8	149.1		563.2		316.0	50	
0.2	31.0		124.4		93.9	100	
			251			0-10	Denton, 1988 - Mean available Pb values from London wide survey
			206			10-50	
			130			>50	

CR - Central Reservation.

Table 2.12 Heavy Metal Concentrations (μg g^{-1}) in Plants at Varying Distances from Highways.

Cd	Pb	Mn	Zn	Distance (m)	References
	583			1	Davies and Holmes, 1972 - Grass, A491, S.W. Birmingham (19267 vehicles day^{-1}).
	208			25	
	406			1	Davies and Holmes, 1972 - Grass, A456, S.W. Birmingham (17497 vehicles day^{-1}).
	312			25	
	514			1	Davies and Holmes, 1972 - Grass, A459, S.W. Birmingham (7473 vehicles day^{-1}).
	292			25	
	550			CR	Rameau, 1972 - Grass, E36 (Utrecht-Arnhem), Netherlands (30000 vehicles day^{-1}).
	135			0	
	110			40	
	33			50	
	38			130	
	3.0			5-10	Havre and Underdal, 1976 - Grass, Nesbyen, Norway (1725 vehicles day^{-1}).
	0.8			10-20	
	1.4			20-30	
	24			1-5	Havre and Underdal, 1976 - Grass, Holmestrand-Semb, Norway (7000 vehicles day^{-1}).
	12			5-10	
	10			10-20	
	875			CR	Little and Wiffen, 1978 - Total vegetation, average of 2 transects either side of M4, Heston, London. (88000 vehicles day^{-1}).
	572, 1180			0	
	390, 770			5	
	228, 628			15	
	226, 228			30	
	83, 162			50	
	75			100	
	88.4		72.4	5	Flanagan et al, 1980 - Available metal in surface deposits on bramble leaves, main road, Strathclyde.
	5.7		10.2	50	
	10.3		8.1	5	Flanagan et al, 1980 - Available metal in surface deposits on rhododendron leaves, main road, Stathclyde.
	19.4		0	50	
2.8,3.0	752, 974			0.5	Muskett and Jones, 1980 - Grass, A40, Hillingdon, Middlesex (40000 vehicles day $^{-1}$).
1.2,1.7	650, 319			3	
0.3-1.0	54-354			10-13	
0.7-1.0	16-143			50-53	
0.6,0.7	14,24			75-78	
0.3,0.3	3,98			110-113	
	270		156	0	Wade et al, 1980 - Total vegetation, combined result for transects either side of 3 major roads.
	142		94	2	
	61		116	5	
	44		110	10	
	48		106	15	
	52		108	25	
	32		107	50	
	33		123	150	
	18	67	40	8	Albasel and Cottenie, 1985 - Available metal in perennial ryegrass, Brussels-Ostend Highway, Aalst, Belgium.
	15	119	35	20	
	100	64	114	1	Albasel and Cottenie, 1985 - Available metal in perennial ryegrass, Brussels-Ostend Highway, Drongen, Belgium.
	19	28	49	5	
	164, 185			0	Deroanne-Bauvin et al, 1987 - Plantain, either side of Bruxelles-Namur Highway.
	105, 55			10	
	58, 63			30	

CR - Central Reservation

particulates. The road kerb itself being a major discontinuity in the road/pavement surface will break up the air flow and will give rise to an area of increased deposition and accumulation.

2.2.3 Street Surface Sediments.

As a result of deposition, particulates will collect in a number of intermediate sites in the highway environment. One of the most important intermediate sites is in the form of street surface sediments and this has has been accentuated by the public concern over Pb in road dusts which have been highlighted as a major source of Pb to the body burden of children, particularly in urban areas (Duggan, 1983; Duggan et al, 1985). Measurements in the locality of highways have shown that metal levels in street dusts are high in relation to the surrounding environment (Table 2.13). This reflects the proximity of such dusts to vehicular sources of heavy metal pollution. Street surface sediments act as accumulation and interchange sites with pollutants being contributed from vehicular sources, roadway materials, vegetable matter and soil from the roadside surroundings (Figure 1.1). The dusts themselves provide a heavy metal source for urban runoff.

2.2.3.1 Variations in Heavy Metals in Street Sediments with Traffic Density and Spatial Location.

Heavy metal levels in street dusts have been shown to be dependent on traffic density (Archer and Barratt, 1976; Harrison, 1979)(Table 2.13). The concentrations found near major roads are generally higher than those found in less heavily trafficked residential roads. Turner (1973), however, found some exceptions to this with regard to Pb. Caswell (1985) also found that Pb concentrations are not necessarily directly related to traffic density with the mean Pb concentrations in pavement dust being 3200, 2387 and 2580 $\mu g\ g^{-1}$ for London streets with traffic densities of less than 30000, 30000 to 60000 and greater than 60000 vehicles per weekday respectively (Caswell, 1985). Day et al (1975) found that while Pb in street dust decreased from major to minor roads,

Table 2.13 Heavy Metal Levels (μg g^{-1}) in European Street Dusts.

Cd	Cu	Fe	Pb	Mn	Zn	Reference
			555			Rameau, 1972 a) Netherlands Street, 14000 veh day^{-1}).
			2000			b) Street in Zurich.
			2700			Turner, 1973-a) Road tunnel, Blackwall, London.
			1200-2300(1800)			b) Heavily trafficked roads, London.
			1100-3200(2500)			c) Residential roads and side streets, London.
			1700			d) Semi-rural dual carriageway, A1, Hatfield.
			1001			Day et al, 1975 - a) Major roads, Manchester.
			888			b) Minor roads, Manchester.
			933			c) Lightly trafficked streets and "play streets".
			963			d) Calculated mean of 3(a)-3(c).
			160-10000(2350)			Archer and Barratt, 1976-a) Gutter, A class road, B'ham
			300-4600(1557)			b) Gutter, 'B' class road, Birmingham.
			220-4300(1050)			c) Gutter, residential road, Birmingham.
			300-13000(1515)			d) Gutter, residential/industrial road, Birmingham.
			160-50000(2574)			e) Gutter, industrial estate road, Birmingham.
			200-5800(932)			f) Pavements in residential areas, Birmingham.
			160-50000(1630)			g)All roadside samples, Birmingham.
			1840			Duggan and Williams, 1977-a) Inner urban roads, Lambeth
			1330			b) Inner urban streets, Islington, London.
			1040			c) Mid-urban streets, Wimbledon, London.
			1040			d) Mid-urban streets, Edgeware, London.
			920			e) Outer urban streets, Harold Wood, London.
			35			f) Rural footpath, Walton on the Hill, London.
			430-3500(1200)			g) All urban samples, London.
			1530			h) Main road gutters, London.
			1460			i) Side road gutters, London.
			1030			j) Main road pavements, London.
			900			k) Side road pavements, London.
			150-2300(960)			Farmer and Lyon, 1977 - Urban streets, Glasgow.
1.3-10.1(4.6)	57-312(143)		920-3560(1880)		200-940(297)	Harrison, 1979-a) Urban roads, Lancaster.
1.0-14.6(7.0)	104-375(206)		2200-15000(6630)		1010-3725(1600)	b) Car parks, Lancaster.
1.0-2.9(2.1)	53-150(79)		150-870(550)		160-710(297)	c) Rural roads, Lancaster.
			840-4530(2130)			d) Town centre streets, Lancaster.
			740-4880(1890)			e) Main roads, Lancaster.
			620-1240(850)			f) Residential roads, Lancaster.
			410-870(570)			g) Rural roads, Lancaster.
			950-51900(12908)			h) Car parks, Lancaster.
			1370-48900(12130)			i) Garage forecourts, Lancaster.
			<1000			Turner et al, 1980-a) Variety of road types, London.
			<1000			b) Urban major road, A406, Neasden, London.
			1000			c) Urban residential road, Neasden, London.
			3000			d) Major urban road junction roundabout, London.
			4000			e) Neasden Underpass, central reservation, London.
2.68	108		2100		539	Harrison et al, 1981- a) Rural major road, Lancaster.
3.66	75		1090		260	b) Urban major road, London.
2.78	199		2540		458	c) Urban major road, Lancaster.
3.22	213		1115		434	d) Rural section of motorway, north of Lancaster.
4.91	71		939		440	e) Open car park, Lancaster University.
0.06-8.7	17-465		35-1750		100-1240	Gibson and Farmer, 1983 - Urban streets, Glasgow.
3.1	237		2346		527	Hamilton et al, 1984-a) A41, Hendon, 1300 veh hr^{-1}.
2.6	174		2291		470	b) Perimeter road, Hendon, London, (100-200 veh hr^{-1})
2.2	181		1045		401	c) Residential road, Hendon. London. (<50 veh hr^{-1})
1.2	54	23592	124	667	230	Harrop et al, 1983 - Chilwell Gardens, Oxhey, Herts.
5.5-20.3(11.9)			1200-9820(4250)		470-2850(1440)	Ahmed, 1985-a) Multi-Storey car parks, Heathrow.
0.5-19.5(6.5)			140-7570(2245)		80-2510(1085)	b) Multi-Storey car parks, Uxbridge.
2.7-107(19.6)			490-3770(1983)		260-2170(1033)	c) Multi-Storey car parks, Slough.
0.8-5.1(2.7)			1170-8880(4040)		340-2330(870)	d) A40, Hillingdon, Middx.
0.7-2.7(1.60			110-4070(1986)		270-1040(527)	e) Other "A"-roads, Hillingdon, Middx.
4.8-7.9(2.8)			680-1410(1130)		240-570(350)	f) Residential roads, Central Hillingdon, Middx.
			1360-5180(2668)			Caswell, 1985 - Pavements, London.
0.1			52		96	Hampton and McKirdy, 1985-Rural road, Scotland.
2.7	149	34370	608		400	Hampton and McKirdy, 1986-Mean levels 1983/4, Glasgow.
3.3-4.3(3.8)	445-628(5146)		3010-4420(3496)	17	825-1206(950)	Warren and Birch, 1987 - A13, Newham Way, London.

Mean values in parentheses

streets with light traffic and "play" streets yielded dusts that exhibited greater concentrations of Pb than minor roads (Table 2.13). From a review of published data (Ellis and Revitt, 1982), it was noted that metal concentrations in urban street dusts often exceeded those found on motorways. The high speed of vehicles and the open nature of motorways may be responsible for the decrease in heavy metal concentrations in the dust due to greater dispersion.

Elevated metal levels in the street dusts of minor urban roads may possibly reflect other sources of pollution and additionally the effects of cold starts, car maintenance and other practices. Cold starts result in greater inputs of heavy metals than those which occur during normal cruise driving modes. During cold start conditions and subsequent acceleration considerable amounts of Pb are exhausted, and up to 2000% of the Pb burned may be emitted owing to re-entrainment of deposited particulates in the exhaust system (Hirschler et al, 1957). Additionally, "accumulation" effects may occur in side streets as municipal street cleaning is often less regular allowing a greater mass of pollutants to collect. Spillages of vehicular fluids and inputs from vehicular products (Table 2.6) resulting from maintenance practices carried out on quiet roads may give rise to additional metal loadings and partially account for the atypical levels on these types of urban streets.

Duggan and Williams (1977) found that there was a slight decrease in Pb concentration in street dust with distance from the centre of London while Day et al (1975) did not find a distinct decrease in Pb concentration with distance from the centre of Manchester. However, a noticeable decrease was observed at a distance corresponding to the edge of the urban area. Brunekreef et al (1983) observed that Pb concentrations in street dusts collected from inner city areas were much greater than those of dust collected in the suburbs. These observations suggest that other sources may well be contributing to the metal levels in urban street dust but the effects of restricted circulation and enclosure as well as those of traffic density may also lead to differences between inner city areas and outer regions. The published data therefore suggests that urbanisation results in elevated levels of

Pb in street dusts which regularly exceed the former Greater London Council guideline for Pb in dust of 500 $\mu g\ g^{-1}$. The majority of samples exceed this value, including the mean values of the Pb levels for residential road samples. Glasgow District Council formulated a set of 'action levels' for metals in street dust based on a figure of five times the yearly average concentration in street dust (Hampton and McKirdy, 1985). These 'action levels' are 11.5 $\mu g\ g^{-1}$, 750 $\mu g\ g^{-1}$, 171850 $\mu g\ g^{-1}$, 3125 $\mu g\ g^{-1}$ and 2450 $\mu g\ g^{-1}$ for Cd, Cu, Fe, Pb and Zn respectively (Hampton and McKirdy, 1986). Table 2.13 shows that Cd and Pb levels have been found in excess of these 'action levels' and recorded levels are generally in excess of the Glasgow yearly average concentrations. This leads to the conclusion that automobile derived metals are a major pollutant of the urban highway environment, even in areas of relatively low traffic density.

The fall-off in concentration of heavy metals with distance from vehicular source can be seen, particularly for Pb, by comparison of pavement and road gutter samples. The latter exhibit higher concentrations (Table 2.13) and this would be expected as the gutter acts as a "collecting wall", creating an area where the effects of dispersal and deflation are minimised (See Section 2.2.2). This leads to a build up of dust particulates and it would be expected that a greater proportion of the road gutter dust compared to the pavement would be in the finer size fractions as the pavement surfaces would be subject to the full effect of dispersive processes.

2.2.3.2 Variations in Heavy Metals in Street Sediments with Particle Size.

The heavy metal content of street dusts is not distributed evenly with particle size. It has been found that Pb concentrations generally increase with decreasing particle size (Rameau, 1972; Duggan and Williams, 1977; Ferguson and Ryan, 1984; Hamilton et al, 1984; Rapsomanikis and Donard, 1985). Cd and Cu levels have also been found to increase with decreasing particle size (Ferguson and Ryan, 1984; Hamilton et al, 1984) as did Mn levels (Ferguson and Ryan, 1984) and Zn levels (Ferguson and Ryan, 1984; Hamilton et al, 1984; Sartor and Gaboury, 1984; Rapsomanikis and Donard, 1985). It has been observed that the trend of metal concentrations to increase with decreasing particle size does not necessarily continue through to the finest particle size. The Pb concentrations of the finest fraction of road dusts has been found to be slightly less in magnitude than the next finest fraction (Rameau, 1972; Ferguson and Ryan, 1984; Warren, 1987). This has also been found for Zn (Sartor and Gaboury, 1984; Warren, 1987).

Some street dusts have been found to be composed mainly of deposited soil (Harrison and Wilson, 1982) although a study of the variation of the metal/aluminium ratio with particle size suggests soils contribute mainly to the larger particle size ranges (Ferguson and Ryan, 1984). Non-soil sources such as exhaust derived aerosols contribute predominantly to the smaller particle size range. The particle size distribution of heavy metals is also dependent on road type (Ellis and Revitt, 1982) and this may considerably affect the heavy metal loadings.

The uneven distribution of heavy metals with particle size has several important consequences. The higher concentrations of heavy metals associated with the smallest particles will be most readily transported by road runoff and contribute to the pollutant loadings of urban runoff. Additionally, this will affect pollutant uptake by humans as the smaller respirable particles will be more liable to accidental ingestion. The efficiency of street cleaning will also be influenced by this particle size distribution (Section 2.3.5).

The mechanism by which the larger particles (>250 µm) that are not emitted directly from exhausts become enhanced with Pb is not entirely clear although it has been suggested that the finer particles coagulate with particles present on road surfaces (Ellis and Revitt, 1982). This theory is substantiated by examination of street dusts by electron microscopy which reveals the presence of aggregated particles (Biggins and Harrison, 1980; Ahmed, 1985).

2.2.3.2 Speciation of Heavy Metals in Street Sediments.

As well as the heavy metal distribution with particle size, the speciation of heavy metals in street dusts will also affect the availability of metals to living organisms and the effects of metals on the environment.

The exchangeable fraction of metals in street dusts was found to be of greater significance than was the exchangeable fraction of metals in soils (Gibson and Farmer, 1984). In street dust Cd exhibits the highest affinity for the exchangeable fraction with a percentage contribution of the total concentration varying from 5 to 32% (Harrison et al, 1981; Ferguson and Ryan, 1984; Gibson and Farmer, 1984; Hamilton et al, 1984). Copper is found predominantly in the organic fraction with a percentage of the total concentration of between 33 and 74% (Harrison et al, 1981; Ferguson and Ryan, 1984; Gibson and Farmer, 1984; Hamilton et al, 1984). Pb and Zn are found in similar concentrations to Cd in the carbonate phase, and of greater magnitude than Cu. The predicted overall availability of metals to the soluble phase and therefore an indication of their mobilisation in the environment, has been predicted to be in the order Cd > Zn, Pb > Cu (Harrison et al, 1981; Hamilton et al, 1984).

The percentage of the total concentration of a metal made up by each phase is known to vary both with total metal concentration (Gibson and Farmer, 1984) and with particle size (Hamilton et al, 1984). The latter effect would be expected as concentration is known to increase with decreasing particle size. The interdependence is illustrated by Pb where the percentage of the total concentration made up by the carbonate phase increases with increasing concentration (Gibson and Farmer, 1984) and decreasing particle size (Hamilton et al, 1984).

2.2.4 Heavy Metals in Soils.

The deposition of heavy metals to soil is another important intermediate site in the highway environment. Unlike street sediments the residence time of metals in the soil compartment of the environment can be substantial. Elevated concentrations of metals are present in the soils adjacent to the highway and the concentration then tends to decrease with increasing distance from the highway (Table 2.11). This is also true for Fe and Mn which are often regarded as indicative of background levels in soils, and of natural processes (Harrop et al, 1983). Although the data is limited it can be seen from Table 2.11 that it could be misleading to assume Fe and Mn are indicative of background levels as they increase with proximity to highways and therefore appear to correlate with pollutants from highway sources.

Following deposition, heavy metals may react with or be transported through the soil and therefore the soil can be considered both as a sink and as an intermediate source site. Lead has been found to decrease with soil depth in soils adjacent to highways (Lagerwerff and Specht 1970b; Chow, 1970; Ward et al, 1975; 1977; Wade et al, 1980; Yassoglou et al, 1987). Similarly concentrations have been observed to decrease with soil depth near highways for Cd (Lagerwerff and Specht, 1970a; 1970b; Ward et al, 1977; Wade et al, 1980), Cu (Ward et al, 1977) and Zn (Lagerwerff and Specht, 1970a; 1970b; Ward et al, 1977; Wade et al, 1980; Yassoglou et al, 1987). In a survey of heavy metal contamination of the Rhondda Fawr valley, South Wales, Burton and John (1977) found that the majority of the high heavy metal levels were concentrated within the top 5 cm of soil. Soil levels of Pb and Cd, in particular, were found to exhibit large maxima associated with main roads.

The bioavailability and mobility of heavy metals in soils is variable and dependent on a variety of factors. These include the concentration of a particular metal in the soil, the chemical form of the metal, soil, pH, the organic content of the soil (both particulate and dissolved) and the physical nature of the soil itself.

Soil pH has been shown to affect the adsorption, and therefore the mobility of Cd (John, 1975; Forbes et al, 1976; Garcia-Miragaya and Page, 1978; Jarvis and Jones, 1980; Jernelov and Johansson, 1983; Singh and Kansal, 1983; Tills and Alloway, 1983; Christensen, 1984; Ram and Verloo, 1985), Cu (McClaren and Crawford, 1973; Forbes et al, 1976; Singh and Kansal, 1983; Ram and Verloo, 1985), Pb (Forbes et al, 1976;

Zimdahl and Skogerboe, 1977; Singh and Kansal, 1983; Tills and Alloway, 1983; Vuorinen, 1983; Ram and Verloo, 1985) and Zn (John, 1972; Gadde and Laitinen, 1974; Forbes et al, 1976; Adams and Sanders, 1983; Singh and Kansal, 1983; Ram and Verloo, 1985). In general the adsorption of these metals increases with increasing pH but other factors must also be considered such as where a shift in pH affects the physical characteristics of the soil (Garcia-Miragaya and Page, 1978).

Organic matter has also been found to affect the adsorption of Cd (Riffaldi and Levi-Minzi, 1975; Eriksson, 1988), Cu (McClaren and Crawford, 1973), Pb (Rolfe and Jennett, 1973; Riffaldi et al, 1976; Soldatini et al, 1976; Zimdahl and Skogerboe, 1977) and Zn (John, 1972). The formation of metal-humic acid complexes is important in the fixation of metals in soils. However, soluble organic matter has been shown to increase the mobility of metals due to the formation of soluble organo-metallic complexes (Singh and Kansal, 1983). Organic matter therefore affects the mobility of metals but whether it increases or decreases the degree of mobility is dependent on the form in which the organic matter is present.

Metal adsorption is also influenced by the presence of Fe and Mn oxides (Gadde and Laitinen, 1974; Zimdahl and Skogerboe, 1977), clay content (John, 1975; Randall et al, 1983; Scokart et al,1983) and the presence of phosphates, carbonates and sulphates (Lagerwerff and Specht, 1970a; Smith, 1976; Newland and Daum, 1982; Scokart et al, 1983). Generally these are variables of secondary importance compared to pH and organic matter in affecting the soil adsorption of metals (Levi-Minzi et al, 1975; Soldatini et al, 1976; Zimdahl and Skogerboe, 1977; Singh and Kansal, 1983).

2.2.5 Heavy Metals in Vegetation.

The adsorption and fixation of metals in soils will in turn affect the uptake of heavy metals by plants, as will airborne concentrations. Consequently the concentrations of metals in plants exhibit decreases with distance from the highway (Table 2.12). Lead can be taken up by plants from the soil, from atmospheric deposition and from soil splash (Royal Commission on Environmental Pollution, 1983), although Rameau (1972) states that Pb in soil appears to be generally immobile and unavailable to plants. There is little translocation of Pb from the roots to the aerial shoots (Ter Haar, 1970; Schuck and Locke, 1970) and relatively large increases in soil Pb are required to produce changes of Pb content in the aerial parts (Motto et al, 1970; Schuck and Locke, 1970; Ter Haar, 1970). However, changes in Pb in air concentrations have been found to have pronounced effects on Pb concentrations found in the aerial parts of plants (Motto et al, 1970, Ward et al, 1977). Soil pH can affect the uptake of Cd by plants (John, 1975) although the atmospheric uptake of Pb and Cd has been suggested to be equal to or larger than that through the root system (Johnsen and Svare, 1983). Davies et al (1984) found that while radishes did derive Pb from soils, atmospheric conditions could cause increases as great as 90% in leaf Pb content. Experiments suggested that 49% of the Pb content found in leaves is due to atmospheric uptake. Plants can therefore be regarded as short term reservoirs of heavy metals within the environment. Heavy metal uptake by plants should not be seen as simply a function of soil or atmospheric concentrations but as a function of both.

It has been found that a significant but not predominant proportion of the heavy metal concentrations found in roadside plants can be explained by deposition of heavy metals from vehicular sources (Ward et al, 1975, 1977). Washing of leaves has been found to considerably reduce the Pb concentrations (Davies and Holmes, 1972; Ward et al, 1975; Ward et al, 1977; Agrawal et al, 1980) and Cd, Cu and Zn concentrations (Ward et al, 1977), with the reductions varying from less than 10% to 40%. The importance of leaf surface characteristics is demonstrated by the data of Flanagan et al (1980). Rough pubescent bramble leaves were found to collect deposited particles and exhibit the trend of decreasing metal concentration with distance from the highway, whereas the smooth, waxy leaves of the rhododendron did not exhibit such a trend. The surface deposits on bramble leaves were found to be five times those of the rhododendron leaves.

2.3 Removal Processes of Heavy Metals in the Urban Environment.

The levels and size associations of heavy metals found in the urban highway environment not only reflect the types and rates of input, but also the removal processes affecting the pollutants.

Removal processes in the urban environment can be summarised as follows;

a) Removal to the atmosphere and subsequent dispersion
b) Washoff/runoff
c) Cleaning practices

Resuspension of contaminants to the atmosphere may occur either as dry particles or aqueous solutions (Section 2.2.1). Some of the resuspended material will remain within the urban highway environment. However, that which remains airborne for long periods of time may become dispersed and removed from the urban highway environment. The rate of removal by atmospheric dispersion will be dependent on the removal efficiency of the metals from the atmosphere and the physical dimensions of the urban environment being considered.

Washoff/runoff is a major removal and transport mechanism for surface deposited heavy metals in the urban environment. Washoff will result in heavy metals being transported through the natural drainage system within the catchment, with the majority of metals eventually entering the subsurface drainage system. Washoff is not 100% efficient and therefore the intermediate washoff of particulates results in transport of heavy metals from one site to another within the environment.

Runoff may also allow interactions and chemical processes to occur; soluble contaminants may dissolve, or alternatively contaminants may precipitate out. Other interactions may include the adsorption of contaminant ions onto insoluble particulates and their subsequent transport by runoff, or the physical breakdown of particles due to attrition during transport. Runoff, therefore, may be responsible for not only the transport of pollutants but also for modifications in their nature and composition.

2.3.1 Removal to Gully Pots.

Immediate removal of pollutants from the paved surfaces to the subsurface drainage system takes place via the gully pots (catch pits) which are a principal contributor to and regulator of pollution loads (Harrop, 1984a). The levels of metals measured in gully pot liquor are presented in Table 2.14.

Table 2.14 Heavy Metal Concentrations ($\mu g\ l^{-1}$) in Gully Pot Liquors.

Total Cd	Total Cu	Total Fe	Total Pb	Total Mn	Total Zn	Ref
					0-570(90)	1
	40(20)		600(170)	620(200)	250(110)	2
<10	10,60		<50,100		40,220	3a
			340-560(520)			3b
13	455		192		407	4a
4	278		121		790	4b
0-200(60)	0-230(20)	0-50000(1240)	0-780(90)	0-2500(210)	0-1180(150)	5

Mean values in parentheses

References
1 Fletcher et al, 1978
2 Mance and Harman, 1978 - Maximum and mean values
3a Dauber and Novak, 1983 - 2 gully pots, 29/10/79
3b Dauber and Novak, 1983 - 2 gully pots, 18/4/80-29/5/80
4a Morrison, 1985 - Maximum, 1 gully pot, 16/7/84-28/7/84
4b Morrison, 1985 - Maximum, 1 gully pot, 6/8/84-15/8/84
5 Pratt et al, 1986 - 3 gully pots, October, 1984-March, 1985

One of the main roles of the gully pot is to act as a settling tank for road runoff solids, however, it has been found that the effects of gully pots on the routing of particulates in road runoff is variable (Mance and Harman, 1978) and their effectiveness at removing particulates less than 1 mm diameter has been questioned (Pratt and Adams, 1984). The aqueous environment within them enables physico-chemical and biochemical reactions to occur resulting in changes in the speciation of some metals (Morrison et al, 1988). Bacterial mobilisation of metals in gully pots has been proposed as an explanation of increased total heavy metal concentrations in gully pots after flushing by heavy rainfall (Mance and Harman, 1978). There is a considerable enhancement of the toxic metals Cd, Cu, Ni, Pb and Zn in the sediments entering the gully pot with respect to the levels found in contributing road surface sediments (Harrop et al, 1983; Harrop, 1984). This enhancement was explained by the more efficient removal of the fine particulates with their relatively high concentrations of associated toxic metals from the above ground sources during storm conditions. It was observed that there was no similar enhancement for the metals Fe and Mn, due to the source being natural soil and not anthropogenic activities. The average total metal removal rates to the subsurface drainage system were found to be 4.0, 28.8, 21.8 and 18.0 mg per day for Cu, Mn, Pb and Zn respectively (Harrop et al, 1983).

The higher total heavy metal concentrations in gully pot liquors compared to urban runoff supports the contention of the ready removal of fine particulate associated metals to gully pots (Mance and Harman, 1978). This suggests that gully pots are a potential source of large quantities of heavy metals and could be major contributors to the "first flush" phenomenon where pollutants are yielded in peak concentrations at the onset of a runoff event. Morrison (1985) found the residence time of Cd, Cu and Zn in the road surface/gully pot system to be approximately that of one storm event whereas Pb owing to its greater association with the solid phase tended to be more persistent. Despite this it was also noted that the efficiency of the gully pot as a detention basin was variable and highly dependent on the hydrological characteristics of the storm (Morrison et al, 1988). Assessment of the storage and discharge of metals from gully pots is therefore important in accurate quantification of metal cycling in the urban environment.

2.3.2 Highway Runoff.

The major contributor to heavy metal pollution in highway runoff has been identified as vehicular traffic (Hedley and Lockley, 1975). Table 2.15 presents the mean concentrations of heavy metals found in highway runoff by various workers. The phenomena of 'first flush' has been observed in relation to road runoff by Pope et al (1978). These workers also found that total metal loadings for bed load and sieve solids (the

Table 2.15 Heavy Metal Levels ($\mu g\ l^{-1}$) in Highway Runoff

Cd	Cu	Fe	Pb	Mn	Zn	Ref
	100-1440(680)	8500-182900(51180)	450-4940(2090)		650-8010(3190)	1
8	33		1110		990	2
	50		340		250	3
1.6-4.9(2.7)	90-193(145)		529-1576(1036)		196-422(272)	4
5.9	97	3420	202		360	5a
5.9	117	5160	245		620	5b
28	58	2180	163		320	5c
0.2-4.1(2.8)	60-188(134.2)	2000-40000(20500)	64-763(424.4)		90-610(378)	6
0.01-20.5(1.78)	14-288(58)	850-17700(5310)	84.8-1260(332)	14.6-288(110)		7
1-27	10-430	4500-78600	62-690		91-740	8a
1-28	10-200	4200-27400	128-920		119-340	8b
1.6	49.2		342.5		247.5	9
1.0-5.3	19-200		24-540			10a
1-3.7	26-145		129-998		155, 211	10b

Mean values in parentheses

References
1 Hedley and Lockley, 1975
   - monthly averages, A38(M), UK.
2 Roberts et al, 1976
3 Dauber et al, 1978
   - N1, Zurich, Switzerland.
4 Pope et al, 1978
   - 6 lane motorway, UK.
5 Klein, 1982
   a) A81, W.Germany; 41000 vehicles/day.
   b) A6, W.Germany; 47000 vehicles/day.
   c) A8/B10, W.Germany; 40600/11500 vehicles/day respectively.
6 Gjessing et al, 1984
   - E6, 4 lane highway, Norway; 19400 vehicles/day
7 Harrison and Wilson, 1984
   - Suspended sediment >0.45µm, M6, UK; 15000 vehicles/day
8 Lygren et al, 1984
   a) Jessheim, Norway - 10cm kerb
   b) Jessheim, Norway - 70cm kerb
9 van Dam et al, 1986
   - City highway, Netherlands; 3200 vehicles/day
10 Svensson, 1987
   a) Car park, Chalmers University, Sweden.
   b) Street area, Chalmers University, Sweden.

latter being suspended solids filtered from stormflow) in storm events were similar in magnitude. However, due to their greater mobility there is a greater probability that the suspended sediments would contribute to environmental metal transport processes.

Levels of pollutants in highway runoff have been found to be elevated in winter compared to summer (Hedley and Lockley, 1975). Winter salting operations may contribute directly to pollutants and also have other side effects such as stimulation of corrosion which further adds to pollutant loads (Hedley and Lockley, 1975). Cold starts and engines using richer fuel mixtures may also add to increased input of Pb from exhausts during winter months.

2.3.3 Roof Runoff.

In separately sewered drainage systems, roof runoff combines with highway runoff and is discharged into receiving streams. Roof runoff occurs prior to runoff from horizontal surfaces such as roads owing to the gradient of the roof surfaces. The contribution of roof runoff to the total pollutants present in urban runoff is of variable importance. The levels of metals and particulates in roof runoff are shown in Table 2.16.

Table 2.16 Suspended Solids and Metal Concentrations in Roof Runoff.

Suspended Solids (mg l^{-1})	Cd	Cu	Fe	Pb	Zn	Reference
1400						Waller, 1972 - Maximum Value
7		740	300	10	580	Malmqvist and Svensson, 1975
38-1507						Harrop, 1983 - Range of Values
309						Harrop, 1983 - Mean Value
	0.6	5		11.1	39.7	van Dam et al, 1986
12		29		37	97	Svensson, 1987 - Maximum Values
4.7		23		17	55	Svensson, 1987 - Mean Values
	1.2	13.7		38.6	22.2	Warren, 1987

(Concentrations $\mu g\ l^{-1}$ unless otherwise stated)

Mance and Harman (1978) concluded that roof runoff was of relatively minor significance as a source of pollutants and caused a dilution effect on road runoff. Waller (1972), however, stated that in some circumstances runoff from roofs may be a significant contributor to the pollutant load in surface runoff and this has been confirmed by Harrop (1984a). Where roofing materials include Cu and Zn, it has been observed that corrosion may lead to high levels of these elements in runoff (Malmqvist and Svensson, 1977; Malmqvist, 1983). Ellis et al (1987) calculated that for a specific catchment the input from roofs and roads to the annual Cd and Pb loadings was approximately equal, while for Cu the contribution from roofs was only 22% of the total and for Zn the roof contribution was 87% of the total. This would suggest that generally the input from roof surfaces can be significant but it may be not only catchment specific but also dependent on the specific metal involved.

2.3.4 Urban Runoff.

Table 2.17 presents data from European studies of stormwater/urban runoff. Urban runoff will be made up of both roof and highway runoff, as well as runoff from any open areas within the catchment concerned. The magnitude of each source will vary from catchment to catchment and results will reflect the proportions of each source so that urban runoff will be found to be, in part, catchment specific.

As with highway runoff the 'first flush' phenomenon has been observed in stormwater runoff, although there appears to be a degree of controversy concerning this phenomena. Sonzogni et al (1980) state that significantly higher concentrations of pollutants do not occur in the early stages of runoff. Peak pollutant concentrations occurring shortly after the initiation of runoff have been observed by Ellis (1977), Wilber and Hunter (1977), Mance and Harman (1978), Revitt et al (1981), Morrison et al (1985) and Morrison (1985). The phenomenon is not a constant feature and Morrison et al (1985) and Revitt et al (1981) observed both storms that exhibited this behaviour and others where peak

Table 2.17 Heavy Metal Concentrations ($\mu g\ l^{-1}$) in Urban Runoff

Cd	Cu	Fe	Pb	Mn	Zn	Ref
1	10		110		130	1
6	270	1000	200	78	465	2
	30-310		60-400		170-570	3
			470			4
0.8	14		140		160	5
	20		280	160	330	6
	50		340		250	7
	30-520		50-820		100-1730	8
	28		205	110	271	9
	250	6700	390		440	10a
	180	4400	160		330	10b
	27	3300	200		240	10c
	19	7000	55		150	10d
4.2-12	49-110.4		125.4-367.1		187.9-276.2	11a
0.9-2.7	90.3-187.7		51-71.5		112.3-230.5	11b
0.7	14.0		72.7		505.5	12
1-29	28-249	4246-29280	268-1970		170-1943	13

<u>References</u>

1 Roberts et al, 1976
2 Horkeby and Malmqvist, 1977
3 Malmqvist and Svensson, 1977
4 Ranchet and Vicq, 1977
5 Roberts et al, 1977
6 VRC, 1977
7 Dauber et al, 1978
8 Lindholm and Balmer, 1978
9 Mance and Harman, 1978
10 Malmqvist, 1983
    a) City centre, Sweden
    b) Residential catchment, 3130 vehicles/day
    c) Residential catchment, 450 vehicles/day
    d) Residential catchment, 340 vehicles/day
11 Morrison, 1985
    a) Residential catchment, UK.
    b) Residential catchment, Sweden.
12 van Dam et al, 1986
13 Revitt, (>0.45µm only) *pers comm*

concentrations occurred later in the storm. Occasionally chemographs demonstrate a succession of peaks and troughs in metal concentrations over the entire storm event. Ellis (1985) considered that while the 'first-flush' phenomenon was over-emphasised, 60 to 80% of storms do exhibit an early flushing regime. Morrison et al (1985) observed this phenomenon in 54% of 190 storms monitored. Various explanations have been put forward to explain such phenomena including the sequential input of pollutants with major contributions from:

a) road surface washoff
b) the removal of in-pipe pollutant deposits
c) the early washout of pollutants which have built up on algal mats within the pipes.

The impact of heavy metal sources increases with the degree of urbanisation (Wilber and Hunter, 1977; Malmqvist, 1983). Thus Pb and Zn concentrations are lower in urban runoff from suburban residential catchments than from a city centre (Lindholm and Balmer, 1978). Similarly, Malmqvist (1983) has shown that runoff exhibited decreases in Cu, Pb and Zn content with increasing distance from a city centre (Table 2.17).

The percentage impervious area within a catchment affects the quantity and quality of stormwater runoff. With increasing impervious area, runoff increases as larger quantities are routed into the drainage system and there are less areas where infiltration into open soil can occur. Lindholm and Balmer (1978) found a significant correlation between increasing pollutant load and increasing impervious area. Helsel et al (1979) found good correlations between Cu, Pb and Zn concentrations and both traffic and percentage impervious area. Impervious area generally increases with urbanisation and will include roads and industrial/commercial areas, both giving rise to Cu, Pb and Zn inputs and subsequent decreases in runoff quality. It was also found that increasing incidence of 'first flush' phenomenon occurred with urbanisation (Helsel et al, 1979). The results of Malmqvist (1983) (Table 2.17) indicate how the concentration of heavy metals in stormwater increase with increasing traffic density within a catchment.

Increases in antecedent dry period length have been associated with increasing stormwater pollution (Marsalek, 1976). However, other studies have found the importance of antecedent dry period to be relatively minor (Ellis et al, 1986; Mance and Harman, 1978). Whipple et al (1977) observed that metal loadings may be similar despite differences in antecedent dry period, and that the highest loadings were not necessarily observed after the longest antecedent dry period. The effects of antecedent dry period on stormwater loadings are not well defined and this may be due to catchment specific factors overriding or masking the effects of the antecedent dry period. Randall et al (1978) found that pollutant load in rainfall correlated well with antecedent dry period in rural areas, although this correlation was not as good in urban areas. However, in order that these observations relating to rainfall can be applied to runoff, rainfall must be the dominant factor in controlling the loadings of pollutants in runoff.

While not finding the effect of antecedent dry period on runoff quality to be statistically significant, Mance and Harman (1978) did find that the characteristics of the current rainfall event were the dominant factor in determining the mass of pollutants discharged in runoff. Aerial deposition was calculated to contribute 96% Cu, 49% Mn, 54% Pb and 38% Zn to runoff. From analysis of input and removal rates, Ellis et al (1986) concluded that aerial deposition provided a major source of most metals entering the road drainage system. Randall et al (1978) found that the majority of pollutants wash out during the first few minutes of rainfall and that subsequent precipitation diluted the total pollutant concentration of the rainfall event. In addition pollutant concentration increased with proximity to metropolitan areas. Pollutant quantities in precipitation are of sufficient magnitude to have a significant impact on the quality of surface water runoff in a large metropolitan area (Goettle, 1978; Randall et al, 1978). Horkeby and Malmqvist (1977) found that atmospheric deposition of Cd and Pb could explain the majority of stormwater Cd and Pb content while for Cu, Fe, Mn and Zn atmospheric deposition could only account for a small fraction of the metal content of stormwater. The influence of aerial deposition on concentrations of metals in stormwater would seem to be significant although possibly variable and dependent on a variety of factors. These include local sources of pollutants to the atmosphere and duration of rainfall, and therefore potential dilution of the input. The storm duration and volume were found by Ellis et al (1986) to be important factors, providing an explanation of 90% of the variation in Cd, Pb, Mn and suspended solids loadings in runoff. It can be seen how the various controlling factors investigated are intimately linked causing difficulties in isolating one prime control parameter.

The removal efficiency of urban runoff will vary with both the magnitude and intensity of the rainfall event, as well as the nature of the sediment removed and the nature of the surface. Simulation of rainfall using irrigation experiments has been shown to result in only partial removal of sediment from the street surface (Malmqvist, 1983). This suggests that removal efficiency will increase with duration of a rainfall event and also probably increase with increased intensity. The removal efficiency will also increase with increasing percentage of fine sediment. The preferential removal of toxic fines by runoff has been suggested as an explanation of the considerable enrichment of heavy metals within the below ground phase of stormwater runoff (Revitt et al, 1981). Harrison and Wilson (1983) suggest that elevated concentrations of heavy metals in stormwater result from the coarser particles removed being concentrated in the bed load while finer material, which is enriched in metals, remains as suspended sediment. This enriched finer material is also able to be mobilized during low flow intensity conditions (Harrison and Williams, 1983). Additionally, the low pH of incoming fresh precipitation is able to effectively react with the surface particulates and produce a mobilised heavy metal leachate.

Removal efficiency will also be affected by the percentage impervious area as runoff percolating into pervious soils will reduce the total pollutant loadings at the outfall. Pollutants may be reduced at the outfall by the settling of suspended solids on soils and additionally adsorption of metals onto soil materials. Adsorption of heavy metals by soils is detailed in Section 2.2.2. The losses of metals to soils will depend on the nature of the soil and the pH of both the soil and the runoff. Storm events may mobilise soil particles and therefore increase stormwater loadings of suspended solids. Runoff may also become enhanced by the leaching of soils if the pH of the runoff is such that it mobilises metals already present as adsorbed forms in the soil. Laxen and Harrison (1977) state, however, that soil Pb causes an insignificant contribution to water pollution. The interaction of stormwater and soil has therefore been shown to both reduce and enhance stormwater pollution, the resulting effect of such interaction will depend on both the stormwater event and soil characteristics.

2.3.5 Street Sweeping.

Street sweeping is carried out to remove quantities of litter and improve the visible signs of pollution but has been found to have varying effects on heavy metals in street dusts and their subsequent removal. The removal of larger surface particulates by street sweeping is well reported. Sartor and Boyd (1972) observed a removal efficiency of greater than 79% for sediment particles greater than 2000 µm, reducing with particle size to 48%, 20% and 15% for the size ranges of 104 µm-246 µm, 43 µm-104 µm and less than 43 µm, respectively. Ellis (1979) found a near total removal of particulates greater than 10 mm and only a reduction of between 15-20% for particulates of grain size less than 60 µm. Beckwith et al (1986b) indicated that street sweeping was particularly efficient for particles greater than 1000 µm, removing 74% of the particulates in this size range. However with regard to the finer fractions it was found that only 29% of the sediment in the size range 106 µm-250 µm was removed. Bender and Terstiep (1984) also noted that particulate loads in the size range less than 250 µm were less affected by street sweeping than the total sediment load. Malmqvist (1978) investigated the particulates collected during sweeping operations and found that only 3.6% of the total weight of street sweepings was made up of particles less than 74 µm. Secondary passes made by the sweeper were found to reduce the remaining sediment by only 50% (Sartor and Boyd, 1979), and further passes removed lower percentage loadings of the remaining sediment and reduced its mean particle size.

Ellis (1977) noted that particles less than 60 µm accounted for 30% of the heavy metals in street sediments and 40-90% of pollutants are associated with particles less than 200 μm. Sartor and Boyd (1972) found that the less than 43 μm fraction of street sediments made up only 6% of the total sediment loadings but was responsible for almost half the heavy metal loadings. The importance of the finer fractions is accentuated, as particulates in stormwater are generally less than 10 μm (Malmqvist, 1978). The failure of street sweeping to remove these finer fractions is further illustrated by Ellis (1979) who found that some areas of the highway surface were cleaner prior to sweeping than after, suggesting that sweeping causes a redistribution of the finer particles. This process of redistribution may also result in particulates being broken down into finer particulates and thus increase their availability to be suspended in stormwater runoff.

Owing to the aesthetic benefits of street sweeping it does appear that the majority of municipal authorities continue to favour it as the predominant method of surface water quality management.

CHAPTER 3 MINERAL MAGNETIC PARAMETERS.

3.1 Historical Use of Magnetic Techniques in Heavy Metal Studies.

Previous use of magnetic techniques in heavy metal investigations has been as a preconcentration procedure (Olson and Skogerboe, 1975; Biggins and Harrison, 1980). Biggins and Harrison (1980) achieved separation of samples into magnetic and non-magnetic fractions by use of an electromagnet while Olson and Skogerboe (1975) used a small hand magnet. In both cases the effectiveness of separation cannot be gauged as no indication of the strength of the magnet was given.

Magnetic techniques have also been used in attempts to characterise sources of heavy metal pollution (Hopke et al, 1980) and subsamples of particulates (Linton et al (1980). Hopke et al (1980) used a permanent bar magnet, held below a sieved subsample which had been placed in a crystallisation dish, to achieve magnetic/non-magnetic separation. The strength of the magnet was not specified.

Linton et al (1980) separated sieved subsamples by repeatedly passing them through a vertical glass tube held between the poles of a 300 mT electromagnet. Linton et al (1980) stress that the designation of particles as magnetic and non-magnetic is entirely a function of the separation technique. This is true of all the applications of magnetic separation and only by use of agreed standardised methods can reliable interpretation of results based on magnetic separation or characterisation be made. This Chapter therefore gives a detailed background of the principles of mineral magnetism and how they are reflected by the measurements to be used in this study. The equipment and measurements used have been adapted from geological techniques and have been used in a variety of environmental applications. Some of the relevant studies where these measurements have been used are also detailed in this Chapter.

3.2 Magnetic Behaviour.

The atoms of any substance have an electronic structure in which electrons may be regarded as circulating in orbits about a central nucleus. Each electron possesses an electrical charge and therefore its motion represents an electrical current producing a magnetic moment. The orbits of the charged electrons are analogous to a wire loop carrying a current. The magnetic moment is the vector produced and is proportional to the strength of the current and the magnitude of the area which it affects, that is the area within the loop. Magnetic moment would therefore be measured in units of current, amperes (A), and units of area, square metres (m^2), i.e. magnetic moment is measured in A m^2.

All electrons possess magnetic moments, but not all elements are magnetic. The electron actually possesses two magnetic moments; the orbital magnetic moment described above, and a spin magnetic moment created by the electron spinning on its own axis. In some atoms the resultant of all the orbital and spin magnetic moments is zero and the moments cancel each other out. In other atoms, for example hydrogen, the formation of a molecule occurs when two atoms possessing electrons of opposite spins are brought together. The individual magnetic moments of the separate atoms cancel each other (McElhinny, 1973). When these atoms or molecules with zero magnetic moment are placed in a magnetic field there is a rearrangement of the spin and orbital motions of the electrons resulting in a net magnetic moment in the opposite direction to the field. This phenomenon is known as diamagnetism and is exhibited by quartz, calcite and water. The diamagnetic moment is weak in comparison to other magnetic behaviour, and is usually masked by these other forms of behaviour. However, diamagnetic effects can be significant for magnetic susceptibility in sediments and rocks which are particularly rich in biogenic silica, calcium carbonate or carbon in the form of organic matter but poor in iron. Diamagnetic effects can also be significant in plastics and this is an important consideration in relation to sampling equipment.

If an atom or molecule has a resultant magnetic moment, the application of a magnetic field tends to cause alignment of the magnetic moments in the direction of the field. This is known as paramagnetism and is exhibited by clay minerals, pyroxenes and amphiboles. This effect is weak, is lost upon removal from the field, and is masked by the stronger magnetic behaviours. However, paramagnetism is significant in rare situations where there are high concentrations of iron and/or manganese compounds which are not in the ferrimagnetic or antiferromagnetic form.

Some substances such as iron, cobalt and nickel exhibit strong magnetic effects known as ferromagnetism. Ferromagnetic substances are distinguished by the fact that they have a greater abundance of valence electrons than metallic paramagnetics. These valence electrons can move freely through the metal so that they become closely packed and react strongly together. Exchange forces between the valence electrons cause their spins to become aligned even in the absence of an applied magnetic field. Ferromagnets, therefore, exhibit spontaneous magnetization (McElhinny, 1973).

Some substances are characterised by a subdivision into two crystal sub-lattices, usually designated A and B. The atomic moments of A and B are aligned although they are antiparallel to each other. If the moments of the two sub-lattices are equal, the ferromagnetic effects cancel each other out and there is no net magnetic moment. This is known as antiferromagnetism (Figure 3.1). Ilmenite exhibits this type of behaviour. If the atomic moments of the sub-lattices are unequal there is a net spontaneous magnetization and a weak ferromagnetism results; this phenomenon is known as ferrimagnetism (Figure 3.1) and is displayed by magnetite. Natural ferrimagnets are often referred to as "magnetite". However, this is a generalisation as magnetites exist in various degrees of impurity and include titanomagnetites in which substitution of titanium for iron has occurred and which is commonly present in basalts.If the equal atomic moments in the two sub-lattices are not exactly antiparallel and a weak spontaneous magnetization results, the substance is known as a canted antiferromagnet. Haematite is an example of such a substance.

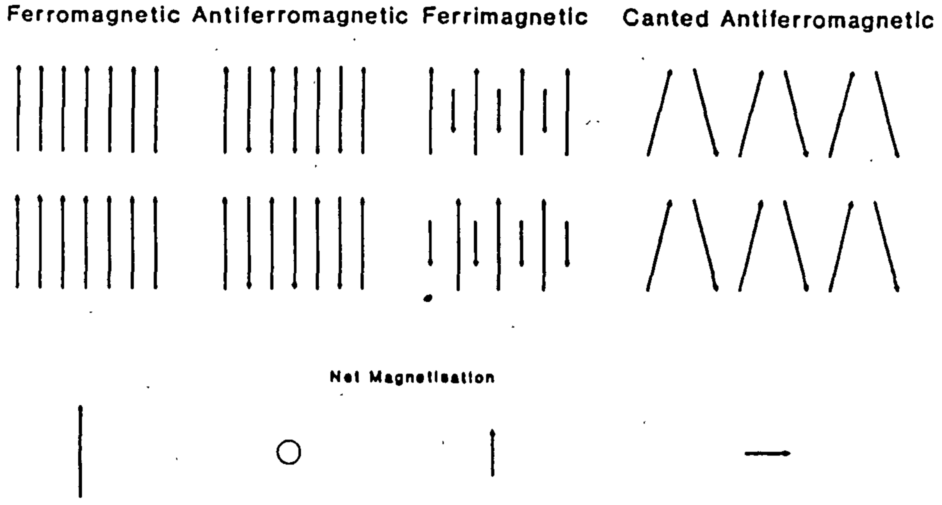
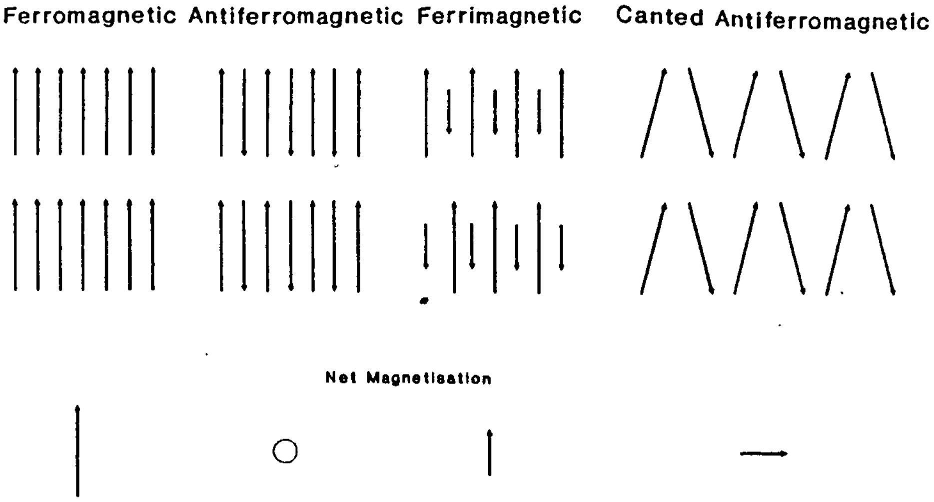


Figure 3.1 Arrangement of Magnetic Moments in Magnetic Materials.

3.3 Domain Theory

If a body is magnetised such that an external field results, the body exhibits a remanent magnetisation, and possesses a magnetostatic energy or energy of self demagnetisation. This magnetostatic energy is dependent on the shape of the body, as it can be preferentially magnetised in some directions rather than others. A long, thin rod for example will prefer to be magnetised along its length rather than across its breadth. In the case of the former there is no internal field opposing the magnetisation, in the latter the elementary magnets tend to rearrange themselves so that each one points in the opposite direction to its neighbour so that similar poles are not adjacent (Figure 3.2). Thus, in the latter case there is a large internal field tending to oppose the magnetisation (McElhinny, 1973).

Within the bulk matrix of a rock iron oxide and sulphide crystals may occur. These are highly ferrimagnetic in comparison to the bulk matrix.



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If a body is magnetised such that an external field results, the body exhibits a remanent magnetisation, and possesses a magnetostatic energy or energy of self demagnetisation. This magnetostatic energy is dependent on the shape of the body, as it can be preferentially magnetised in some directions rather than others. A long, thin rod for example will prefer to be magnetised along its length rather than across its breadth. In the case of the former there is no internal field opposing the magnetisation, in the latter the elementary magnets tend to rearrange themselves so that each one points in the opposite direction to its neighbour so that similar poles are not adjacent (Figure 3.2). Thus, in the latter case there is a large internal field tending to oppose the magnetisation (McElhinny, 1973).

Within the bulk matrix of a rock iron oxide and sulphide crystals may occur. These are highly ferrimagnetic in comparison to the bulk matrix,

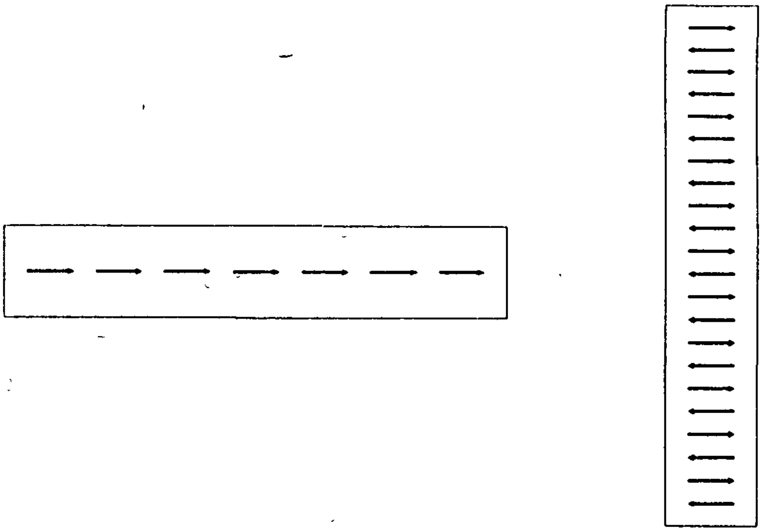


Figure 3.2 Schematic Representation of the Ease with which a Rod can be Magnetised Along its Length Compared with at Right Angles to its Length.

which is usually paramagnetic in nature, owing to its siliceous composition. The crystals are the magnetic grains that usually dictate the mineral magnetic characteristics of the rock (Stacey, 1959). Magnetic constituents are a small proportion of the bulk, possibly only a few percent (Neel, 1955).

Ferro-, ferri-, and canted antiferromagnetic grains attempt to minimise their magnetostatic energy by subdividing into sub-regions which are magnetised in different directions. The regions are called magnetic domains and are separated by domain walls through which there is a progressive rotation of atomic magnetic moments. Domain walls have been calculated to be in the order of a few thousand to several tens of thousands of nanometres thick (Neel,1955). Movement of domain walls in response to magnetic fields may be restricted by defects in the crystal lattice, such as dislocations, lattice vacancies and impurities.

Some magnetic grains are so small that it is energetically uneconomical to divide into domains. Therefore, these grains only possess a single domain, (<<1μm), whilst large grains are multi-domained. The magnetic behaviour of large multi-domained grains is similar to that of bulk material (Amar, 1958). It should be noted that while magnetic grain size is not independent of particle grain size the two are not the same. Coarse particles can be characterised by fine magnetic grains and the resulting magnetic parameters will reflect the size of these grains, not particle grain size.

The alignment of domains at any time will reflect both their response to external fields and their adjustment to each other, so that they achieve the most energetically economical state possible. In large multi-domained grains the domain walls usually find suitable positions such that the magnetostatic energy is zero. In consequence these grains may be demagnetised so as to have no net magnetisation.

In contrast to this, the single domain grains have moments that can be reversed but not destroyed. In small multi-domain grains the walls may not be able to find positions necessary to give zero magnetostatic energy and therefore the moments of these grains may be reversed but not demagnetised. As a result the grains behave in a similar manner to single domain grains and are accordingly called pseudo single domain grains, (PSD) (McElhinny, 1973). The domain state of a magnetic grain therefore greatly influences the behaviour of the grain when subjected to a magnetic field. The resulting magnetic measurements made both at the time it is subjected to such a field and subsequent to exposure to the field will reflect this. This effect will be discussed in greater detail in Sections 3.5 and 3.9.

The boundary between single domain and multi-domain grains is not precise. It is affected greatly by the presence of impurities and by grain shape. For example, the maximum size of single domain grains increases with increasing grain elongation. Dunlop (1973) deduced that the single domain - multi-domain boundary for equant magnetite grains lies between 0.035 μm and 0.05 μm. In the case of haematite the boundary is much larger, approximately 0.15 cm (McElhinny, 1973).

3.4 Superparamagnetism and Magnetic Viscosity.

Below the stable single domain grain size (<≃0.03 μm) the grains are too small to retain a magnetic remanence at room temperature. Any magnetic moment induced by an applied field will be lost due to thermally excited spontaneous reversals of the direction of magnetisation upon removal from the magnetic field. This behaviour is the same as that exhibited by a paramagnetic material. However, since the atomic moments are larger than for a normal paramagnetic material the alignment in the field is much stronger and the effect is termed superparamagnetism.

Between superparamagnetism (SP) grains and stable single domain (SSD) grains there is a range of grains, (diameter ≃0.03 μm-0.05 μm), which are termed viscous. Their response to changes in magnetic field is delayed with respect to time. Multi-domain (MD) grains also display magnetic viscosity which, however, only seems to be true in respect to "quadrature" measurements and not to the growth of viscous remanence or viscous loss of remanence. This effect is thought to be due to thermally activated domain wall movements upon removal from a field, the walls finding more energetically economical positions. This viscous behaviour by MD grains is some two orders of magnitude less than the viscosity of "viscous" grains. Viscous grains can be identifed by susceptibility measurements as they give rise to a "quadrature" or out-of-phase component when compared to susceptibility measurements made at differing frequencies.

3.5 Specific Magnetic Susceptibility and Quadrature.

The magnetic susceptibility is the ratio of magnetisation to the applied field. The magnetisation is the magnetic moment per volume and is therefore measured as $(A\ m^2)/m^3$ or alternatively $A\ m^{-1}$. The applied field is proportional to the current and inversely proportional to the length of the coil and is therefore proportional to amperes per metre $(A\ m^{-1})$.

Magnetic susceptibility is therefore dimensionless:

$$k = M/H$$

where k is magnetic susceptibility
M is magnetisation
H is magnetic field (Am^{-1})

The total magnetic moment per unit mass divided by the applied field is called the mass or specific magnetic susceptibility. It is related to k by converting volume to mass, i.e. dividing by density (Mullins, 1977).

$$\chi = k/\rho$$

$$\chi = M/H\rho$$

where χ is specific (mass) susceptibility
ρ is density

As k is dimensionless, the units of χ are the inverse of density, that is $m^3\ kg^{-1}$.

Susceptibility is shown on the hysteresis loop diagram (Figure 3.3) as the initial gradient of the curve expressing magnetisation versus field strength. In the case of ferrimagnets the initial gradient is steep in comparison to that of antiferromagnets where the gradient is more gentle. The susceptibility of magnetite is about a thousand times that of haematite. In both cases this initial magnetisation is reversible.

In terms of magnetic grains, the overall susceptibility is caused by;

a) the alignment of SP grains

b) the slight rotation of the grain magnetic moments in alignment with the field in SSD grains.

c) the slight rotation of moments of individual grains towards the field and enlargement of domains whose moments are aligned more or less parallel to the field.

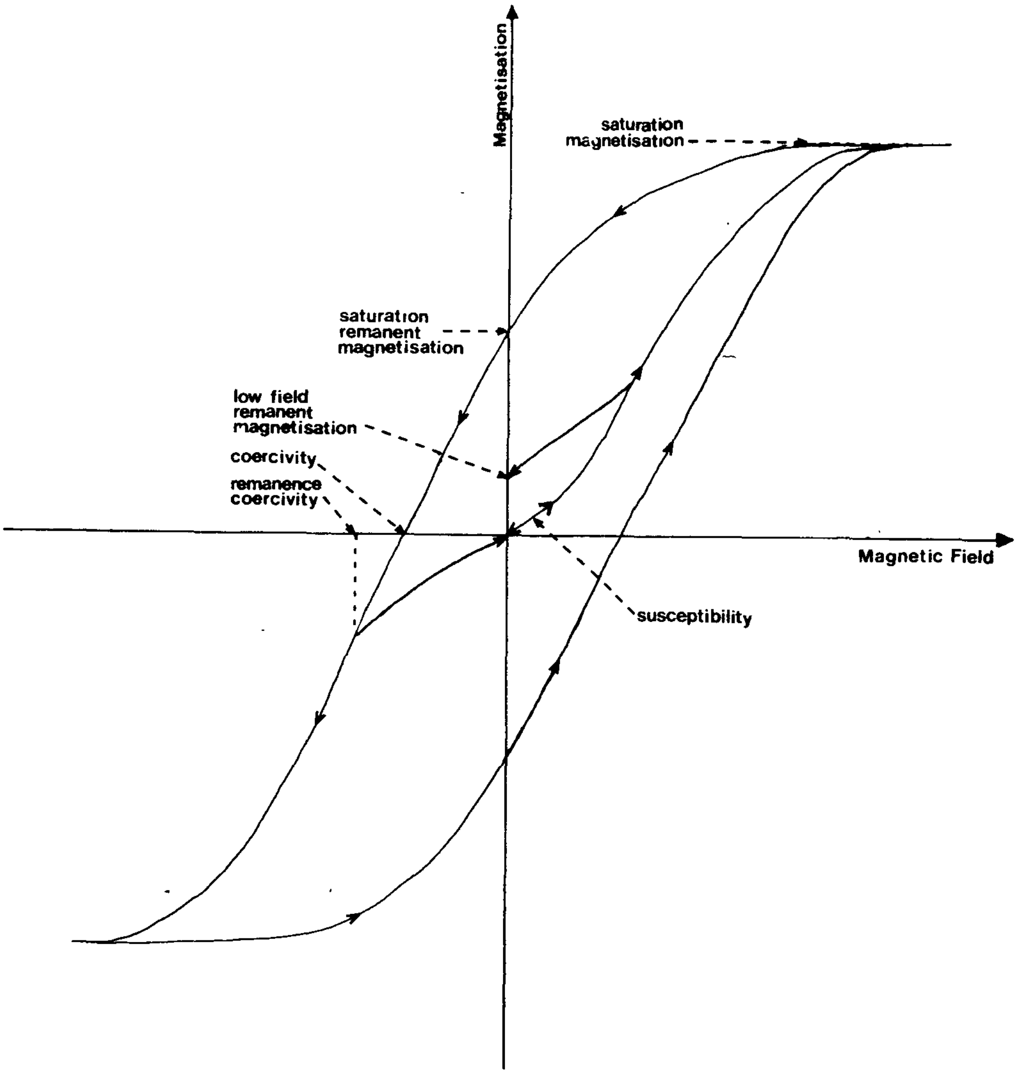


Figure 3.3 Magnetic Hysteresis Loop and Initial Magnetisation Curve.

All three reactions are temporary and the grains return to either random alignments in the case of SP grains or the grains return to their original states before placement in the field in the case of SSD or MD grains.

Susceptibility is indicative of the volume concentration of magnetic minerals in a sample. It is also affected by magnetic grain size, internal stress and other nonintrinsic parameters (Thompson et al, 1975). Table 3.1 shows the results of magnetic measurements of dispersed, sized magnetic powders. A slight decrease in susceptibility is seen with decreasing sediment grain size. The domain status of the sample varies from multidomain to single domain and as the size

Table 3.1 Variation of Mineral Magnetic Parameters With Sediment Grain Size.

Grain Size (μm)	χ (cm^2kg^{-1})	IRM_{300mT} (Am^2kg^{-1})	IRM_{300mT}/χ (kAm^{-1})	$(B_o)_{CR}$ (mT)	REFERENCE
Magnetite					
220	752	0.483	0.642	12	1
200	560	0.849	1.516	9.2	2
150-250	715	1.06	1.483	16.5	3
120	582	1.41	2.42	17	4
100-150	741	1.15	1.552	17.1	3
100	728	1.16	1.59	14	1
100	500	1.2	2.4	15	5
88	509	1.49	2.92	18	4
75-100	749	1.29	1.722	17.6	3
58	534	1.47	2.75	19	4
55-75	746	1.47	1.971	18.2	3
40-55	726	1.56	2.149	18.6	3
37	728	1.29	1.78	20	1
37	631	1.04	1.65	20	1
37	703	1.14	1.62	19	1
37	534	1.85	3.47	20	4
30-40	736	1.95	2.649	19.3	3
25-30	726	2.44	3.361	19.5	3
21	509	1.74	3.41	23	4
20-25	722	2.66	3.684	21.2	3
19	461	2.32	5.03	22	4
15-20	707	3.22	4.554	22.8	3
15	679	3.48	5.12	25	4
12	-	2.7	-	23	4
10-15	675	4.26	6.311	24.9	3
6	461	4.05	8.79	23	4
5-10	618	6.34	10.529	28.3	3
<5	536	11.2	20.896	39.7	3
1.5	485	11.2	23.1	38	2
1.5	388	5.85	15.1	32	4
1.5	461	5.79	12.6	34	4
<1	500	12	24.0	50	5
0.22	708	10.2	14.4	-	6
0.1	679	17.9	26.4	-	6
0.076	650	21.8	33.5	-	6
0.076	650	21.8	33.5	-	6
0.037	572	26	45.5	-	6
0.03*0.02**	451	41.8	92.6	-	6
Haematite					
100	0.3	0.075	250	500	5
Unknown	6.0	0.2	33.3	700	7

References

1) Parry, 1980
2) Parry, 1979
3) Hartstra, 1982
4) Parry, 1965
5) Thompson and Morton, 1979
6) Dunlop, 1972
7) Thompson and Oldfield, 1986

decreases to where single domain grains only are present the susceptibility correspondingly increases.

Quadrature and frequency-dependent susceptibility are diagnostic of fine viscous grains. The magnetisation response of viscous grains in an applied alternating field gives rise to an asymmetric wave form. The resulting susceptibility readings can be expressed as 'in-phase' and quadrature ('out-of-phase') components. The quadrature component will increase with increasing number of viscous grains.

A similar indication of the presence of viscous grains is given by measuring suseptibility at different frequencies. At low frequency the magnetisation response remains in phase with the alternating field giving rise to a response curve that can be envisaged as a complete waveform . The 'in-phase' susceptibility has a value close to that of direct, static susceptibility (Thompson and Oldfield, 1986). At high frequency, however, the delayed response of the viscous grains and the lack of time between successive alternations in field due to the higher frequency give rise to an incomplete waveform. This is due to the prior response not decaying to zero before the next response to the alternating field occurs.

There is a resultant difference between the waveforms at low frequency and high frequency and this difference, the 'out-of-phase' component, is commonly expressed as a percentage of the total susceptibility (χ_{fd}/χ) and is calculated using the formula;

$$\chi_{fd} = ((\chi_L - \chi_H)/\chi_L)*100$$

where χ_{fd} is frequency-dependent susceptibility
χ_L is the susceptibility reading at low frequency
χ_H is the susceptibility reading at high frequency

3.6 Saturation Isothermal Remanent Magnetisation (SIRM; IRM_{sat}; J_{rs}; M_{rs}).

Isothermal remanent magnetisation is the magnetisation induced in and retained by a sample after it has been placed at room temperature in a magnetic field. Saturation isothermal remanent magnetisation is the largest IRM that a substance or assemblage can possess using laboratory equipment.

The units of SIRM, and any other induced IRM, are defined by the magnetisation per unit mass, that is amperes per metre divided by density;

SIRM = magnetisation per unit mass

$\mathrm{SIRM} = (\mathrm{A\ m^2/m^3})/(\mathrm{kg/m^3})$

$\mathrm{SIRM} = \mathrm{A\ m^2\ kg^{-1}}$

Susceptibility is illustrated as the initial gradient of the magnetisation curve at which stage the phenomenon is reversible (Path 'a', Figure 3.4). If the field strength is increased this region of the curve is exceeded and the reaction is not reversible. The magnetisation then does not follow the curve to zero but reduces along a new path retaining an isothermal remanent magnetisation (IRM) (Path 'b', Figure 3.4).

In domain theory this is explained as the field which has sufficient energy to overcome some of the energy barriers separating the easy directions of magnetisation and causing individual grains to flip through 180° to align with the field. This reaction is non-reversible as the grains do not have sufficient magnetostatic energy to overcome these barriers outside the applied field.

Variations in IRM of a substance or SIRM between substances can also be explained in terms of grains. The stability of grains varies with that of MD grains being lower than that for SSD grains. A large energy barrier must be overcome in order to change the remanence of an SSD grain whereas in MD grains, domain wall movements may occur in

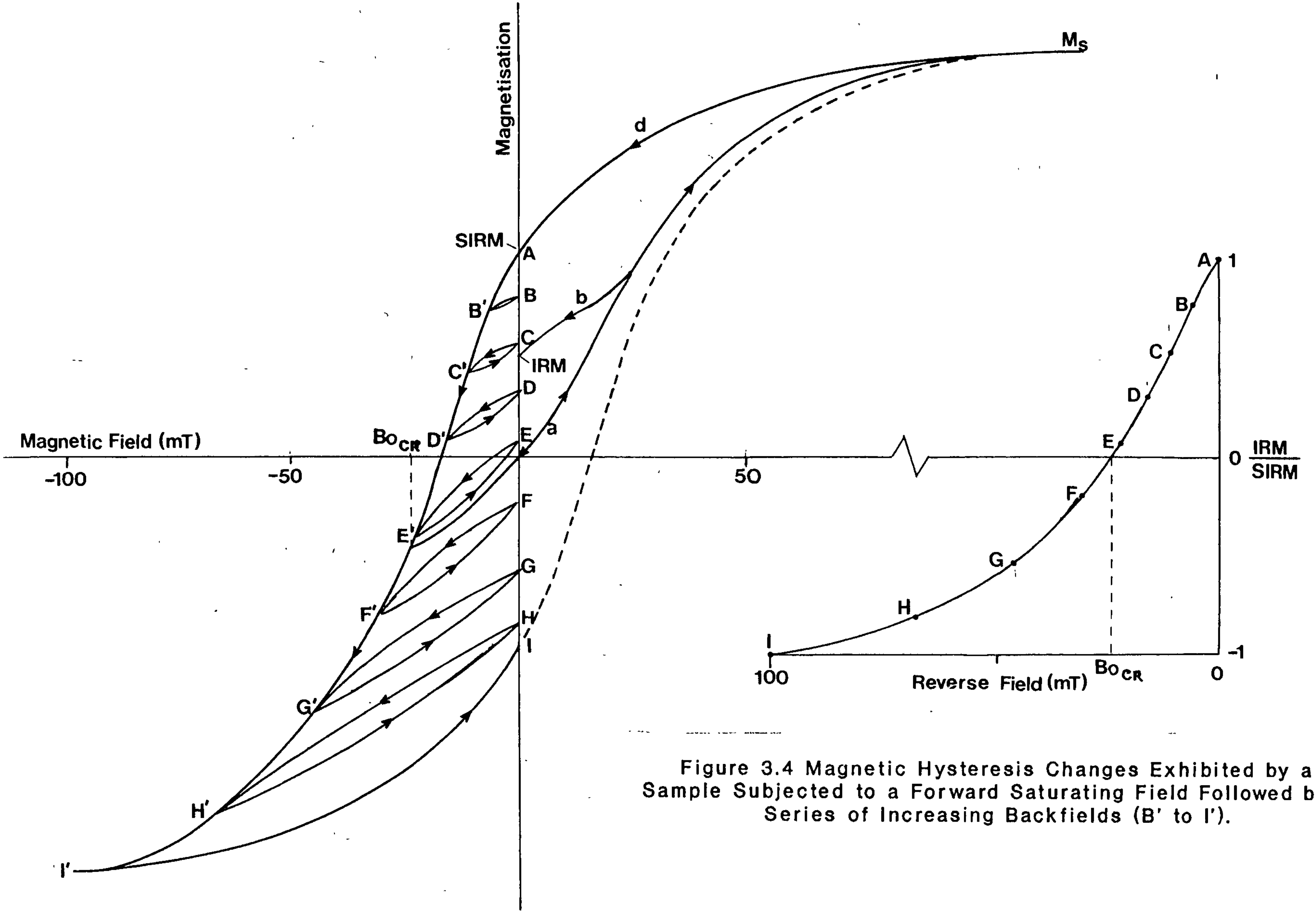


Figure 3.4 Magnetic Hysteresis Changes Exhibited by a Sample Subjected to a Forward Saturating Field Followed by a Series of Increasing Backfields (B' to I').

relatively low fields. If the field is increased in steps and the IRM recorded at each step the magnetisation curve can be drawn up (Figure 3.4). The increase in remanence can be viewed as the increasing numbers of grains whose energy barriers have been progressively overcome.

A point is reached where subsequent increases in the magnetic field produce no further increase in magnetisation. This is termed saturation magnetisation (M_S). Upon removal from the field the magnetisation decreases slightly but does not reach zero. The remaining magnetisation is called the saturation remanent magnetisation (M_{RS}). The highest isothermal remanent magnetisation which can be produced within the laboratory may not actually be the true saturation remanence. It may only be an isothermal remanent magnetisation produced on the approach to saturation. This can occur when haematite is a constituent material of the sample under investigation. The laboratory measurements in this study are therefore described as isothermal remanent magnetisation (IRM) induced on the application of a particular field, the magnetic field designated by an attached subscript. Other studies have utilised the term SIRM to describe the greatest isothermal magnetisation produced using laboratory equipment (Thompson and Oldfield, 1986).

The decreases of magnetisation from M_S to M_{RS} and the reduction of magnetisation to IRM upon removal from the field is explained by the destruction of the alignment of the SP grains by thermal disturbance upon removal from the field. There is also a rotation of magnetic moments to align with the easy axes of magnetisation in SD grains and in MD grains there is a readjustment to the domain configuration. This reduction can be viewed as the reversible reaction which is seen in susceptibility. The same phenomenon occurs within the grains accounting for both reactions.

M_{RS} or SIRM are not affected by weak magnetic behaviour such as diamagnetism and paramagnetism as these are lost upon removal from the magnetic field. M_{RS} or SIRM are also indicative of the volume concentration of magnetic minerals in a sample. The data in Table 3.1 shows that there is a significant increase in the SIRM value of magnetite with decreasing grain size and this parameter is at a maximum in stable single domain grains. Smaller grains exhibiting viscosity and SP, however, will exhibit negligible SIRM.

3.7 Coercivity of Remanence $(B_0)_{cr}$.

Following the measurement of SIRM, a reverse magnetisation can be induced in the sample by placing the sample within a reversed magnetic field. On application of a reverse field the net magnetisation results from;

a) the SP grains aligning with the reverse field

b) the alignment in the reversed field of the moments of stable domains whose individual coercivities have been exceeded by the applied field.

c) the reversible changes in configuration of MD grains so that the moments of the domains align to a greater extent with the reversed field direction.

In addition the net magnetisation is made up of the contribution of those domains whose coercivities have not been exceeded and which are still aligned in the directions obtained before the reversal of the field.

When the reversed field is reduced to zero or the sample is removed from the field there is a net loss of magnetisation. This is due to the thermal randomisation of the alignment of SP grains and the relaxation of the alignment of the moments of the domains in MD grains.

In order that a complete curve of reverse magnetisation can be drawn the sample is placed in a series of reverse fields of increasing field strength. With continued applications of reversed fields a point is reached at which forward and reversed "in-field" magnetisations cancel each other out and the net assemblage magnetisation is zero. The field at which this occurs defines the "coercive force" or coercivity of the assemblage, $(B_0)_c$ (Figure 3.3).

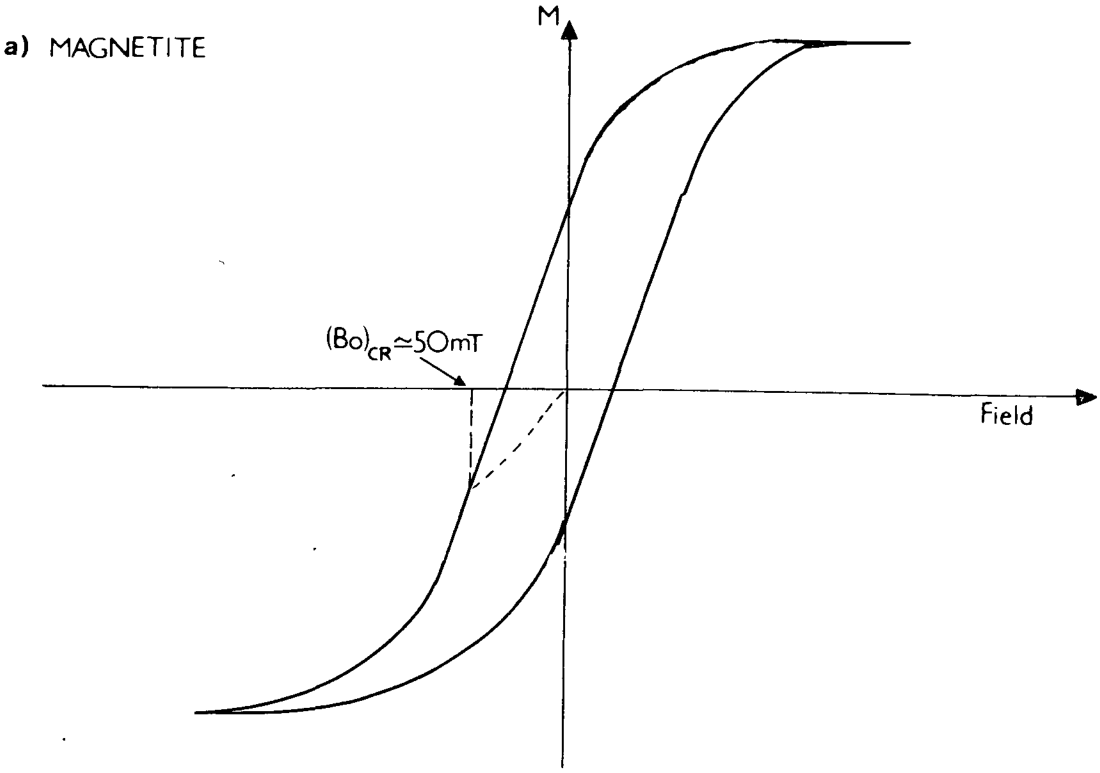
The coercivity of remanence, $(B_o)_{CR}$, is the point where with reduction of the reversed field to zero the forward and reversed remanent (out of field) magnetisations cancel each other out and the net assemblage remanence is zero (Figure 3.3 and 3.4).

If the reversed field is increased further the assemblage will acquire a negative magnetisation which will increase with increasing field strength until the assemblage is saturated in the reversed direction.

The coercivity curve of an assemblage can be plotted by division of each IRM value, recorded at each successive application of a reverse field, by the SIRM value for the assemblage. In the case of Figure 3.4 the coercivity curve on the right is plotted by calculating B/A; C/A; D/A through to I/A. This curve allows $(B_o)_{CR}$ to be evaluated accurately, as opposed to estimation made from the hysteresis loop. The coercivity curves obtained from a sample are roughly diagnostic of the magnetic mineral assemblage present (Dunlop, 1972).

It has been found that convenient measures to use for a series of samples where the coercivity curves are to be compared are ratios of several discriminating reversed fields. This has the advantage of being clearer when plotted on one graph as opposed to series of curves that generally tend to be confused making it difficult to discriminate between characteristic curves or properties for particular samples. In previous work the ratio of a reversed field IRM divided by SIRM has been designated "S". This is no longer thought to be a useful designation as for differing suites of samples it has been found that the particular reversed field that is most discriminatory between samples may vary depending on the material present. In consequence, it is preferred that the actual ratio should be stated in full.

Reversed field ratios, $(B_o)_C$ and $(B_o)_{CR}$ are generally considered normalised parameters which are independent of concentration. However, like the actual shape of the hysteresis loop they are characteristic of the type of magnetic minerals present. "Soft" magnetic minerals such as magnetite tend to have steep hysteresis loops (Figure 3.5a), while "hard" magnetic minerals, such as haematite, tend to have flat



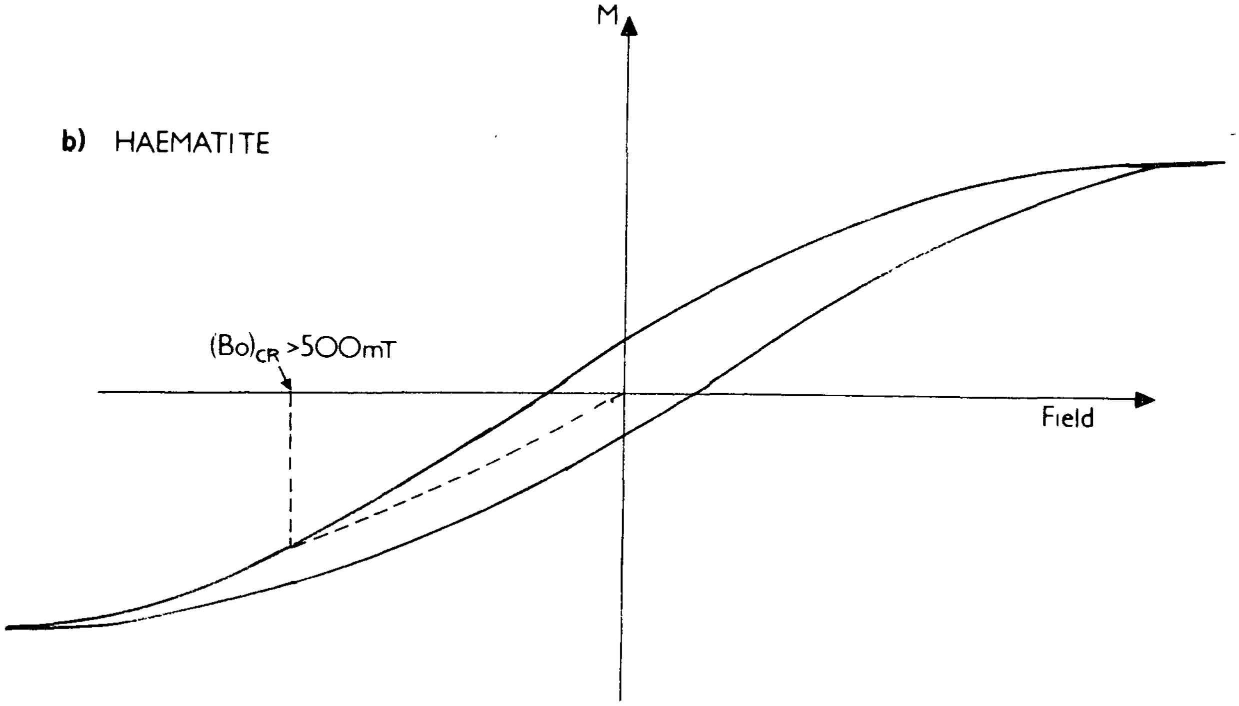


Figure 3.5 Typical Magnetic Hysteresis Loops of Magnetite and Haematite.

hysteresis loops (Figure 3.5b). These normalised parameters are also indicative of magnetic grain size.

$(B_o)_{CR}$ and reversed field ratios and, to some extent, SIRM/χ (See Section 3.8) also reflect changes caused by environmental processes such as fire, pedogenesis and authogenesis.

3.8 SIRM/χ

This ratio reflects the type, size and shape of magnetic minerals in a sample (Walling et al, 1979; Thompson et al, 1980; Hunt et al, 1984) and can be used as a rough estimate of magnetic grain sizes (Thompson and Oldfield, 1986). It is also independent of ferrimagnetic concentration. The units of this parameter (Am^{-1}) are calculated from the units of the appropriate parameters:

$$\text{Units of SIRM / Units of } \chi$$

$$= A\ m^2\ kg^{-1} / m^3 kg^{-1}$$

$$= A\ m^{-1}$$

Where SIRM and χ are proportional, and therefore SIRM/χ is constant, SIRM can be used as an alternative measure of the concentration of magnetic minerals. Oldfield et al (1981) found that in measurements made on a suite of core samples the susceptibility was normally too weak to be measured. Where both SIRM and χ could be measured they were found to be directly proportional in all samples the constant ratio of SIRM to χ could be used for calculation of the unknown parameter. From Table 3.1, SIRM/χ can be seen to be indicative of grain size variations, showing an increase with decreasing grain size so that the maximum SIRM/χ value occurs in stable single domain grains.

3.9 Application of Mineral Magnetic Parameters in Environmental Studies.

Mineral magnetic measurements are of considerable environmental interest. Magnetic minerals derived both naturally and from anthropogenic activities can be distinctive and this can allow scientists to gain information relating to the sources of magnetic minerals, their supply and the rates of sedimentation and deposition.

Mineral magnetic parameters have been applied to studies of land use impact, particularly with regard to erosion (Rummary et al, 1979), to lacustrine and marine stratigraphical studies (Thompson et al, 1975; Oldfield et al, 1977; Thompson et al, 1980), to paleaoenvironmental studies (Oldfield et al, 1980) and to particulate pollution studies (Oldfield et al, 1981a; Hunt et al, 1984).

3.9.1 Mineral Magnetic Studies of Lake Sediments.

Initial work carried out on lake sediments indicated that magnetic susceptibility represented a rapid and non-destructive technique which could be used to correlate between cores (Thompson et al, 1975; Oldfield et al, 1978a). It was also suggested that as a majority of magnetic parameters are derived from allocthonous material, magnetic measurements could yield information on erosion rates and patterns (Oldfield et al, 1978a; Foster et al, 1985; Stott, 1987). The sediment influx into lakes has been assessed by use of mineral magnetic parameters (Bloemendal et al, 1979; Dearing et al, 1981). The use of magnetic susceptibility measurements has allowed the calculation of total sediment influx versus time and the differentiation of sediment influx from channel erosion and slate debris inwash from spoil tips. The dominant sediment type in sampled sediments could be identified from their significantly different mineral magnetic signatures (Dearing et al, 1981).

3.9.2 Mineral Magnetic Studies of Marine Sediments and Particulates.

Several studies of marine particulates utilising mineral magnetic parameters have indicated that, where the particulate pollution is distinctive with regard to mineral magnetic parameters, the particulates can be traced.

Scoullos et al (1979) found by plotting the values of χ for surface marine sediments in the Elefsis Gulf, Greece that the concentration of magnetic minerals increased with proximity to the suspected point source of the particulates which was an iron and steel works discharging effluent containing iron oxides directly to the sea. Good linear correlation between iron concentration and mineral magnetic parameters measured on sampled marine particulates was observed. By use of χ and SIRM the spatial distribution patterns of particulate output from these major sources could be determined (Oldfield and Scoullos, 1984).

Further studies have indicated that linkages between heavy metal concentrations and mineral magnetic parameters exist in marine sediments. A strong linear relationship between Zn and SIRM was found and was thought to be due to a binding mechanism , probably adsorption, of Zn onto magnetically active particles that are rich in Fe (Scoullos, 1981). Additionally χ and SIRM were seen to correlate closely with concentrations of Cu, Pb, Mn, Fe and Zn in sediment cores taken in the Elefsis Gulf (Scoullos and Oldfield, *in press*). Investigations into metal-magnetic relationships in estuaries have revealed that there is a close parallelism between magnetic susceptibility and Cu and Zn concentrations, and in some cases Cr and Ni concentrations, for sections of the estuarine sediment cores. Both mineral magnetic parameters and physical measurements indicate that clay or clay-sized particles are the major carriers of trace metals in these sediments (Scoullos and Oldfield, *in press*).

3.9.3 Mineral Magnetic Studies of Fluvial Processes and Suspended Sediments.

Identification of suspended sediment sources through the use of mineral magnetic parameters has been reported by Oldfield et al (1979) and Walling et al (1979). Their work was carried out in the Jackmoor Brook basin, near Exeter. Bulk samples of the possible source materials were collected and the coercivity curves compared to the curves for suspended sediment samples. The dominant source of suspended sediments during storm events was concluded to be cultivated top soil (Oldfield et al, 1979). The source materials appeared to be well defined allowing ready identification. High SIRM values and a tendency to greater similarity between the coercivity curves of suspended sediment and the cultivated top soil source at storm peak flow suggested that this source increased in its relative importance during major flood events at peak flow (Oldfield et al, 1979; Walling et al, 1979). Channel scour as a source of suspended sediments could also be distinguished such that an indication of the relative importance of slope and channel sources could be ascertained both during and between storm events (Walling et al, 1979). These studies indicate that mineral magnetic parameters allow not only a qualitative characterisation of source of suspended particulates but also an insight into the relative dominance of the source.

Research has also been carried out into the application of mineral magnetic parameters to the investigation of urban pollution in stormwater suspended sediments (Revitt et al, 1981). Variation in mineral magnetic characterisations of the suspended sediments throughout storm events suggested that different sources contributed to the suspended sediment load of a storm at different times. The suspended sediments sampled towards the end of a storm event appeared to have high SIRM values and it was postulated that these sediments may have resulted from scouring of toxic particulates from street surfaces as it is known that vehicular derived particulates have high concentrations of magnetic minerals (Revitt et al, 1981; Thompson and Oldfield, 1986). Good correlation was observed between SIRM and the heavy metals Cu, Pb and Zn, suggesting sources of particulates high in magnetic minerals and heavy metals may be the same or closely associated. Cadmium did not exhibit a good correlation and no pattern of sequencing over storm events was evident (Revitt et al, 1981).

Further studies of fluvial processes have been carried out utilising artificially enhanced sediments (Oldfield et al, 1981b; Rummery, 1981; Arkell et al, 1983; Leeks et al, 1988). It was found that sediments subjected to forest fires exhibited increased χ and SIRM values. These were used to date lake sediments and to trace soil erosion resulting in sediment input into these lakes (Rummery et al, 1979; Rummery, 1981). It was found that the mineral magnetic characteristics of sediments could be artificially enhanced by the application of heat (Oldfield et al, 1981b). Sediments from the natural bedload of drainage ditches and rivers were artificially enhanced such that the sediments exhibited large χ and SIRM values in the natural bedload of drainage ditches and rivers (Arkell et al, 1983; Leeks et al, 1988). The bedload movement could subsequently be traced. As the natural bedload was used the tracing was effective for all size ranges affected by the fluvial process and this is an obvious advantage over artificial sediments (Arkell et al, 1983; Leeks et al, 1988).

3.9.4 Mineral Magnetic Studies of Atmospheric Particulates.

The atmospheric fallout of magnetic spherules has been documented by a number of workers (Parkins et al, 1970; Doyle et al, 1976) and the possible sources of these spherules have been cited as volcanic, extra-terrestrial and industrial (Puffer et al, 1980; Thompson and Oldfield, 1986). The abundance of magnetite spherules in air particulates, lake, marsh and beach sediments has been found to decrease with distance from industrial centres and it has been suggested that the presence of magnetite spherules of industrial origin could be used as indicators of post-industrial age deposition (Puffer et al, 1980).

This aspect has been investigated in research carried out on samples and cores from ombrotrophic peat bogs. An ombrotrophic peat bog derives its nourishment entirely from atmospheric sources. The bog surfaces are built up above the ground water table so that deposited particulates are not affected by water movement post deposition. This, in turn, can lead to a record of atmospheric deposition from the time of isolation of the bog surface from surface and ground water to the present.

Vertical cores taken from such bogs have been analysed and the variation in mineral magnetic parameters through the core have been recorded. These studies indicate that levels of parameters relating to magnetic mineral concentrations found in near-surface peats are orders of magnitude larger than those found in peat samples at the base of the cores (Oldfield et al, 1978b; Oldfield et al, 1981a). The vertical variation represents temporal variation in deposition and the dramatic increase in concentration related parameters observed in nearly all cores studied is ascribed to the onset of industrialisation. It was also found that as well as vertical variation, spatial variation was present with peats within the vicinity of major conurbations having values of concentration related mineral magnetic parameters which were orders of magnitude greater than those of peats remote from industrial activity (Oldfield et al, 1981a).

Investigations into the relationship between mineral magnetic parameters and heavy metal concentrations in peat bog cores have also been carried out. Oldfield et al (1980) found good agreement between magnetite deposition rates, as calculated from mineral magnetic measurements, and measured total iron deposition rates. From this it was concluded that mineral magnetic procedures could be combined readily with methods for monitoring heavy metal pollution based on the chemical analysis of *Sphagnum* moss. A further study of ombrotrophic peat bog cores indicated strong similarities in the distribution of SIRM, χ and the metals Cu, Pb and Zn. The persistence of the heavy metal-magnetic mineral associations was suggested to support the process-orientated linkage rather than "co-existence" (Jones, 1985).

Mineral magnetic parameters have been applied to investigating contemporary particulate pollution. Samples of particulates from predominantly vehicular sources collected in road tunnels, samples of fly-ash from a power station and leaf samples from the environs of the power station were investigated by Hunt et al (1984). The mineral magnetic characterisations were observed to be significantly different. The ratio of SIRM, to heavy metals was consistent for each source while being characteristic for that source, suggesting that such methods could be used to identify and differentiate pollution sources (Hunt et al, 1984; Thompson and Oldfield, 1986).

A survey by Maxted (1983) indicated that mineral magnetic measurements of leaves in urban areas and their associated particulates could yield information on pollutant concentrations. Mineral magnetic concentration related parameters such as χ and SIRM increased with increasing pollutant concentration. The coercivity values have been found to vary with the relative haematite content allowing roadside particulates to be distinguished from power station fly ash (Oldfield and Maxted, 1984). Further studies involving mineral magnetic measurements on leaves and their associated particulates have exhibited good correlations between trace metals and mineral magnetic parameters in tracing pollutants from industrial sources (Oldfield, 1988).

Studies of airborne dust samples collected on board ship in the Mediterranean and Atlantic further reinforce the prospect that mineral magnetic parameters are useful tools to differentiate particulates. Mineral magnetic parameters have been found to clearly differentiate between dusts of Sahara origin and dusts of South American origin (Thompson and Oldfield, 1986).

The overall evidence provided from previous studies on the application of mineral magnetic parameters to environmental problems are that they can be reliably used to identify sediments and particulates from a variety of sources and situations. These applications are only successful, however, if there is a significant difference in one or more of the mineral magnetic characteristics of the source materials.

In the case of heavy metal pollutants it is expected that they would be associated with particulates with characteristic mineral magnetic signatures as a result of the anthropogenic nature of both the metals and the particulates. The mineral magnetic characteristics of the particulates would reflect the physical and chemical forces to which the particulates are subjected during their formation. This would appear to be indicated by the results of Hunt et al (1984) and Oldfield and Maxted (1984). This has important implications for environmental studies since it may be possible to trace heavy metals by the mineral magnetic characteristics of the particulates with which they are associated.

CHAPTER 4 SAMPLING AND ANALYTICAL METHODS.

4.1 Introduction.

As illustrated by the data presented in the review of sources of heavy metals in the urban environment (Chapter 2) the pattern of distribution of heavy metals will primarily reflect the presence of industrial inputs owing to the magnitude of these point sources compared to the minor more widespread inputs from domestic and vehicular sources. In order that the impact of the input of pollutants from vehicular and highway associated sources can be assessed, a sampling site relatively removed from industrial sources was required. A previously instrumented catchment in Oxhey to the north-west of London (Wilkinson,1956; Harrop 1984a) was found to match these requirements and was therefore used. The research was carried out in two distinct areas; primarily in a small limited sub-catchment with clearly defined boundaries; and in the main parent catchment.

4.2 The Research Catchments.

4.2.1 The Chilwell Gardens Sub-Catchment.

Chilwell Gardens is an arterial road located in Oxhey, S.W. Hertfordshire (Figure 4.1, Plate 4.1). The highway is typical of many such residential roads found within the main parent catchment. The section of the road which comprises the experimental sub-catchment is bordered by residential units to the west and by the South Oxhey Community Centre to the east. The housing units were built in the late 1940s and consist of terraced blocks of four houses of similar design which are constructed of brick with a cladding of cement. Roofing materials consist of sand-cement mix tiles with iron guttering (Plate 4.2). Several dwellings in the parent catchment have garage facilities, but there is only one in the sub-catchment area. The contributing areas to surface runoff are therefore roofs and the road surface together with adjacent pavements (Figure 4.2). The gardens within the sub-catchment do not contribute as they are inclined away from the road or at a level

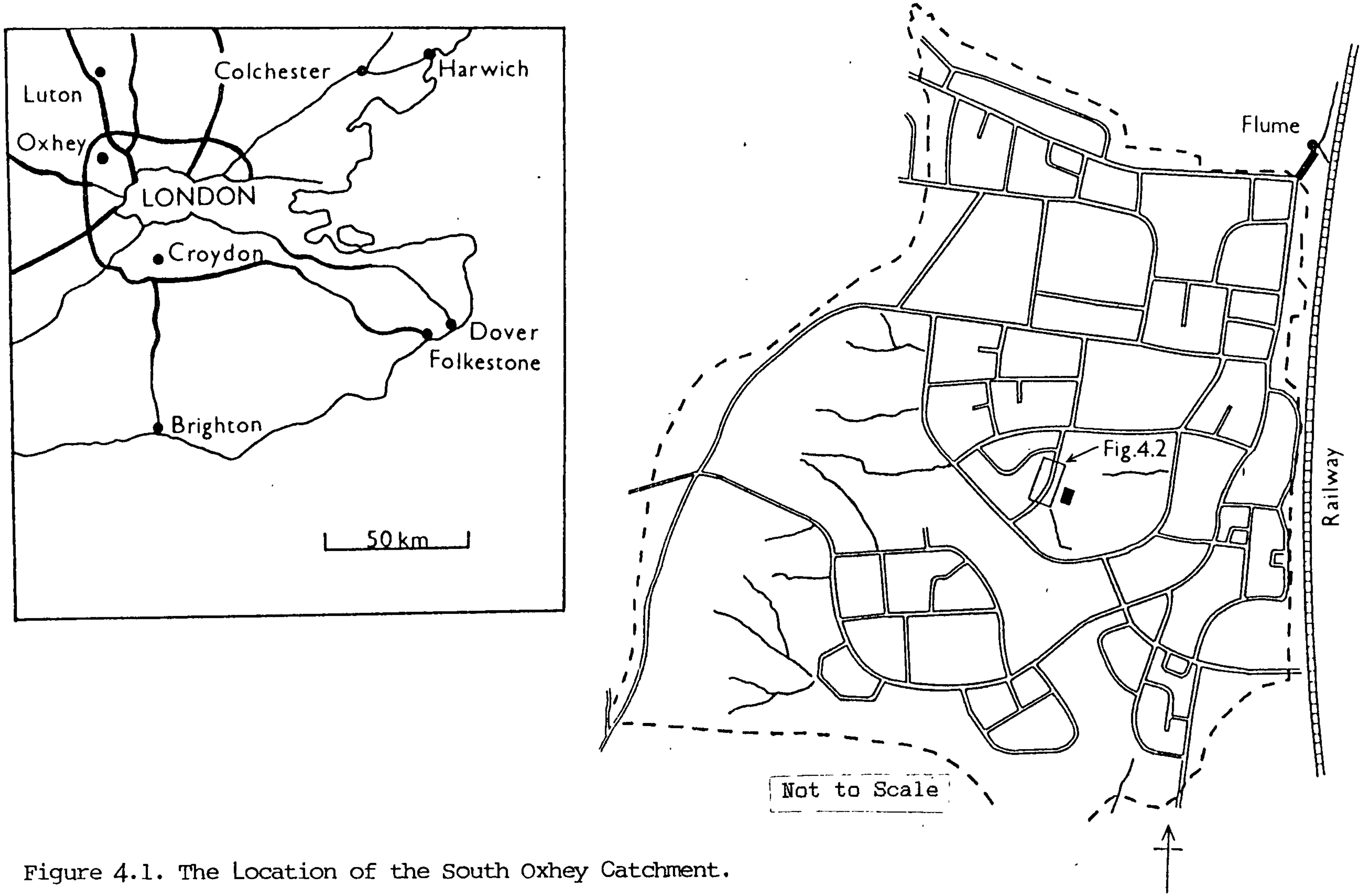


Figure 4.1. The Location of the South Oxhey Catchment.

Plate 4.1 The Chilwell Gardens Sub-Catchment.

Plate 4.2 Typical House Adjacent to Sub-Catchment (from which roof sediment samples were collected).

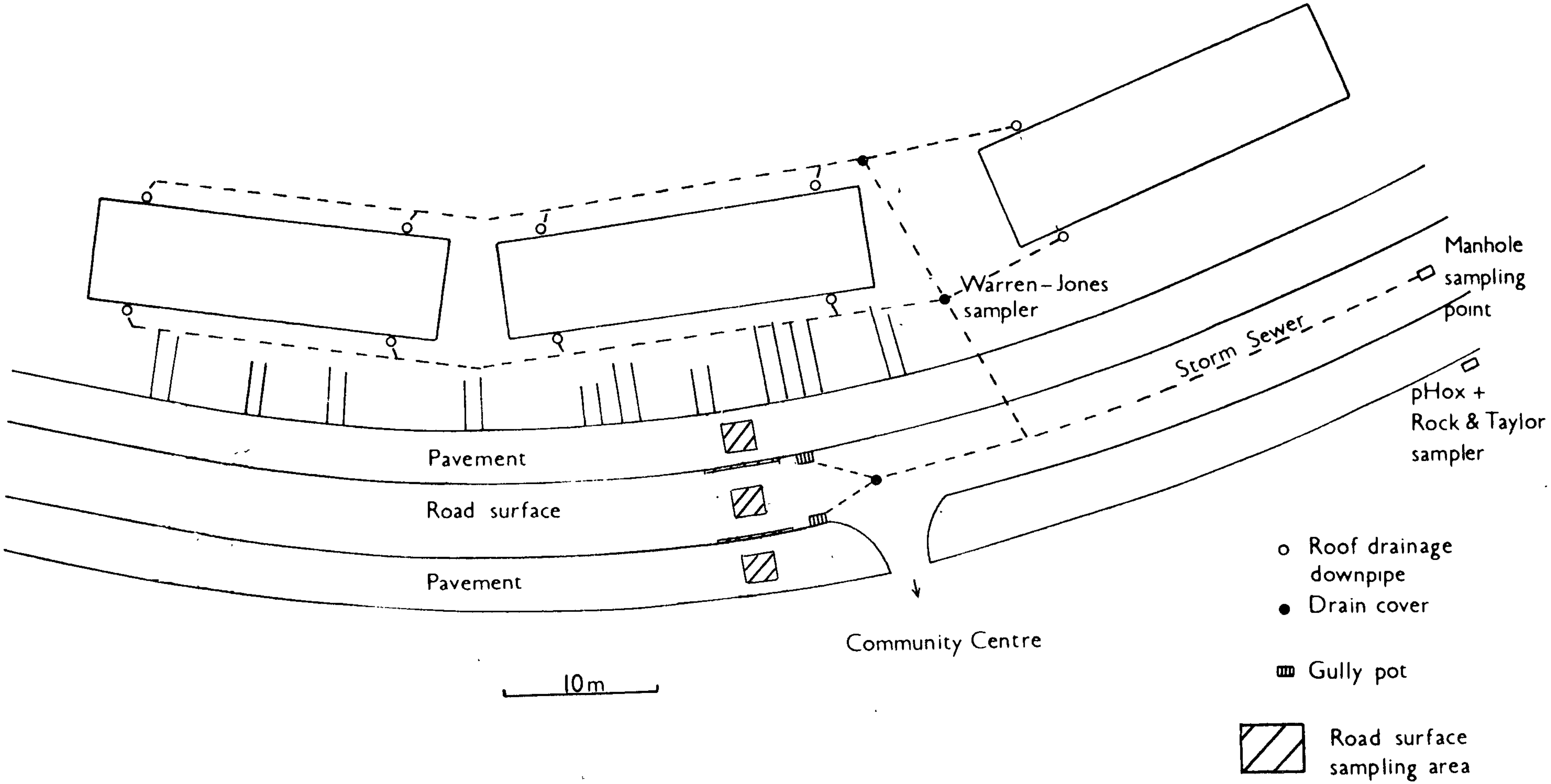


Figure 4.2 Sampling Locations and Drainage System at the Chilwell Gardens Sub-Catchment.

below the pavement surface. The total area of the sub-catchment has been ascertained by Harrop (1984a) to be 533.09 m^2, and measurements made in this study are in agreement with this figure. Harrop (1984a) found that 96% of the catchment area is impervious.

Table 4.1 Characteristics of the Chilwell GardensSub-Catchment.

Paved Surface Area		533m^2
consisting of;	Pavement (East)	157m^2
	Pavement (West)	155m^2
	Road Surface	221m^2
Roof Surfaces		
	Total roof surface area	614m^2
	Horizontal area equivalent	412m^2
Total Contributing Area		945m^2

4.2.1.1 Road and Path Surfaces.

Chilwell Gardens connects two other residential roads within the catchment, consequently the road is lightly trafficked being restricted mainly to local traffic serving the houses with some additional load provided by traffic to the community centre. The road is of typical construction for the estate consisting of a concrete base of approximately 30.5 cm overlying a hardcore platform placed on the local boulder clay. The concrete base is covered by a layer of hardcore and cinders which is topped with a layer of tarmacadam. In March 1981 the road was resurfaced with a thin surface of tar and loose coarse Mount Sorrel granite chippings.

The pavements adjoining the road are of rolled tarmacadam, with a foundation of approximately 50 cm of cinder and hardcore. The texture of the rolled surface is variable owing to repairs carried out on several occasions and in certain areas tree root penetration as well as parking practices have led to extensive cracking and damage to the pavement surface.

4.2.1.2 Drainage.

The drainage system is of the separate sewer type. Roofs are drained to iron guttering and down pipes of which there are four on each housing block linked by 10.2 cm pipes to the storm drain. The road surface of the sub-catchment is drained by two gully pots which are similarly connected to the storm drainage system (Figure 4.2). The pipes are of glazed clay and were laid in 1946-1947. The main storm drainage pipe is 21.6-22 cm in diameter and is set in cement. Within the sub-catchment there are two manhole covers which allow inspection of the drainage system. Due to age and settling some of the pipes are subject to leakage. The drainage sytem of Chilwell Gardens is linked to the main drainage system of the estate, eventually leading to the flume outfall.

4.2.2 The South Oxhey Catchment.

The parent catchment, of which the Chilwell Gardens catchment is a part, is typical of post-war London overspill developments and comprises grass verges, gardens, woodlands and open spaces with semi-detached and terraced housing, schools, shops and public buildings. The catchment is 243 ha in area. There is no industrial or commercial development on the estate. Housing density is approximately 3.2 units per hectare over the built-up area with an overall housing density of 2.02-2.43 houses per hectare (Harrop, 1984a), although with recent residential development projects this figure is increasing.

The catchment is 19.8% impervious (Harrop, 1984a) and is drained via the separate stormwater pipes that outfall to the Hertsbourne River which is a tributary of the River Colne.

4.2.2.1 Geology and Pedology.

The underlying geology of the catchment is impermeable London Clay which is 60.96-91.44 m thick with a 10.67-19.81 m overlay of Woolwich and Reading beds. The soil across the larger catchment is primary Windsor Tertiary clay (Soil Survey of England and Wales, 1982) which consists of permeable but seasonally waterlogged clayey soils mostly with brown subsoils.

4.2.2.2 Drainage.

The estate is drained by a totally separate sewer system with a typical dendritic pattern of stormwater drainage pipes. The surface stormwater runoff is drained via the outfall pipe to a trapezoidal long throated flume. The flume was constructed originally by the Transport Road Research Laboratory for investigations into urban surface road runoff (Watkins, 1962). It is a prefabricated concrete structure and was originally calibrated by Kent instruments in the early 1950's but refurbished and recalibrated by the Middlesex Polytechnic Urban Pollution Research Centre in 1980 (Harrop, 1984a; Ellis et al, 1986b).

4.3 Sampling Strategy.

Discrete samples of all bulk sediment types were collected in order that heavy metal concentrations and loadings throughout the highway sub-catchment could be assessed. The source sediments were also investigated for their mineral magnetic characteristics to characterise and "fingerprint" source sediments. Bulk sediment samples were sieved into size fractions such that specific size associations of heavy metals or mineral magnetic parameters could be identified if they existed. Discrete samples of sediments throughout the drainage system were collected to assess if sediments could be traced by their heavy metal levels or mineral magnetic properties. Samples relating to possible input sources of heavy metals and magnetic minerals were also investigated in an attempt to trace the dominant input source in the non-industrialised urban environment. These included atmospheric inputs, vehicular sources, constructional materials and litter.

Stormwater suspended solids were sampled at the sub-catchment and main catchment outfalls to assess the possibility of using mineral magnetic parameters to type sediments over storm events and to allow the calculation of heavy metal loading from the main catchment to the receiving stream. Further bulk sampling was carried out throughout the larger catchment to type further land uses and to investigate the consistency of the results found in the sub-catchment.

4.4 Sediment Sampling Methodology.

Roadside dusts were sampled using vacuum techniques whenever possible. A Shelton J-Vac wet/dry type vacuum cleaner was used, fitted with a 5 µm nylon mesh stretched over the normal drum filter to reduce losses of the fine particles. The importance of the fine particles has been illustrated in Section 2.2.4 where it was seen that heavy metal concentrations increase with decreasing particle size. The collected sample was removed by brushing out the vacuum cleaner barrel with a cleaned nylon brush into a plastic bag. When only wet or damp sediment was available, sampling was carried out using a dustpan and brush to avoid losses due to sticking of the sediment in the pipe of the vacuum cleaner. The drum of the vacuum cleaner was supplied covered with a phenolic epoxy coating which reduced the possibility of sample contamination. Any exposed metal parts were covered by adhesive tape prior to sampling. The use of vacuum techniques has been reported to be highly efficient for collecting particles from street surfaces. A collection efficiency of greater than 95% has been reported for this technique (Pitt, 1979; Warren 1987) compared to 92% of the particulates for other methods (Warren, 1987).

Samples of road dusts were collected from areas chosen to represent the differing paved surfaces associated with the highway. Pavement samples were collected from a 2 m square area on both sides of Chilwell Gardens. The road centre samples were collected from a centrally located 2 m square area on the road surface of Chilwell Gardens. As the road was approximately 5 m wide it was felt inappropriate to divide it further. Road gutter samples were collected from an area 5 m long and 0.3 m wide, the length being parallel to the kerb. The longtitudinal centres of the sampling areas were points on a transect of the road perpendicular to its central line (Figure 4.2). Other roadside dusts sampled in the larger catchment were collected in a similar fashion.

Surface soil samples were collected using a plastic scoop and placed in plastic bags. Core samples of soil were taken by using 40 mm diameter stainless steel core tubes, the cores being extruded upon return to the laboratory.

Roof sediments collected from the tiled surface were sampled using a pre-cleaned plastic dustpan and brush. The same area of eight tiles was sampled on each occasion. The roof gutter samples were collected using a pre-cleaned plastic scoop and a nylon brush. The same metre length of guttering was sampled on each occasion.

Sub-surface chamber, pipe and sewer sediment samples were taken as grab samples with no attempt to quantify the sample in terms of pollutant loadings. The nature of the sampling environment made it impossible to take a sample over a unit area or a representative unit volume on a repeatable basis. Gully pot samples were taken by use of a "dipper", which initially consisted of a polypropylene beaker attached to a wooden pole. This was later replaced by a commercially produced dipper which consisted of a polypropylene beaker as before but instead of a wooden pole the beaker was attached to a polypropylene covered metal handle. Prior to the sampling scheme being implemented, the gully pots were suction cleaned by Three Rivers District Council. In-pipe samples were collected by scooping up sediment lying in drainage pipes at inspection points with an acid-cleaned plastic scoop.

The sediment samples were oven dried at 40°C for a minimum of 48 hours, depending on the weather conditions when sampling occurred or whether the sample came from the sub-surface drainage system. The low drying temperature was chosen so as not to affect the mineral magnetic properties of the samples. The sediments were then desiccated, weighed and stored to await further analysis. Specific source particulates were also sampled by appropriate methods and these are detailed in Section 7.4.

4.5 Sediment Sample Analysis.

4.5.1 Sediment Pretreatment.

All dust and soil sediments were sieved to remove extraneous particles. A sieve aperture of 1000 µm was chosen as a preliminary separation procedure on the basis that initial sampling revealed identifiable anomalous objects in all fractions greater than 1000 µm; these included sweet papers, can ring pulls, cigarette ends and nails. Previous workers investigating the variation of heavy metals with particle size have used coarse sieves of differing apertures, 500 µm (Duggan and Williams, 1977; Warren, 1987), 600 µm (Harrison et al, 1981), 963 µm (Ferguson and Ryan, 1984), 1700 µm (Rameau, 1972) and 2000 µm (Harrop, 1984). The aperture size selected can be seen to be within the range of the previously used cut off sieve apertures.

In the case of sediments sampled during the first eight months of sampling the sieved sample was divided into two portions according to the total sample weight. From one portion a plastic sample pot was filled and stored awaiting mineral magnetic analysis, and subsequently for heavy metal analysis. The second portion was sieved into fractions. The sieves used were 500 µm, 250 µm, 125 µm, 63 µm, 38 µm and a base collector pan. If the second portion was found to be in excess of 100 g the subsample was quartered and a quarter sieved. Generally it was found that roadside dust samples were dominated by the larger grain sizes and this led to some problems with the sieves of larger aperture being "blinded" by particulates lodging fast in the apertures and thus preventing the passage of finer particles. Reduction of volume of the the sieved sample alleviated this problem but a balance had to be reached in order to provide a sufficiently large fine fraction for analysis. Another drawback with sieving is that it can lead to the break up of sediment by abrasion and collision leading to an artificially inflated weight of fines.

After the first eight month period the samples were only passed through the preliminary sieve (1000 μm) prior to subsamples being taken to fill the plastic sample pots for further analysis.

4.5.2 Mineral Magnetic Analysis.

4.5.2.1 Sample Preparation.

In order to obtain representative determinations several procedures were carried out prior to measurement. The plastic sample containers used for the magnetic analysis were thoroughly acid cleaned as the sediment samples would be later subjected to metal analysis. The sample pots were rinsed three times with deionised water including a 10 minutes wash in an ultrasonic bath. One out of every twenty pots was tested for the presence of mineral magnetic parameters and if significant the batch of twenty were discarded. For samples of low weight or samples suspected to have low values of IRM_{300mT}, indicated by levels of χ that could not be measured, the mineral magnetic parameters of the sample pots were measured prior to placement of the samples in them. If these measurements were found to be significant the pot was discarded. For minor variations from zero the readings for the sample could be adjusted accordingly.

Mineral magnetic parameters are related to magnetic grain alignment in an applied field and therefore it is important that factors such as physical movement of the grain which affect the magnetic grain alignment should be avoided. This was achieved by tightly packing the sediment particles into the sample pots with mineral magnetically inert materials such as cotton wool, paper towelling or polyurethane foam. Both the cotton wool and paper towelling were found to be less reliable in terms of mineral magnetic signal cleanliness than the foam. It was found that the reliability of the foam could be increased by the removal of its external edges immediately prior to use.

4.5.2.2 Magnetic Susceptibility.

Measurements of magnetic susceptibility were carried out using a Bartington Instruments Susceptibility Meter and dual frequency sensor (Plate 4.3). The instrument was zeroed using a cleaned plastic pot filled with foam as a blank and readings of pre- and post- sample measurements of the empty sensor allowed adjustment for drift using one of the following formulae depending on the scale used:

1.0 Scale $k = R_S - (Z_1 + Z_2 / 2)$

0.1 Scale $k = ((R_1 + R_2) - (Z_1 + Z_3)) / 2$

where k is volume susceptibility
R_S is susceptibility reading for a sample on scale 1.0.
R_1 is second susceptibility reading after placement of sample in sensor
R_2 is third susceptibility reading after placement of sample in sensor
Z_1 is susceptibility reading prior to placement of sample in sensor
Z_2 is stabilised susceptibility reading after removal of sample from sensor
Z_3 is second susceptibility reading after removal of sample from sensor

A 10 mT alternating magnetic field is produced by the sensor. The operating frequency of the alternating field is either 0.47 kHz or 4.7 kHz. The frequency is selected prior to determination of susceptibility of a sample. The selected frequency is modified by the placement of a sample within the sensor and the resulting change in frequency is converted to a reading of magnetic susceptibility. The range of determination of volume susceptibility by the instrument is 0.01 to 125.65. The measurement period of the sensor was 1.1 seconds.

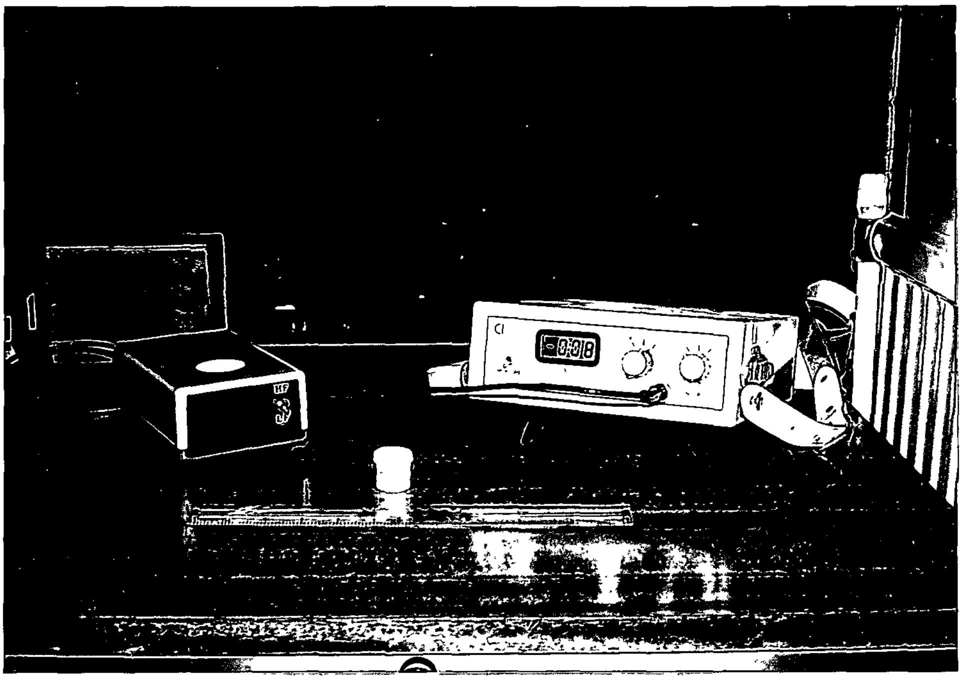


Plate 4.3 Bartington Instruments Susceptibility Meter.

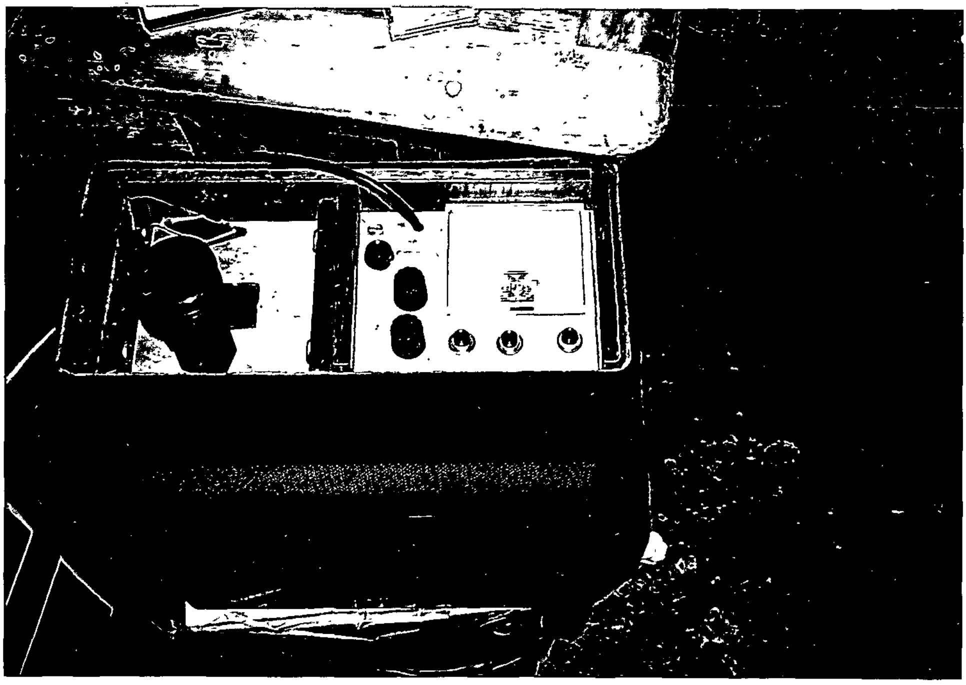


Plate 4.4 Molspin Pulse Magnetiser.

4.5.2.3 Isothermal Remanent Magnetisation (IRM).

IRM was induced using a Molspin Pulse Magnetiser generating a uniform field of 300mT over the full volume of the sample (Plate 4.4). The resulting IRM was measured on a portable Minispin fluxgate magnetometer (Plate 4.5). Readings from the magnetometer were corrected for weight by division of the reading by the sample weight, and were corrected for shape alignment within the meter by multiplication of the reading by 12.9 (Oldfield *pers comm*). "Reverse field" or "back field" IRM measurements were made after measurement of the initial IRM_{300mT} and subsequently placing the sample in the pulse magnetizer in reverse fields of 20 mT, 40 mT, 100 mT and 200 mT, and measuring the IRM at each stage. All IRM measurements were carried out using facilities located in the Department of Geography, University of Liverpool (Plate 4.6).

4.5.3 Heavy Metal Analysis.

4.5.3.1 Digestion Technique.

There are many acid digestion techniques for heavy metal analysis that have been cited in past research and most of these involve heating the samples with concentrated acids, such as sulphuric, hydrochloric and nitric acids. In the selection of an appropriate digestion method several factors were considered, including comparability to other work, ease of method, time of method, safety and expense. Use of hydrofluoric acid was ruled out, particularly on the grounds of safety factors and the time involved per sample analysed.

It has been observed that digestion methods that include the use of sulphuric acid give rise to anomalously low results for Pb (Davis and Carlton Smith, 1983; Tinsley et al, 1983) and this has been suggested to be due to the formation of insoluble salts (Tinsley et al, 1983) and co-precipitation of Ca and Pb sulphates (Davis and Carlton Smith, 1983). The accurate analysis of Pb was important to this research and therefore methods utilising sulphuric acid were not considered to be appropriate.

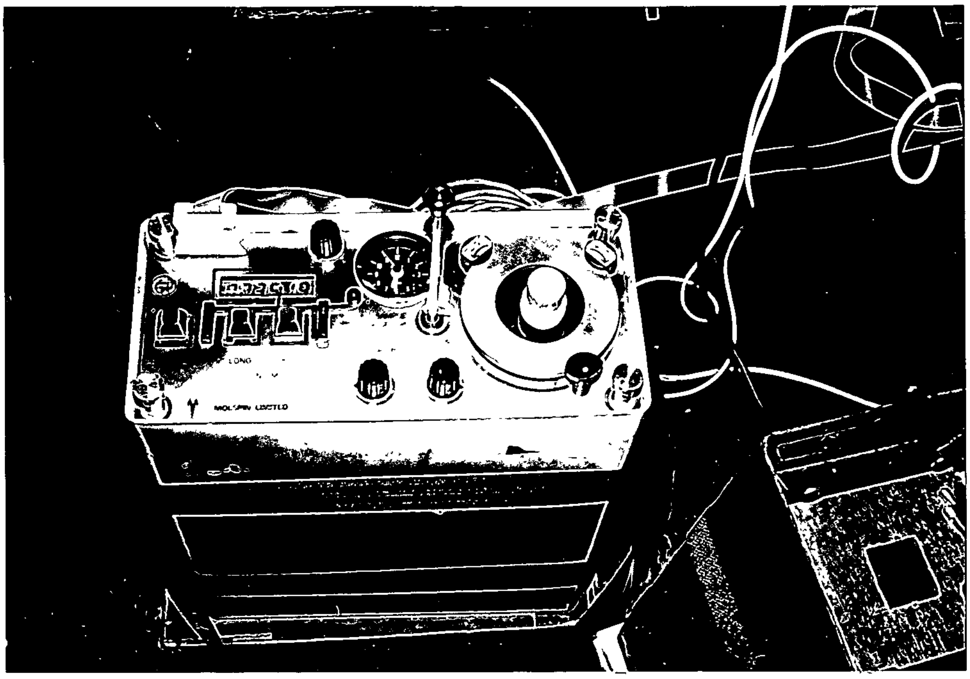


Plate 4.5 Minispin Fluxgate Magnetometer (Sample in raised position prior to measurement).

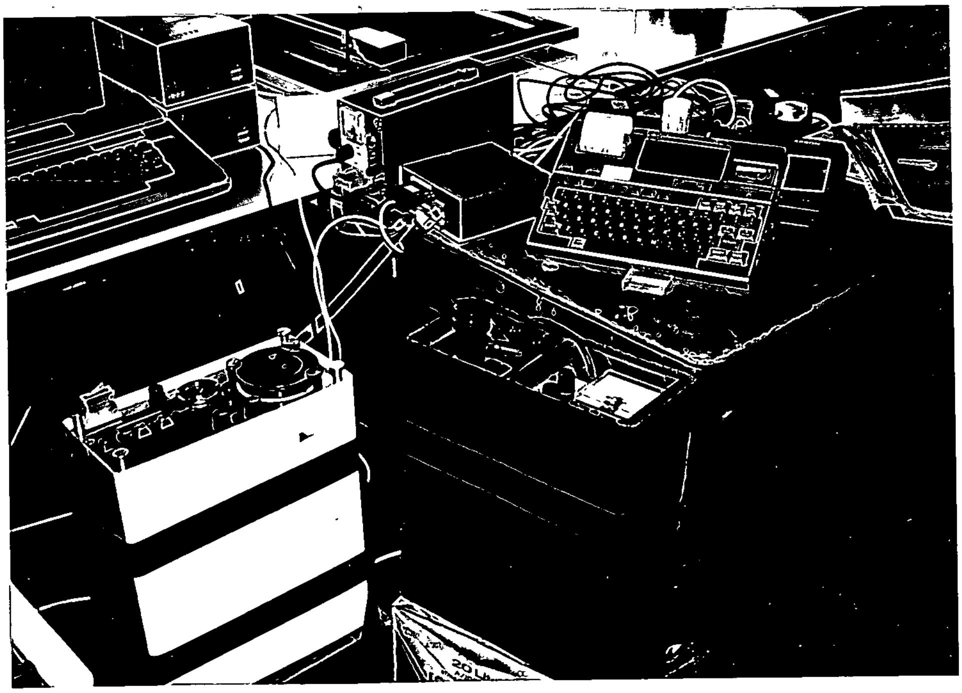


Plate 4.6 Work Station at Department of Geography, University of Liverpool.

Tinsley et al (1983) have compared a number of extraction techniques and produced a statistical ranking of the methods. Discounting those digestions involving sulphuric acid, concentrated hydrochloric acid and 2M nitric acid were ranked as preferable methods. The use of a nitric/perchloric acid mixture in a 3:2 ratio has been found to yield accurate results for fly ash when compared to US National Bureau of Standards results for analysis of a standard material (Stolzenburg and Andren, 1980).

Comparisons of extraction efficiencies of the different methods have been made. Veneman et al (1982) found that in the analysis of orchard soils, a combination of nitric-perchloric acids proved more efficient for the extraction of Pb than nitric or hydrochloric acids used individually. In an inter-laboratory comparison of metal determinations in sewage sludge and soil it was found that the greatest extraction of Ni, Pb and Zn was acheived by a nitric-perchloric acid combination as opposed to nitric acid individually or a nitric acid-hydrogen peroxide combination. The latter technique was, however, found to produce highest results for Cd (Davis and Carlton Smith, 1983). For Cu, the nitric-perchloric acid combination was found to be the least effective of the three methods (Davis and Carlton Smith, 1983).. Ahl and Lindevall (1977) found that nitric acid was more efficient individually at extracting Cu from marine sediments than in combination with perchloric acid. The combination, however, proved to be more satisfactory for Mn and Zn, and comparable for the extraction of Fe. Krishnamurty et al (1976) found that results from a method using a combination of nitric acid and hydrogen peroxide gave good agreement with published results for US National Bureau of Standards Standard Reference Materials and also gave satisfactory precision.

From the published data it appears that digestion of samples with concentrated nitric acid alone, and in combination with other reagents is a common and satisfactory method for heavy metal analysis. In order that a method could be decided upon prior to the commencement of a major sampling programme a comparison of three digestion methods utilising nitric acid singly and in combination with other reagents was carried out. In all cases AnalaR grade reagents were used.

1) Concentrated Nitric Acid (HNO_3):

Approximately 2.5 g of road dust was weighed into a 100 ml beaker and 30 ml of concentrated nitric acid was added. The beaker was then placed on a sand bath and heated almost to dryness. 30 ml of 0.1 M nitric acid was added and the beaker warmed for 30 minutes. The contents of the beaker were filtered through a Whatman No. 54 filter paper into a 100 ml volumetric flask. The residue was washed with further amounts of 0.1 M nitric acid and the filtrate was made up to 100 ml and analyzed by atomic absorption spectrophotometry.

2) Nitric Acid - Hydrogen Peroxide (H_2O_2):

Approximately 0.5 g of road dust was weighed into a 100 ml beaker, 10 ml of concentrated nitric acid was added and the beaker covered by a watch glass prior to being warmed on a sand bath for 2 hours. The beaker was allowed to cool before 3 ml of 30% H_2O_2 was added dropwise to the extraction mixture. Heating was continued for 1 hour with intermittent swirling of the beaker. The cooled digestate was filtered through a Whatman No. 54 filter paper into a 50 ml volumetric flask. The residue was washed with deionised distilled water until the filtrate was made up to 50 ml and this was then analyzed by atomic absorption spectrophotometry.

3) Nitric Acid - Perchloric Acid ($HClO_4$):

Approximately 2.5 g of road dust was weighed into a 100 ml beaker and 27 ml concentrated nitric acid was added. 3 ml $HClO_4$ was added and the beaker was heated on a sand bath until the beaker contents were almost dry. The beaker was cooled and 30 ml of 2% hydrochloric acid (HCl) was added and the beaker warmed for 30 minutes. The digestate was filtered through a Whatman No. 54 filter paper into a 100 ml volumetric flask. The residue was washed with deionised distilled water and the resulting filtrate (100 ml) analysed by atomic absorption spectrophotometry.

The three digestion methods were used in the analysis of two different road dust samples, one sampled from the hard shoulder of the M1 motorway (Sample 1), the other from a major trunk road in North London (Sample

2). Six replicates of dust sample 1 and four of sample 2 were digested. The results of the comparison of these digestion methods are given in Table 4.2.

The results of the comparison were subjected to statistical testing to establish whether any significant difference between the means and distribution was present. Analysis of variance indicated no such significant differences existed except for the Cu analyses of Sample 1. The Cu analysis results for the $HNO_3:H_2O_2$ technique are significantly lower than those of the other two methods. despite the fact that such a variation did not recur with sample 2. This, combined with the fact that H_2O_2 is known to be relatively unstable and therefore the reagent can be affected by storage conditions ruled out this method. The lack of significant variation between the other two methods did not discriminate between their applicability. The HNO_3 method is a simpler procedure but the $HNO_3:HClO_4$ method was adopted as it is known to be efficient for samples with high organic contents (Cantle, 1982; MAFF, 1985). This is particularly relevant to gully pot samples which have a high organic content due to the leaves which collect in the catchpits. The smaller sub-catchment of Chilwell Gardens is lined with trees and during Autumn substantial leaf fall contributes to the total sediment mass. A similar method, utilising $HNO_3:HClO_4$, has been used by Warren Spring Laboratories for airborne particulate analysis (Rogers et al, 1983). Analysis of airborne particulates is encompassed in this research and is reported in Section 7.1. It was, therefore considered that the $HNO_3:HClO_4$ was likely to be the most suitable method.

Further testing of the $HNO_3:HClO_4$ method was carried out by comparing results when the digestate was either filtered or centrifuged. In order that the digestate could be centrifuged the digestion was carried out in a large centrifuge tube (approximately 130 ml) instead of a beaker. After the addition of 2% HCl the tube was warmed and then centrifuged at 4500 revolutions per minute for 15 minutes and the supernatant poured into a 100 ml volumetric flask. A further 30 ml of 2% HCl was added and centrifuging repeated after warming. The supernatant was made up to 100 ml with deionised distilled water.

Table 4.2 Results of Comparison of Acid Digestion Methods.

	Cd (µg g^{-1})	Cu (µg g^{-1})	Fe (mg g^{-1})	Pb (µg g^{-1})	Mn (µg g^{-1})	Zn (µg g^{-1})
SAMPLE 1 (M1)						
HNO_3						
Range	1,7-2,6	99,1-121,8	28,0-31,6	1498,6-1598,2	671,1-739,4	502,8-532,7
Mean	2,2	109,8	29,3	1529,3	703,1	511,3
$HNO_3:HClO_4$						
Range	1,7-3,6	98,3-126,3	28,6-30,0	1504,8-1547,2	651,8-732,4	486,1-531,5
Mean	2,6	115,4	29,5	1532,8	702,2	507,6
$HNO_3:H_2O_2$						
Range	1,1-2,7	74,9-94,2	27,6-29,8	1457,3-1539,7	641,3-710,1	459,8-524
Mean	2,0	85,4	28,7	1502,3	686,0	496,1
F-value	1,8	17,8	1,3	1,7	0,8	1,1
99% critical F-value: 6,36						
SAMPLE 2 (A41)						
HNO_3						
Range	1,1-2,3	91,3-99,4	20,8-22,8	1351-1417,1	748,1-783,3	485,2-515,1
Mean	1,6	96,7	21,49	1384,2	763,0	500,3
$HNO_3:HClO_4$						
Range	1,4-2,6	83,2-119,7	20,0-22,6	1264-1387	711,2-796,1	508,7-545
Mean	1,8	100,2	21,5	1338,7	748,6	524,2
$HNO_3:H_2O_2$						
Range	2,0-2,4	83,8-112,2	19,9-22,5	1350,8-1455,8	755,6-786,8	469,4-504,6
Mean	2,2	99,7	21,09	1390,7	769,6	494,0
F-value	2,2	0,1	0,2	1,4	0,8	4,2
99% critcial F-value: 8,02						

The comparison involved the digestion of two road dust samples, one from the M1, sample 1 in the previous comparison, and road dust collected from the same major road in North London (Sample 2 as previously) but which was collected on a different occasion. Four replicates were performed on the latter, and six on the former. The results are presented in Table 4.3.

There is no significant difference between the two methods in terms of mean values (Table 4.3). The standard deviation about the mean, however, is greater for all metals, except Cd, for filtered compared to centrifuged digestates. The method of digestion adopted was therefore that which incorporated the use of HNO_3 and $HClO_4$ followed by centrifugation of the digestates as it was thought this would lend itself to comparison with other work and also give greater precision of results.

The same digestion procedure was adopted for all collected sediment samples. Replicate digestions were carried out for the majority of samples. In some cases the total weight of a subsample was less than 0.1 g. This was often found to be the case with the finer sieved fractions i.e. 63 μm and less. The analysis of such a small sample by first splitting into replicates would result in a digestate of low metal concentration, possibly close to the detection limits of the spectrophotometer. This would make accurate determinations of concentration more difficult owing to background interferences. For this reason with subsamples of low weight the total amount of sediment was digested and the digestate volume was limited to 25 ml.

4.5.3.2 Atomic Absorption Analysis.

Heavy metal concentrations for the majority of samples were determined by conventional atomic absorption spectrophotometric analysis. Atomic absorption spectrophotometry is a versatile and sensitive analytical technique which is widely used for trace metal analysis.

Analysis of samples was carried out on a Pye Unicam SP2900 instrument.

Table 4.3 Results of Heavy Metal Analyses using Filtration and Centrifuge Techniques.

	Cd (μg g^{-1})	Cu (μg g^{-1})	Fe (mg g^{-1})	Pb (μg g^{-1})	Mn (μg g^{-1})	Zn (μg g^{-1})
<u>SAMPLE 1 (M1)</u>						
<u>Filtration</u>						
Range	2,6-4,1	93,4-129,8	28,6-31,1	1327,8-1593,0	648,7-750,5	443,1-531,9
Mean	3,3	105,8	29,6	1521,1	705,8	505,2
S,D,	0,6	13,9	0,9	100,0	38,1	31,7
<u>Centrifuge</u>						
Range	1,7-3,6	98,3-126,3	28,6-30,0	1504,8-1547,2	651,8-732,4	486,1-531,5
Mean	2,6	115,4	29,51	1532,8	702,2	507,6
S,D,	0,7	10,8	0,5	18,5	29,7	19,1
t-value	1,8	1,2	0,1	1,3	0,2	0,1
Significant t-value; 2,23						
<u>SAMPLE 2 (A40)</u>						
<u>Filtration</u>						
Range	1,9-3,5	146,4-157,7		1684,2-1796,8		532,0-564,9
Mean	3,0	152,3		1735,3		546,5
S,D,	0,7	4,6		46,6		13,7
<u>Centrifuge</u>						
Range	2,9-3,4	146,9-154,6		1744,2-1805,2		532,1-555,7
Mean	3,2	150,4		1783,8		547,3
S,D,	0,2	3,6		27,1		11,1
t-value	0,5	0,6		1,6		0,1
Significant t-value; 2,45						

Acetylene-air flame atomic absorption procedures were used (Pye Unicam, 1980) with a single slot burner. The instrumental settings were restricted to a slit width of 0.4 nm and a burner height of 10 mm. Determinations of over-range concentrations were therefore achieved by dilution or in the case of Fe by the selection of a less responsive wavelength. The following wavelengths were used; Cd (228.8 nm), Cu (324.75 nm), Fe (248.3 nm and 386.0 nm), Pb (217.0 nm), Mn (279.48 nm) and Zn (213.86 nm).

The instrument was calibrated using freshly prepared standard solutions, made up from stock solutions to the appropriate required concentrations. The stock solutions were diluted with 2% HCl such that the calibration solutions would be subject to similar matrix interferences to the sample solutions analysed.

The calibration curves become increasingly curved at high concentrations therefore standards were used such as to give a visually straight line when plotted, and samples diluted so that concentrations could be read off this portion of the calibration curve. A Hewlett Packard data centre compatible with the Pye Unicam SP2900 was used to convert absorbances to concentrations rather than by reading from the plotted curve. For Zn the segment of the calibration curve that consisted of a straight line was limited and in this case the data centre was used to produce a curve of best fit. Values were cross checked against the plotted graph and any anomolous readings repeated with a diluted sample.

4.6 Atmospheric Particulate Sampling.

4.6.1 Sampling Methodology and Pretreatment.

In order to ascertain the contribution of atmospheric particulates to heavy metal and magnetic mineral concentrations in the catchment, an atmospheric sampling station was set up on an exposed section of the flat roof of the South Oxhey Community Centre, which is situated directly to the the east of the sub-catchment. The sampling station was approximately 60 m from the road.

Samples of airborne particulates were collected by drawing air through a pre-weighed Millipore MF-Type membrane filter (47 mm diameter; 0.8 μm nominal pore size) using a low volume Casella pump. The volume sampled was measured directly on a UGI gas meter. The average flow rate was approximately 2 l minute^{-1}. The filter was mounted in a Millipore 47 mm polycarbonate sampling head, which in turn was mounted in a vertical face down position approximately 1.5 m above the roof surface and protected by an inverted funnel so as to prevent contamination by rainfall. Millipore filters were used as they have been shown to have low metal content and are "clean" with respect to mineral magnetic parameters. The filters were dried at 40°C and then placed in a desiccator while they cooled to room temperature. The weight of airborne particulates was then determined using an Oertling Analytical balance to accurately weigh the filter and particulates correct to four decimal places.

Total bulk deposition was collected in acid cleaned plastic bottles attached to a plastic funnel which was covered with a plastic grid of aperture 5 mm. This grid was used to prevent contamination by large wind blown particulates such as leaves and to prevent the ingress of insects. The bottle and funnel were mounted in an upright position 1.5 m from the roof surface. The sample was collected as soon as possible after a rainfall event and returned to the laboratory for filtration and analysis. Atmospheric particulates were filtered out by passing the sample through a pre-weighed Millipore membrane filter (47 mm diameter; nominal pore size of 0.45 μm). The filters were supported in an acid cleaned specially designed plastic filtration unit and the volume of filtrate was recorded after filtration.

The filter containing the collected atmospheric particulates was placed in a previously acid washed and triple rinsed plastic sample pot and then dried in an oven at 40° C for 48 hours. The sample pots containing filter and collected atmospheric particulates were placed in a desiccator overnight and the filter and atmospheric particulates weighed. The use of the plastic pots in the drying process meant that the filter dried in such a position that it fitted the pot. The sample pots were marked and stored safely in a sealed container until they were analysed for mineral magnetic parameters.

Rainfall volume was measured directly from the volume collected in the bulk deposition bottle and additionally by a Rimco autographic raingauge. The raingauge was situated on the roof surface and was linked to a data logger by a short length of two-core cable. All data was logged onto ferric oxide tape casettes on a Microdata event recorder, the data interval selected being 30 seconds. The data recorded was processed as described in Section 4.8.

4.6.2 Mineral Magnetic Analysis.

Mineral magnetic analysis of suspended sediments was limited by the weight of material collected. As the weight of sampled particulates was typically between 0.0003 g and 0.02 g, susceptibilty readings could not be carried out with any reliability. The use of the plastic sample pots similar to those used for mineral magnetic analysis of soil and dust samples meant that the analysis for IRM_{300mT} and backfield ratios was carried out in an identical manner to that of low weight soil and dust samples. The only difference was that the suspended sediment samples were not packed down with inert foam. However, the drying of the particulates onto the filter and the drying of the filter within the pot meant that little or no movement occurred in the sample during analysis for mineral magnetic parameters.

4.6.3 Heavy Metal Analysis.

4.6.3.1 Digestion Technique.

The filters were digested in a similar manner to the digestion of soil and dust samples, however, owing to the low weights of collected particulates AristaR grade reagents were used. A filter was placed in a centrifuge tube and 9 ml AristaR concentrated nitric acid and 1 ml AristaR perchloric acid was added. The centrifuge tube was heated on a sand bath until the filter was totally dissolved and the contents had reduced to less than 1 ml. The tube was cooled and 10 ml of 0.1M HNO_3 was added. The use of 0.1M HNO_3 rather than 2% HCl, as used in the previous methodology for sediments, was to avoid the presence of chlorides which could cause interferences in determination of metals by anodic stripping voltammetry. The use of anodic stripping voltammetry was necessary as the concentrations in the digestate were normally below those determinable by flame atomic absorption spectrophotometry. The centrifuge tube was warmed after the addition of the 0.1M HNO_3 and subsequently centrifuged. This was repeated and then the digestate made up to 25 ml with 0.1M HNO_3.

4.6.3.2 Anodic Stripping Voltammetry.

Anodic stripping voltammetry is an electrochemical technique that can be used for the determination of concentrations of metals below the detection limits of flame atomic absorption spectrophotometry. This technique can only be applied to a limited range of metals, including Cd, Cu, Pb and Zn. The technique involves the plating of metals present in a sample solution onto the surface of a mercury cathode suspended in the solution. The cathode is kept at a predetermined controlled negative potential for an accurately timed period. The amount of metal plated onto the electrode is proportional to the concentration of metal in solution. The plated metals are then sequentially stripped from the mercury by applying a reversed potential which is both varied and pulsed. The "sweep" of reverse potentials can be adjusted to include those reverse potentials that are characteristic for the metals to be determined. With the mercury now the anode, the metals are stripped at characteristic potentials and a current is passed as each metal is stripped. The current produced is proportional to the amount of metal plated which in turn is proportional to the concentration of the element in the solution. By plotting the peak current against concentration a calibration curve can be drawn up and the metal concentration in subsequent samples determined. The solution is de-aerated by bubbling nitrogen through the solution prior to the determination as the reduction of dissoved oxygen causes interferences. A side effect of this is that the pH is raised due to the removal of dissolved carbon dioxide from the solution. The sample solution must therefore be buffered prior to analysis.

The instrument used in this research was a Princeton Applied Research Model 384 Polarographic Analyser in the differential pulse anodic stripping voltammetry (DPASV) mode.

4.7 Stormwater Sampling Methodology.

4.7.1 Roof Runoff.

Suspended sediments in roof runoff were collected by use of a Warren Jones WJ40 effluent sampler placed at a convenient inspection point in a drain leading from the roof down-pipe to the road drainage system. The sampler is suitable for collecting samples from small diameter sub-surface drains. It consists of a polypropylene container with an inlet protected by a cowling at the front of the sampler. At the top of the container an air flow regulator allows air to leave the sampler and water to enter at a limited rate. The sampler has obvious advantages in that it does not require a power source and can be placed beyond the reach of vandals. The disadvantage is that the sample is a single integrated sample of the first phase of a runoff event and sequencing over a storm event cannot be investigated. In addition the overall sampling period is not known in relation to the rainfall event.

After collection the sample was placed in an acid cleaned pre-washed polypropylene bottle and returned to the laboratory for analysis.

4.7.2 Chilwell Gardens.

Stormwater samples were collected from the surface water drain downstream of all drainage connections from the sub-catchment (Figure 4.2). At the sampling position, a 90° V-notch weir plate has been located by a previous researcher (Harrop, 1984a). The weir housing carries a submersible pump, water level sensor and air reaction dip tube to provide a full sampling and flow rating facility. Three core cabling links the pump and sensor to a pHox multi-parameter water quality monitor located above ground in a custom built instrument cabinet. This equipment was overhauled prior to commencement of this project and it was hoped to use it to measure flow at the weir plate. Flow, together with water quality parameters, is measured when the water level reaches a sensor collar and the instrument is activated. Flow level is measured by the air reaction dip tube linked to two air pump lines, the data being recorded on a Microdata logger. An interface unit allows synchronisation with real time units from logger interface cards. As stated in Chapter 8 problems were experienced with this equipment and flow measurement was not always obtained.

Stormwater samples were collected by use of a Rock and Taylor multipurpose liquid sampler. This was located in an extension of the instrument cabinet housing the water quality monitor. An external float switch was placed in the inspection chamber on the air reaction dip tube of the water quality meter such that it was at the height that both the water quality monitor and the liquid sampler triggered at the same depth of water. The float switch is activated and closes a single pole switch fed from the sampler. Once the water rises and the float switch closes, the sampler is also activated and water is sampled from the small reservoir behind the 90° V-notch weir. Water is drawn up to the sampler by a separately housed peristaltic pump, therefore avoiding contamination by metallic parts of the pump. The period of sampling is set by timers on the unit, one timer relating to the period during which water is drawn up the sampling line and the other relating to the period when the pump reverses and the line is cleared. This avoids cross contamination of samples. The total sampling time is the sum of the time taken for both operations and at the Chilwell gardens catchment was set to 5 minutes. The line is 8 mm polypropylene piping which has been found to be the optimum diameter to overcome cohesive forces both within the water and between the water and the pipe (Roberts, 1985). The water drawn up the line is routed to collection bottles held in racks on the sampler by a distribution mechanism consisting of a control gear and a top plate of 52 funnels in a circular path, 48 of which are connected by tubes to elbows above each bottle. The polypropylene bottles, each with a capacity of 568 ml are held in the sampler in three racks of sixteen. Preparation of the bottles is detailed in Section 4.8.1. The remaining four intake funnels, marked START-PUMP-FINISH, are for testing of the sampler, and lead directly to an outlet. This allows the first sample of a storm to be discarded automatically so that any liquid remaining in the line from previous sampling does not contaminate the storm samples. The sampler completes the sampling cycle and clears the tube that is engaged at the time the float switch opens.

The sampler has a sampling flow rate equivalent to 568 ml in 180-300 seconds and this together with the velocity of the flow being measured will control the maximum particle size sampled. Particles up to 40 μm were sampled consistently by a similar sampling arrangement used by Roberts (1985). The sampling efficiency decreases for the larger fractions with a noticeable reduction for 350 μm particles and an operating maximum for sampled particles of 1000 μm (Ellis pers comm).

4.7.3 Oxhey Flume.

The present research utilised the instrumentation and flow recording housing installed by Harrop (1984a, 1984b) and Morrison (1985) although before this could be reliably operated the flume and related stilling well had to be cleared of accumulated sediment.

The trapezoidal throated flume was originally installed by TRRL and is a type appropriate for accurate gauging of a wide range of discharges (Harrop, 1984a, 1984b). The complete installation consists of a measuring channel, a throat structure, a down stream channel and a stilling well for water level determination. Since its installation, the flume had fallen into disrepair and the subsequent re-commissioning of the structure is detailed by Harrop (1984a, 1984b).

Water level in the flume is measured in a stilling well which reduces the effects of water surface irregularites. The vertical well is connected to the approach channel by an inlet pipe situated 0.06 m below the lowest level to be gauged and which is flush with the approach channel wall. The pipe is at right angles to the approach channel.

The equipment for water level measurement and recording is housed in a cabinet built over the stilling well. Water level is measured by use of a float suspended upon a wire across a pulley system. The float has adequate clearance in the well being at least 0.075 m from all walls; additional depth is provided to prevent the grounding of the float on the well bottom or any accumulations of silt. The float rotates a potentiometer by an intermediate 200 mm circumference pulley. This potentiometer produces a voltage proportional to its angular position, a 360° rotation producing a charge of 3.33 volts. This is equivalent to 200 logger steps and therefore each logger step is equivalent to 1 mm. The potentiometer is continuous such that it can fully rotate as many times as needed and therefore measure the range of water levels required.

In order to overcome problems at the end of the potentiometer track two other potentiometers are driven in a similar manner by the same shaft. The second is a replica of the first but fixed at 180° to the first. The third potentiometer is geared to measure the full level range within one rotation. The output from the three potentiometers are logged on separate channels on a Microdata logger.

The zero-base setting of the flow recording device is equal to zero flow and this is checked by a dip flash unit installed in the cabinet above the well. The unit is accurately levelled into the cabinet with reference to the level of the invert at the throat. A metric metallic tape is attached to a fixed support on the cabinet bench and the tape passes a levelled reference point into the well. Attached to the tape is a broken circuit flash unit which when in contact with water makes a completed circuit, the water connecting the two exposed terminals, and a light indicating the completed circuit. The water level can be calculated by subtraction of the tape length from the height of the unit above the invert, which is 2944 mm.

Water sampling was again carried out by use of a Rock and Taylor multipurpose liquid sampler. The float switch was relocated after the well was cleared out as the screws holding the switch had corroded away. From the original studies conducted by Harrop (1984a, 1984b), the height of the float switch was 64 mm above the base line flow. When relocated it was found to be 74 mm above base line flow. The sampling period set for the current investigation was 6 minutes which includes both filling of the bottles and subsequent purging of the intake line.

4.8 Stormwater Sample Analysis.

4.8.1 Stormwater Pretreatment.

Stormwater samples were collected in polypropylene bottles as detailed in Sections 4.7.1., 4.7.2 and 4.7.3. The bottles were prepared by soaking in an acid bath containing chromic acid for at least 48 hours. Following this the bottles were rinsed out with distilled water and soaked in 20% nitric acid for 24 hours after which they were triple rinsed with deionised water and air dried. The bottles were collected as soon as possible after the sampled storm event; usually within 24 hours of the end of the storm. Upon return to the laboratory, the pH value of the sampled water in each bottle was determined using a Radiometer electronic autocal pH meter, type pHM83. Using an immediate slow filtration technique, a full storm sequence of forty eight bottles could take up to two weeks to filter. The bottles awaiting filtration were therefore kept in a refrigerator at less than 4°C. Suspended sediments were filtered out by passing the sample through a Millipore membrane filter (47 mm diameter; nominal pore size of 0.45 μm). The filtrate was discarded after the volume had been recorded. The filter with the collected suspended sediments was placed in a previously acid washed and triple rinsed plastic sample pot and then oven dried at 40°C for 48 hours. The sample pots containing filter and collected suspended sediments were then treated similarly to the bulk deposition samples, the weight of suspended sediment being calculated and the samples stored for mineral magnetic analysis.

4.8.2 Mineral Magnetic Analysis.

Mineral magnetic analysis of suspended sediments was limited by the weight of material collected. The quantites of suspended sediments collected at the flume were between 0.03 and 0.44 g and between 0.0063 g and 0.16 g at Chilwell Gardens. As in the case of the airborne particulate samples, susceptibilty readings could not be carried out with any reliability on such small sample weights. Use of the plastic sample pots in the filter drying process meant that the analysis for IRM_{300mT} and backfield ratios was carried out in an identical manner to that of airborne particulates (Section 4.6.2).

4.8.3 Heavy Metal Analysis.

The filters were digested in a similar manner to the atmospheric particulates (Section 4.6.3.).The weight of stormwater particulates varied as did the concentrations such that for samples collected at the Oxhey flume heavy metals could be determined using flame atomic absorption spectrophotometry with the exception of Cu which was determined using anodic stripping voltammetry. For the stormwater particulate samples collected at Chilwell Gardens, only Fe and Mn were determined using flame atomic absorption spectrophotometry. Copper, Pb and Zn concentrations were determined using anodic stripping voltammetry.

4.9 Data Collection, Processing and Analysis.

The automatic recording system used in this research was the Microdata Environmental Data Logging System. Rainfall and water level data were recorded on a M200L logger. This records data at predetermined intervals onto ferric oxide cassette tapes. The logger is contained in an aluminium housing with a neoprene seal between the two halves. The lid contains the rechargeable batteries and is connected to the rest of the logger by a lead, din plug and socket. A stepping motor drives the tape transport mechanism and as the tape moves forward the data is written onto the tape. Full details of the installation and use of this and the associated interface units are given in Harrop (1984a; 1984b).

The casette tapes were processed firstly onto paper tape by use of a Microdata translator unit (M200) linked to a 1180 series tape punch DDTM 047. The paper tape was then used to feed the data into a mainframe DEC 10 computer via a LRP - 300 paper tape reader in conjunction with a controller program RDPT8. The data is still in binary format and the data is transformed by use of the Fortran program "Oxhey", as used by Harrop (1984a, 1984b) and Morrison (1985). The data is stored as a data file on the mainframe computer before checking and editing. Further processing for print was carried out by simple basic subroutines in which readings for battery status and large sections of zero readings were edited out.

Full details of the data processing procedures are given in Harrop (1984a; 1984b).

CHAPTER 5 HEAVY METAL LEVELS AND MINERAL MAGNETIC PARAMETERS FOR SEDIMENTS FROM THE CHILWELL GARDENS SUB-CATCHMENT.

5.1 Introduction.

In order that source sediments occurring in an urban catchment could be identified and typed in terms of heavy metal concentrations and mineral magnetic parameters, discrete bulk samples were collected as described in Section 4.3. The main sources of sediment within the Chilwell Gardens sub-catchment consisted of two types of impermeable area; roof surfaces and highway associated surfaces, i.e pavement and road surfaces. In order that the two source areas could be investigated more thoroughly they were split into sub-areas. For the roof surfaces this involved dividing the total area into the tiled roof surface and the guttering, while for the highway associated surfaces, sampling was directed such that pavement, road gutter and central road surfaces could be defined (Section 4.3).

Further sediment samples from intermediate sites throughout the drainage system were also collected, including gully pots and deposits of sediment found within the stormwater drainage pipes.

It was important that the samples be representative of sediment types in terms of both spatial and temporal distribution, as these samples were to form the data base against which stormwater samples were intended to be typed. Spatial distribution was accounted for adequately by selection of appropriate areas over which dust samples would be collected. It was decided that bimonthly sampling over a two year period would be sufficient to allow temporal variation to be taken into account. Sampling took place between February 1983 and December 1984. The time interval between samples would allow a sufficient build up of sediment to take place, while the overall duration would allow anomalous results to be distinguished from seasonal trends.

5.2 Heavy Metals in Sediment within the Chilwell Gardens Sub-Catchment.

The results obtained from the two year sampling programme (1983/4) at the Chilwell Gardens sub-catchment are summarised in Table 5.1. These results indicate that the concentrations of Cu, Pb and Zn are generally higher in sediments associated with the paved surfaces, particularly the road gutter, road centre and the road drainage system, compared to the roof surface and roof drainage sediments. Cadmium concentrations do not appear to vary significantly with sampling location. Iron exhibits higher concentrations in sediments sampled from the roof and roof drainage system, including the end-of-catchment sewer where the roof drainage has joined the road drainage. Manganese generally exhibits similar concentrations at all locations although there is a slight tendency to find lower concentrations in roof gutter and roof drainage sediments.

5.2.1 Heavy Metals in Road and Pavement Sediments.

Comparison of Table 5.1 and Table 2.13 suggests that Cu and Pb concentrations found in the sediments collected from the street surfaces of the catchment are within the normal range of concentrations found in UK street sediments although being slightly lower than the average. This may be due to the fact that the catchment is a low trafficked road and the quoted ranges include highly trafficked roads or roads in the proximity of high traffic densities, such as the A13 (Warren and Birch, 1987), the M4 and A406 (Turner et al, 1980) and the A41 (Hamilton et al, 1984). The Zn concentrations, however, are fairly typical of concentrations found in the other studies cited in Table 2.13. It can also be seen that the values of heavy metals are comparable to previous studies undertaken in the same catchment (Harrop et al, 1983).

5.2.1.1 Spatial Variation of Heavy Metals in Road and Pavement Sediments.

Spatial variation was investigated by comparing the results from samples

Table 5.1 Heavy Metal Concentration Ranges and Means for Sampled Bulk Sediments in the Chilwell Gardens Sub-Catchment.

	Cd (μg g^{-1})	Cu (μg g^{-1})	Fe (mg g^{-1})	Pb (μg g^{-1})	Mn (μg g^{-1})	Zn (μg g^{-1})
Pavement (East*) n=13	0-8.1 (1.7)	35.5-40.4 (43.1)	17.0-29.7 (22.7)	23.0-299.7 (126.8)	483.8-779.5 (620.8)	115.7-292.2 (188.92)
Road Gutter (East*) n=13	0-4.1 (0.7)	32.3-78.6 (49.6)	14.4-31.0 (20.1)	146.6-1075.7 (449.5)	283.3-739.2 (537.1)	141.1-397.1 (263.6)
Road Centre n=13	0-2.4 (0.5)	26.6-190.2 (110.6)	22.3-37.3 (30.1)	295.2-2843.5 (791.1)	330.2-589.8 (436.9)	229.3-849.8 (422.1)
Road Gutter (West†) n=13	0-1.7 (0.7)	36.5-125.3 (61.3)	17.0-29.8 (22.1)	190.3-790.3 (397.7)	302.6-831.4 (516.2)	189.4-456.8 (339.5)
Pavement (West†) n=13	0-5.8 (1.4)	30.5-81.4 (49.6)	12.0-26.2 (21.1)	29.6-162.6 (103.2)	479.1-685.0 (588.0)	131.6-445.3 (244.5)
Roof Surface n=5	udl-2.8 (1.5)	17.3-30.9 (24.2)	30.9-41.0 (34.3)	206.7-480.1 (357.3)	294.1-644.3 (472.8)	300.4-510.4 (387.6)
Roof Gutter n=5	udl-4.6 (1.5)	24.7-33.8 (29.3)	33.2-49.6 (39.9)	279.3-700.3 (470.9)	250.0-468.1 (344.6)	79.7-335.3 (249.5)
In-Pipe n=4 (Roof drain)	udl-5.3 (1.9)	17.2-30.0 (22.6)	28.8-35.3 (31.2)	85.2-438.5 (293.7)	193.3-227.8 (208.4)	74.1-290.5 (198.5)
Gully Pot (East) n=6	1.4-4.7 (2.51)	39.2-87.6 (56.7)	11.5-23.1 (15.98)	217.4-1448.3 (644.3)	285.7-443.0 (349.4)	286.4-800.9 (431.7)
Gully Pot (West) n=6	0-3.4 (2.1)	38.0-101.2 (61.0)	12.8-27.5 (18.78)	242.6-654.9 (471.7)	244.2-502.1 (351.6)	282.6-616.9 (440.5)
In-Pipe (Gully drain)	3.1	68.7	26.1	474.7	734.4	393.9
In-Pipe (Combined drain)□ n=6	0.5-3.2 (1.6)	13.0-130.9 (65.4)	22.9-43.8 (32.6)	235.6-908.5 (465.4)	346.9-590.8 (434.4)	320.9-499.8 (404.3)

Mean values in parentheses udl - under detection limit

* - East refers to Community centre side of the road (Figure 4.2)

† - West refers to Housing side of the road (Figure 4.2)

□ - Drainage point of catchment below the confluence of roof and road drainage taken from the differing sampling areas along the transect perpendicular to the road (Table 5.1). The overall mean values for Cd suggest that there is a pattern of decreasing Cd concentrations towards the road centre. The highest Cd concentrations were found in pavement sediments although this was not the case in every sample set collected, i.e. in every set of samples collected from across the transect (Figure 5.1). This may reflect a predominantly random distribution of the metal, although it may also be a result of working close to the analytical detection limits for this metal.

Copper, Pb, and Zn concentrations increase from the pavement to the road gutter with a further increase in the road centre sediments (Figures 5.2, 5.4, 5.6). Lead exhibit this trend most markedly as it is consistently shown by each set of bimonthly samples (Figure 5.4). The same pattern is observed for Zn in over half the sample sets collected (Figure 5.6). In those sample sets where all five samples of the set did not conform to this trend. It was found that there was only one aberrant Zn concentration. In the case of Cu the pattern of concentrations across the transect is less marked, although still recognisable (Figure 5.2). For Cu, Pb and Zn the mean concentrations confirm these overall trends (Figure 5.7).

The concentrations found in samples on either side of the roadway for a particular metal were not always equally balanced (Table 5.1). Statistical analysis using "Students t-test" indicates no significant differences between the means of the Fe and Pb concentrations for either pavement or road gutter sediments at the 5% level of significance. However for Cu, there is a significant difference between the means of the pavement sediments on either side of the road and for Zn there is a significant difference between the means of both road gutter and pavement sediments on either side of the road. Copper values on the west side of the roadway tend to be greater than those on the east, both in terms of overall mean and range of road gutter and pavement sediments. Zinc concentrations in paved surface sediments are also biased towards the west side. The difference in concentrations may reflect the presence of parked cars which are often found on the west side outside the houses but rarely on the east side. This may result in an extra input of heavy

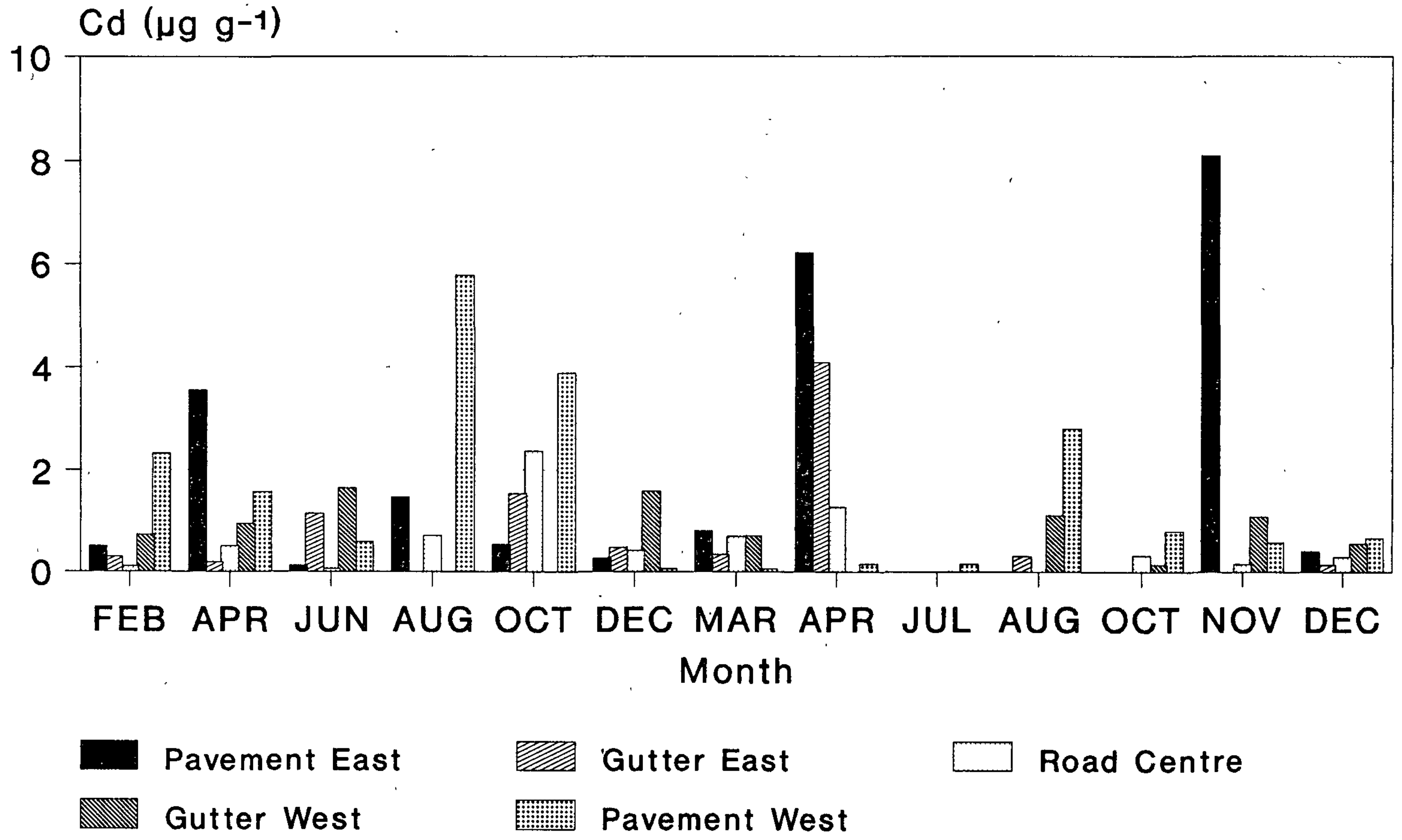


Figure 5.1 Temporal Variations in Cadmium Concentrations in Highway Associated Sediments.

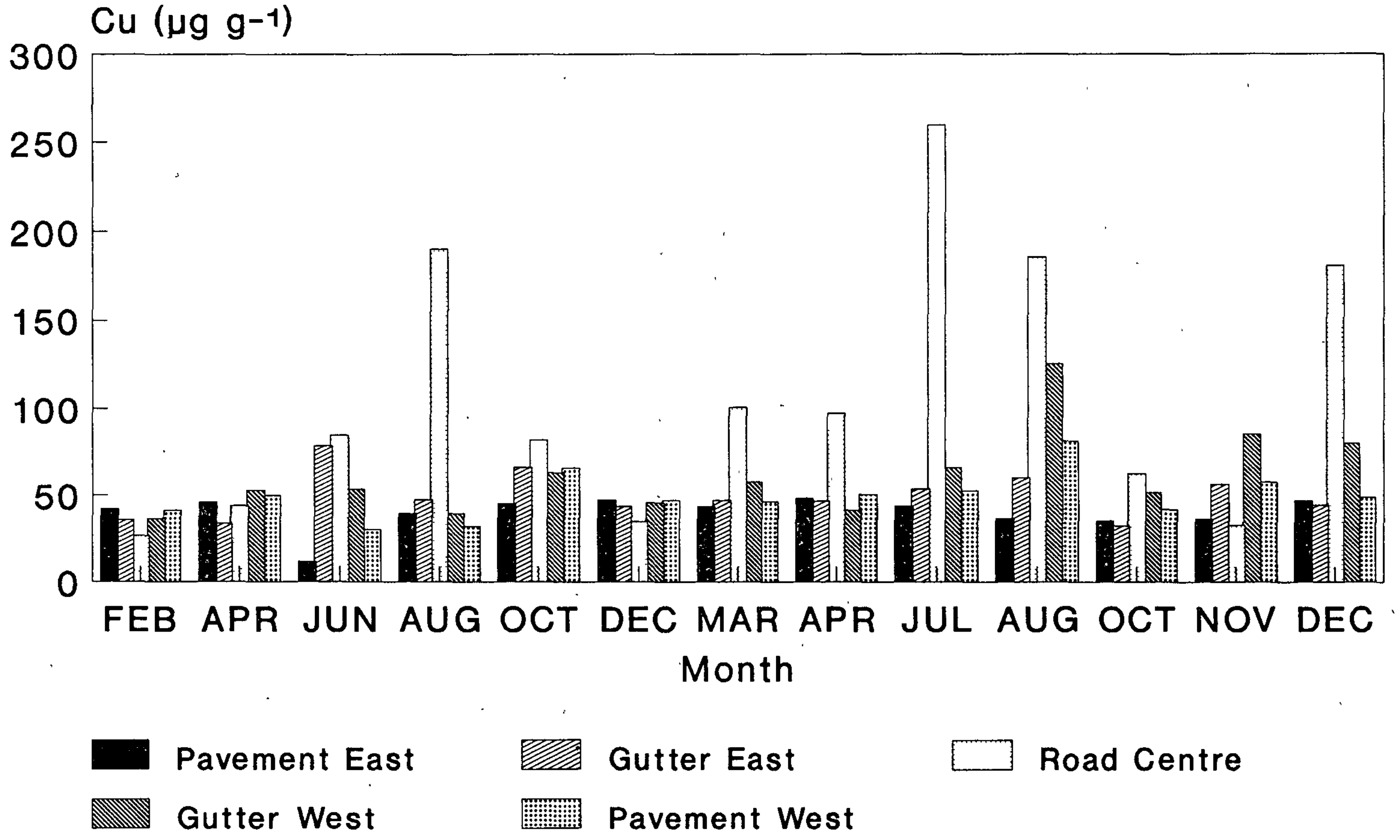


Figure 5.2 Temporal Variations in Copper Concentrations in Highway Associated Sediments.

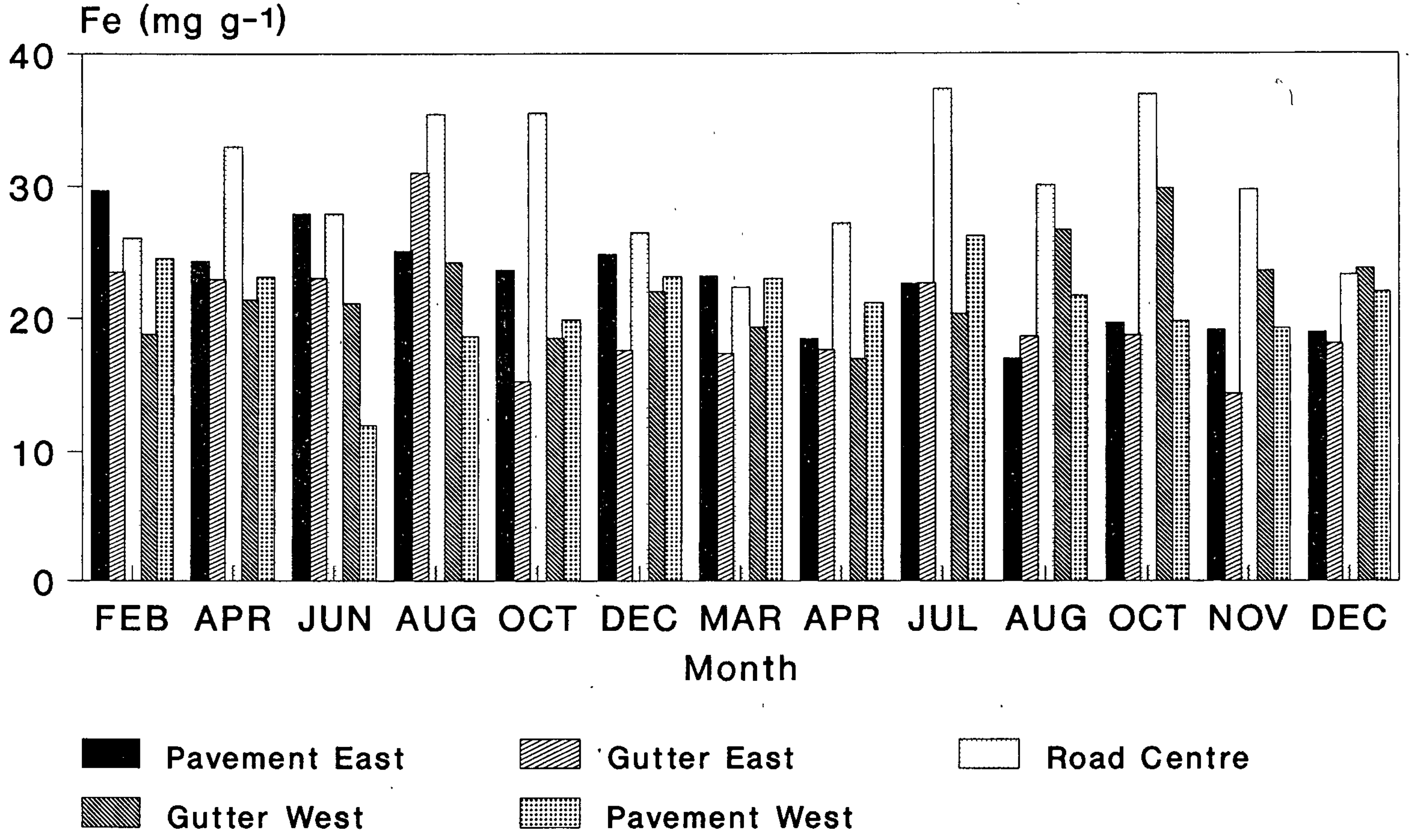


Figure 5.3 Temporal Variations in Iron Concentrations in Highway Associated Sediments.

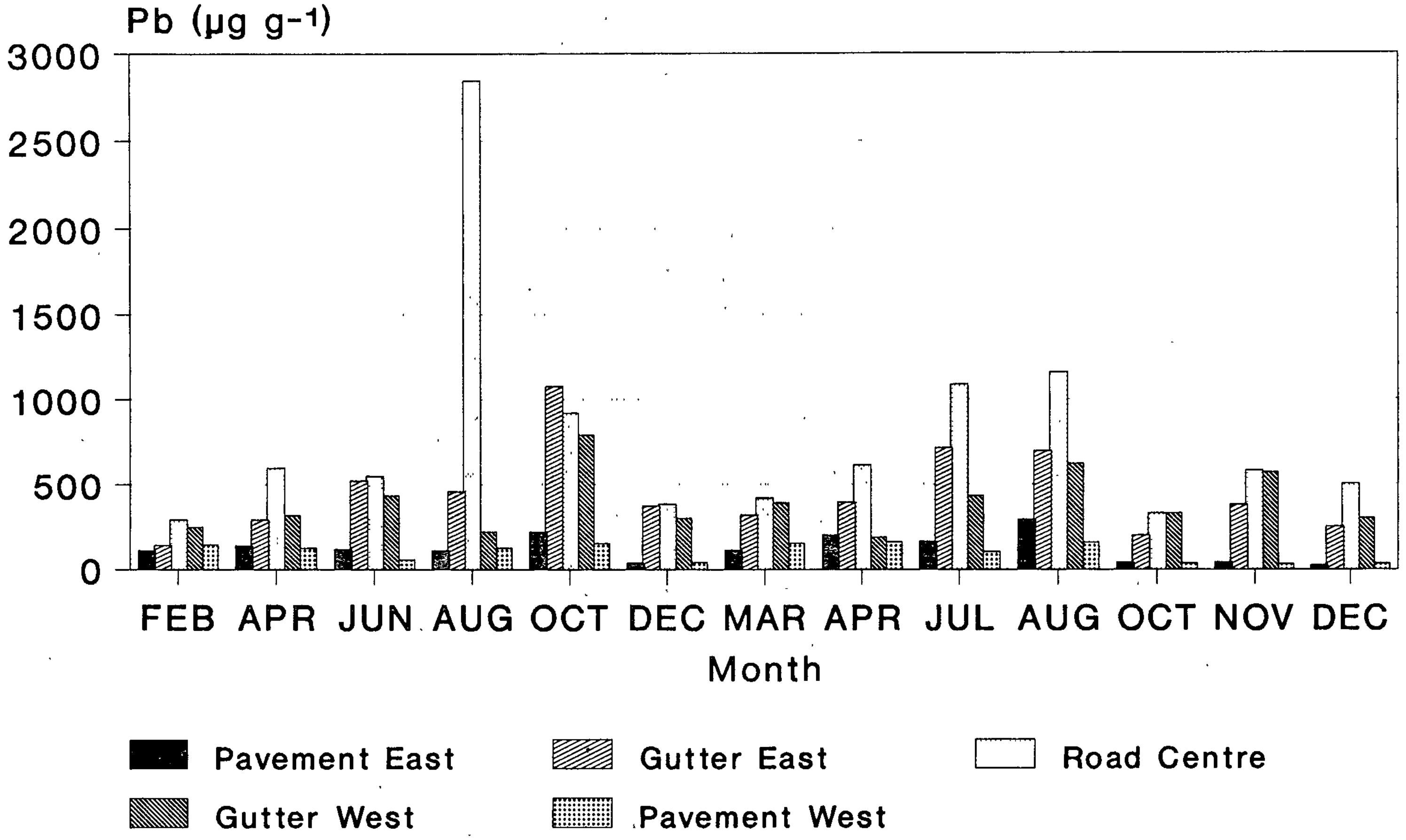


Figure 5.4 Temporal Variations in Lead Concentrations in Highway Associated Sediments.

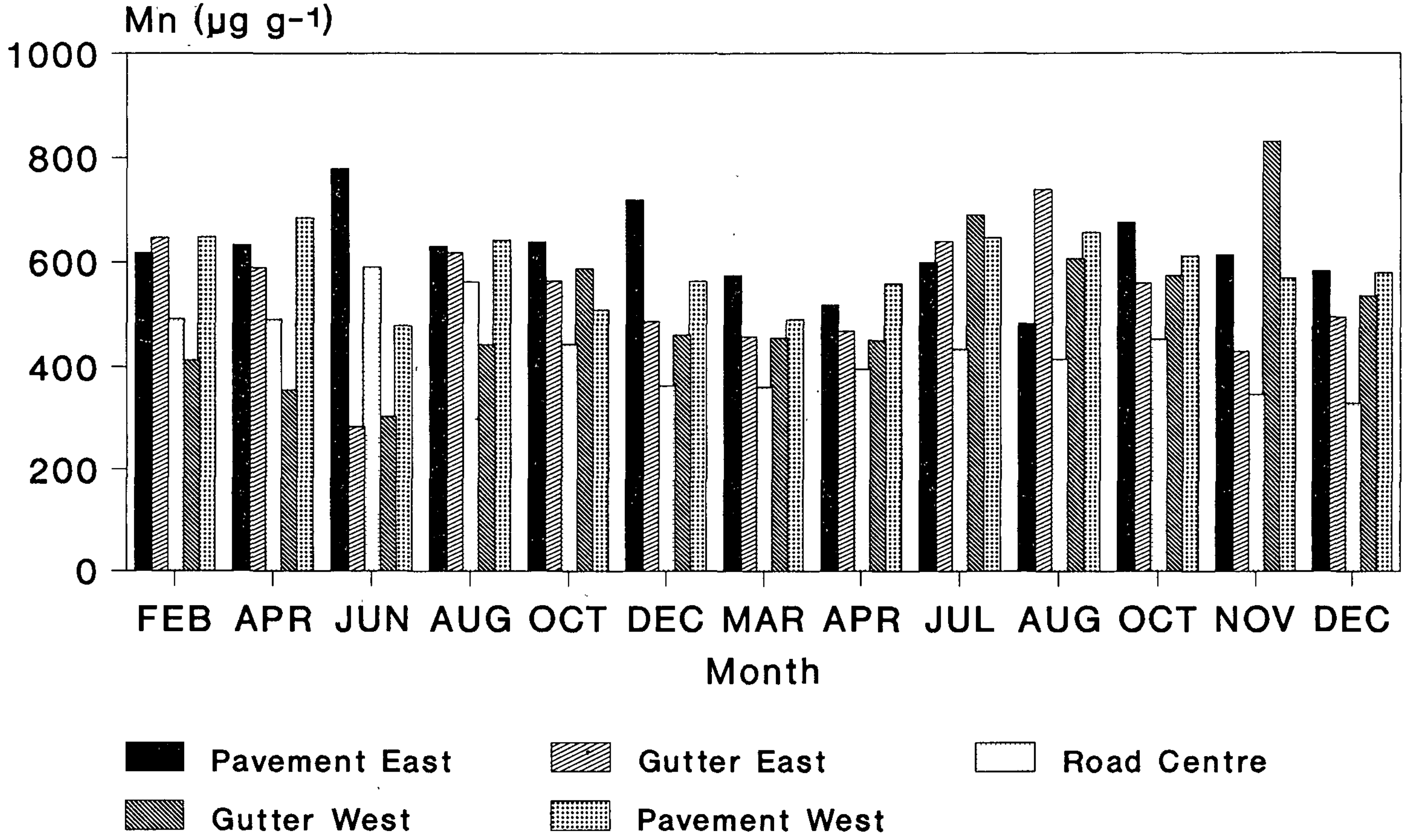


Figure 5.5 Temporal Variations in Manganese Concentrations in Highway Associated Sediments.

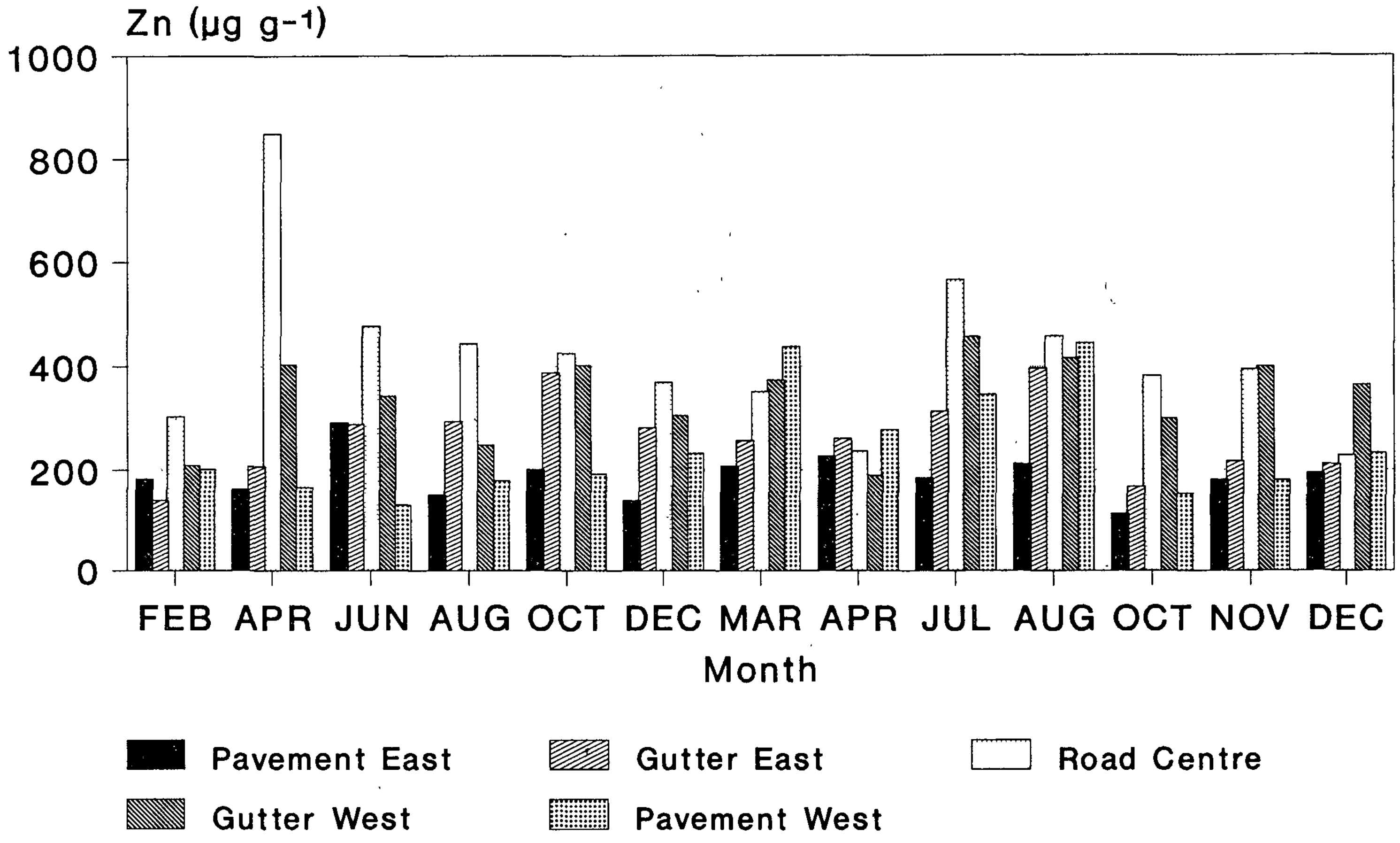


Figure 5.6 Temporal Variations in Zinc Concentrations in Highway Associated Sediments.

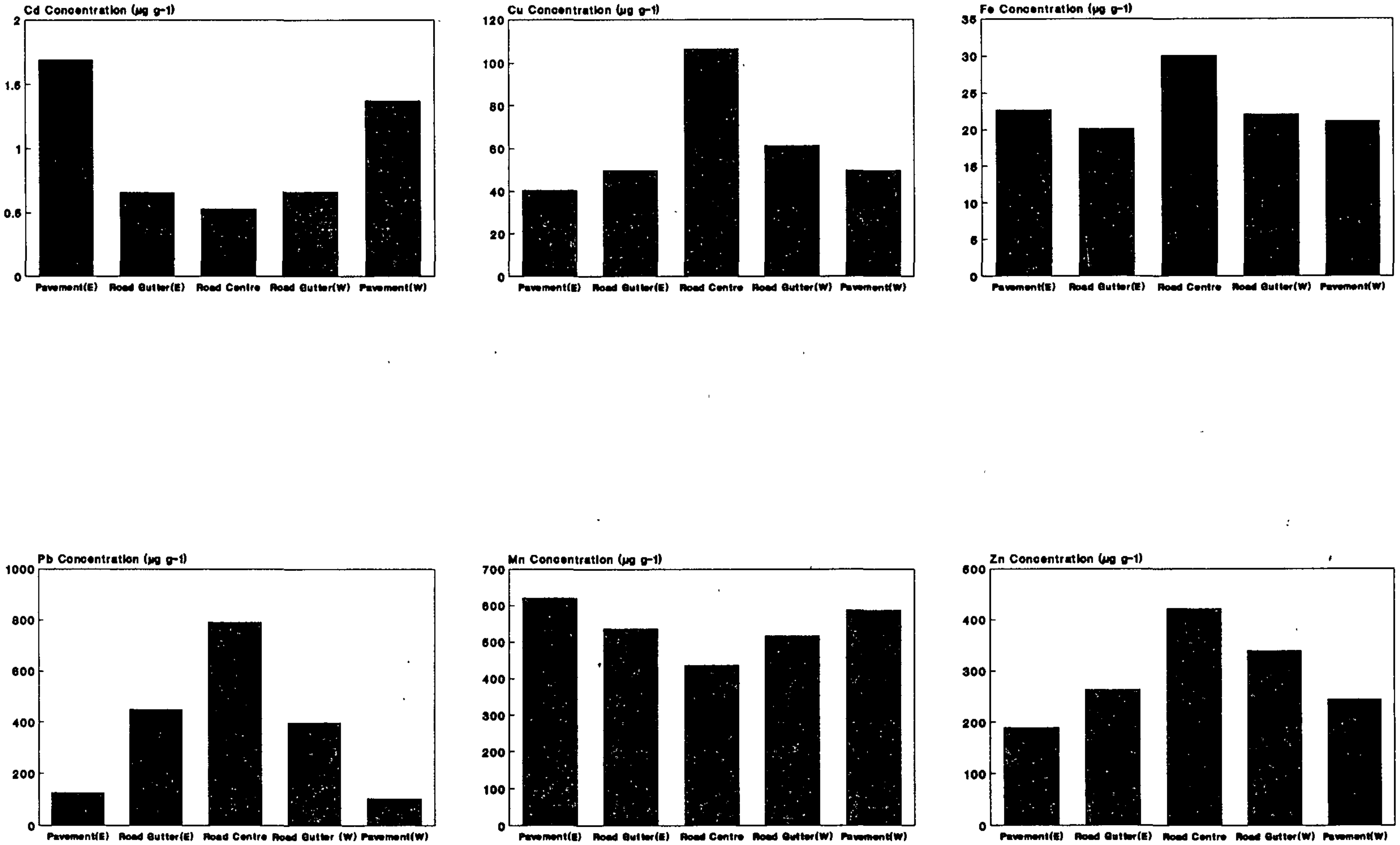


Figure 5.7 Mean Heavy Metal Concentrations in Highway Associated Sediments.

metals from maintenance practises and sump drippage, or from corrosion and attrition products released from the parked cars onto the road surface. The effects of resuspension and deflation of particulates would also be decreased.

Comparison of the concentrations of Pb found in paved surface sediments on the east and west sides of the road centre reveals a reversed pattern to that of Cu and Zn, although statistically this can be accounted for by the variation between samples. Given that the metals are likely to occur from a similar source, this suggests that different processes may affect metal distribution, such that products containing predominantly Cu and Zn are concentrated rather more on the west side and products containing Pb are dispersed evenly or may be concentrated to a minor degree on the east side. Alternatively it may be that maintenance practices result in an extra additional source of Cu and Zn but not of Pb on the western side.

Cold starting is known to cause large amounts of Pb-containing particulates to be emitted. These emissions, however, may be equalled or outweighed by moving vehicle emissions resulting in the slight non-significant bias of Pb concentrations on the eastern side of the road. The Pb-containing particulates are known to be of small dimensions (<50 μm) and as such may become dispersed across the highway surface. The use of streets for carrying out car maintenance practices involving brakes and anodised exhaust pipes may also give rise to additional Cu and Zn inputs on the western side. Certainly, tyre wear from wheel-kerb contact during parking would be one extra source of Zn-containing particulates that might be expected to predominantly occur on the western side but not the east. The particulates from these sources are probably larger than exhaust particulates and therefore may not be readily dispersed across the highway surface and so result in the elevated concentrations found.

Manganese, like Cd, does not consistently exhibit the same trend (Figure 5.5) and the mean values decrease towards the road centre (Figure 5.7). The Mn concentrations may be reflecting the amount of soil and vegetation derived metal present in a sample at any specific time.

Manganese concentrations are slightly higher on the eastern side which would be consistent with this explanation as there are many more large trees overhanging the road on this side and less barriers to wind transportation of soil from the adjoining sub-catchment. This is extremely speculative especially as the difference in the means of the two sides of the road, for both pavement and road gutter sediments is not significant at the 5% level of significance.

The mean values of Fe concentrations do not exhibit a uniform increase from roadside to centre but the distribution of concentrations is less random than for Cd and Mn (Figure 5.3). There is some indication, in a minority of sample sets, of an increase from pavement to road centre. The variation in concentration between the two sides of the roadway is minimal and not significant. It may be that the background level of Fe is such that the affects of the pollutant are masked by the high level of Fe that occurs naturally.

These results suggest that a heavy metal source, particularly of Cu, Pb and Zn, is present in the centre of the road and that removal processes distribute the heavy metals towards the roadside edges. This is not unexpected considering that motor vehicles are known major sources of heavy metals (Table 2.7). The relative concentrations of Cu, Pb and Zn are not constant with the relative mean concentrations at the road centre and the road gutter being in the order Pb > Zn > Cu, whereas at the pavement the order is Zn > Pb > Cu. This suggests that while the three metals have a similar dominant source either there is a secondary source of Zn or a greater background contribution. Alternatively, the Zn associated particulates occur in a different particle size range which result in a greater dispersion of particulates with high Zn concentrations.

5.2.1.2 Temporal Variations of Heavy Metals in Road and Pavement Sediments.

The concentrations of heavy metals found in sediments sampled from the road and pavement surfaces were also examined with regard to their temporal variation. The sampling interval was generally two months and this has precluded any detailed conclusions being drawn, although certain general seasonal trends can be seen. The seasonal variation appeared to be most obvious in the road centre sediments, with trends being less accentuated in the road gutter sediments and hardly noticeable in the pavement sediments. There was found to be a significant difference in the winter concentrations (October to March) and summer concentrations (April to September) for the metals Cu, Pb Mn and Zn at the 5% level of significance in road centre sediments. No significant differences between the means of metals for winter and summer concentrations were found for road gutter sediments and only those for Pb were found to be significant in pavement sediments. In all cases where a significant difference between summer and winter mean concentrations was found, the summer mean tended to be greater than that for winter.

In order that the effects of variations between east and west sides of the road did not interfere with the analysis, where there had been found to be a significant difference between either side of the road, the winter and summer sample groups were carried out for each side of the road separately.

The variation of heavy metal concentrations in road centre sediments with regard to time can be seen in detail in Figures 5.1-5.6. Cadmium does not appear to exhibit any distinct temporal trends with time. Copper, Pb and Zn can be seen to peak during the summer months (July to August) for both sampling years. In the first year Zn exhibits peak concentrations in the road centre and the western road gutter in April. These values were found to be untypical and thought to result from a singular pollution incident, possibly linked to car maintenance practices. The temporal variation of Fe and Mn appears to be smoothed and less distinct than for Cu, Pb and Zn. In the case of Mn the peaks are less accentuated while for Fe the peaks appear to be less accentuated and are smoothed such that they continue into October and December.

The evidence provided above, points to a temporal variation of inputs or accumulation controls of particulates in the sub-catchment. The influence of this variation is limited and is most significant in areas closest to vehicular sources. Not all metals are affected in the same manner which suggests that inputs of particulates other than those from motor vehicles, such as leaf fall in Autumn, do not simply dilute the heavy metal levels. The contributing metal inputs to each location may be inherently variable over time or the physical characteristics of the metal containing particles are such that they are affected differently by processes operating on deposited particles within the sub-catchment. The similarities between temporal variations of Cu, Pb and Zn suggest that these metals may result from the same or similar pollutant source, or alternatively that they are associated with particles of similar characteristics.

The difference in temporal variation of Cd, Fe and Mn concentrations suggests that these metals arise from different sources to those of Cu, Pb and Zn. Inferences on the source of Cd are difficult to make owing to the lack of any observed pattern. Levels of Mn found in non-industialised catchments have been cited as representing natural background soil levels (Section 2.2.3) and therefore these should not be distributed with respect to any point source. It is difficult to explain why Mn should exhibit an inverse spatial variation to the metals Cu, Pb and Zn while exhibiting a similar, even though less accentuated, temporal variation to these metals. A possible explanation is that the spatial variation is due to Mn concentrations resulting from wind-blown soil input whereas the temporal variation results from similar physical processes affecting particulates and the results of these processes are most accentuated in the road centre.

It would seem therefore, that the alternative explanations would be that the source of pollution increases in the summer or that heavy metal removal processes are more dominant in Winter. The probable source of heavy metals is indicated as road traffic, from both spatial variations and current knowledge. It is viewed as unlikely that traffic increases significantly in summer, yet it is known that the more prevalent wet conditions in winter may lead to greater removal of particulates by more efficient washoff. The more probable explanation would appear, therefore, to be that physical processes are the dominant factor in controlling the temporal variation.

The overall variation of metals in highway associated sediments was investigated. Significant relationships between Cu, Fe, Pb and Zn were found (Table 5.2). Cadmium and Mn were not found to exhibit significant relationships. This reinforces the proposed co-origin of Cu, Fe, Pb and Zn.

Table 5.2 Correlation Matrix for Metal Concentrations in Highway Associated Surface Sediment Samples.

	Cd	Cu	Fe	Pb	Mn	Zn
Cd	1.0	-0.09	-0.16	-0.11	0.07	-0.16
Cu		1.0	0.45	0.68	-0.24	0.44
Fe			1.0	0.43	-0.03	0.5
Pb				1.0	-0.17	0.54
Mn					1.0	-0.18
Zn						1.0

Correlation coefficient 99%: 0.33

5.2.2 Heavy Metals in Roof Sediments.

There is relatively little information available on heavy metal concentrations in roof sediments, although work by Malmqvist (1978) on roof runoff suggests that heavy metals found in roof particulates are governed mainly by the nature of construction materials. The results of metal analysis suggest this appears to be true in this study.

Generally, concentrations of Cu in roof sediments were found to be less than those encountered in paved surface sediments (Table 5.1). Concentrations of Pb and Zn were less than those found in road centre sediments but generally similar to those of the road gutter. This similarity of concentrations is unexpected and while it is thought possible that resuspension processes are carrying deflated particulates from the adjacent road to be redeposited on the roof surface it was deemed necessary to investigate atmospheric inputs to ascertain the scale of this contribution. Atmospheric contributions would affect the concentrations found in all sediments and therefore could be responsible for an elevated background concentration upon which the metal pollution from motor vehicles or other sources is superimposed.

An additional potential source of Pb was the weathering of lead flashings around the chimney structures on the roof. This may account for the concentrations found in roof surface and gutter sediments being greater than those of the pavement sediment. Cadmium concentrations were found to be similar to those found on paved surfaces with mean values in roof and pavement sediments being similar (Table 5.1). Manganese concentrations were also found to be similar to, although slightly lower than, those of the paved surface sediments. Iron concentrations were found to be elevated in comparison to concentrations found in paved surface sediments and this was thought to be due to the presence of cast iron guttering and iron rich sandstone tiles.

5.2.3 Heavy Metals in Sub-Surface Sediments.

The heavy metals found in sediments in the sub-surface drainage system tend to reflect the source sediments (Tables 5.1). Accordingly, gully pot sediments exhibit similar concentrations to those of the highway associated sediments. Cadmium, however, while being within the range of the highway associated sediments, does seem to have an elevated mean value compared to all catchment sediments. This suggests that Cd concentrations found in gully pot sediments are enhanced in respect of surface source materials. From the physical position of the gully pots it would be expected that the greatest similarity in concentrations would be between road gutter sediment concentrations and those found in gully pot sediments. This only appears to be true for Cu and also possibly for Pb although the concentrations of these metals are slightly elevated compared to the mean concentrations of road gutter sediments. The mean value for Zn shows greatest similarity to the road centre mean. The mean values for Fe and Mn are significantly less than any of the mean values of the highway associated impermeable surface sediments.

This would appear to imply a trend for the gully pot sediments to be reflecting the road centre concentrations. The mean value for Cd however, is greater than the mean values for all the highway associated impermeable surfaces and if the gully pot were reflecting a large contribution of road centre sediments then the Cd value should have been less than that of pavement and road gutter sediments. The concentrations found in gully pot sediments are therefore not thought to purely result from a mixture of contributing sediments but may also reflect other factors such as physico-chemical reactions including adsorption and acid solubilisation (Section 2.3.1).

It should be noted that the above comparison was made between paved surface concentrations determined on sediments collected over the full two year sampling period and gully pot sediments sampled only during the first year. Comparison was also therefore made of concentrations as found in the gully pot sediments to the concentrations of heavy metals found in the highway associated sediments collected in the first year. It was found that the overall concentrations in highway associated sediments did not vary significantly between the two years and comparison with either data set, that of the first year of sampling or both, will result in the same observations and inferences being drawn.

Concentrations of heavy metals found within in-pipe sediment collected from the roof drain were found to be similar to roof sediments. However, both the range and mean of the values suggest slightly lower concentrations being present than those found in the roof sediments. This was thought to be due to the removal of the fines with only the coarser sediment being deposited in-pipe. As has been shown in Section 2.5, heavy metal concentrations increase with decreasing particle size and removal of the fine particles would result in a sediment with a lower concentration.

The concentrations found in the sediment sampled at the weir plate, marking the boundary of the sub-catchment, do not give much indication of the dominance of the roof or road sediments. Generally it would appear that the Fe input from the roof is always noticeable in the sediment sampled at the weir plate. Both Cu and Zn tend to be higher than the concentrations found in roof sediments but similar to concentrations found in the gully pot and road centre sediments. Lead and Mn concentrations are similar to the mid-range of combined roof or combined highway associated sediments, thus little can be inferred as to the dominance of the roof or road as a source.

The grab samples of in-pipe sediments were collected from above the weir plate which acts as a barrier against which particles collect. Larger particles would be the first to be deposited and collect against the weir plate, particularly as runoff volume decreases at the end of a storm event. The finer particles are less readily deposited under continuous flow conditions. A small amount of runoff was seen to occur for extended periods after storm events and was thought to result from land and french drain drainage connections to the pipe network. The size distribution within the in-pipe sediment is likely to depend on the volume and persistence of this residual flow. Additionally, if the particulates from the roof and road surfaces are of differing mean densities or the distribution of heavy metals with particle size is skewed to a larger extent in one of the source areas, any supposition of dominance would be erroneous as it would be based on the assumption that the same processes are affecting the sediment from both sources. Before conclusions can be made as to dominance of either roof or highway derived sediment within the drainage system, further investigation of the physical characteristics of the sediment is required and this is detailed in the following Chapter.

5.2.4 Heavy Metal Loadings.

It has been established that heavy metal levels at Chilwell Gardens do not represent natural background but reflect the input from one or more point or area sources. The concentrations of the metals in sediment samples can be indicative of the proximity of the source and the severity of the pollution. Threshold limits for exposure to pollutants are normally given as a concentration. In order that total risk could be assessed and to understand the dynamic system, metal loadings were investigated. The loadings give indications of the total metal present in surface dusts and this can be useful in assessing the size of the inputs and outputs to the system. By considering the temporal variation it can be seen whether there is a net gain or loss or whether the system is in equilibrium.

The heavy metal loadings were calculated from the product of the concentration in each sample and the sample weight after preliminary sieving. The result was divided by the total area of the sampling location giving a unit value of weight per square metre. In interpreting the road gutter loadings per square meter it should be borne in mind that the sampling of the road gutters was over an area of 5 metres length by 0.3 metres width within which approximately 90% of highway particulates have been found to occur (Ellis, 1977).

The heavy metal loadings for the highway associated surfaces and roof surfaces are presented in Table 5.3. Generally the heavy metal loadings of the highway associated impermeable surfaces appear to be dependent on the sediment loadings rather than variation in concentrations of metals in sediment samples when compared across a transect (Tables 5.1 and 5.3). The road gutter sediment samples are sufficiently large to dominate the sediment loadings at all other sites and consequently the road gutter metal loadings are also dominant.

With regard to temporal variation, maximum sediment loadings occurred in April/June in the first year of the sampling programme, and to a greater extent in March/April of the second year (Figure 5.8). The majority of metals exhibited a loading pattern similar to that of sediment loadings in that peak loadings occurred in March and April. Minimum sediment loadings were found to occur in October and November. The decrease in sediment loadings may be due to more efficient removal of sediment by washoff resulting from the onset of autumnal rainstorms. There was some tendency for metal loadings in the road centre to peak in summer, particularly July and August, as a consequence of the high observed metal concentrations compensating for the decrease in sediment loadings.

Cadmium exhibited the most aberrant behaviour from the sediment loading pattern with maximum Cd loadings occurring in April for the pavement

Table 5.3 Sediment and Heavy Metal Loadings in the Chilwell Gardens Sub-Catchment.

Sample Area	Sediment ($g\ m^{-2}$)	Cd ($\mu g\ m^{-2}$)	Cu ($\mu g\ m^{-2}$)	Fe ($mg\ m^{-2}$)	Pb ($\mu g\ m^{-2}$)	Mn ($\mu g\ m^{-2}$)	Zn ($\mu g\ m^{-2}$)
Pavement (East)	3-118,4 (38,6)	0-735 (85)	110-5732 (1709)	58-2186 (845)	125-24393 (6572)	1842-37777 (22810)	546-26960 (7852)
Road Gutter (East)	12,6-263 (90,0)	0-1078 (115)	408-14864 (4590)	231-4644 (1833)	2525-104033 (37223)	6921-123416 (44077)	2118-68646 (23685)
Road Centre	1,2-27,9 (10,3)	0-27 (6)	42-3410 (1292)	38-646 (300)	396-18847 (7909)	443-10039 (4378)	456-16659 (4728)
Road Gutter (West)	16,5-425,5 (86,2)	0-289 (46)	1080-17535 (4324)	440-7231 (1702)	7193-80969 (26765)	10015-52889 (38460)	6882-80587 (24438)
Pavement (West)	2,7-137,5 (34,90)	0-258 (42)	153-6923 (1696)	51-2912 (724)	78-22358 (4575)	1509-76856 (20123)	477-38306 (9627)
Roof Surface	0,7-4,8 (2,6)	0-6 (3)	15-137 (64)	22-199 (92)	135-1495 (950)	192-3122 (1354)	334-1721 (932)
Roof Gutter*	18,2-427,9 (182,1)	0-449 (160)	615-7200 (2838)	701-11926 (4162)	5814-203168 (65801)	6372-96167 (35132)	6102-24591 (18399)

Mean values in parentheses

* Loadings per metre of guttering - each metre of guttering serves approximately 5,2 m^2 of roof surface.

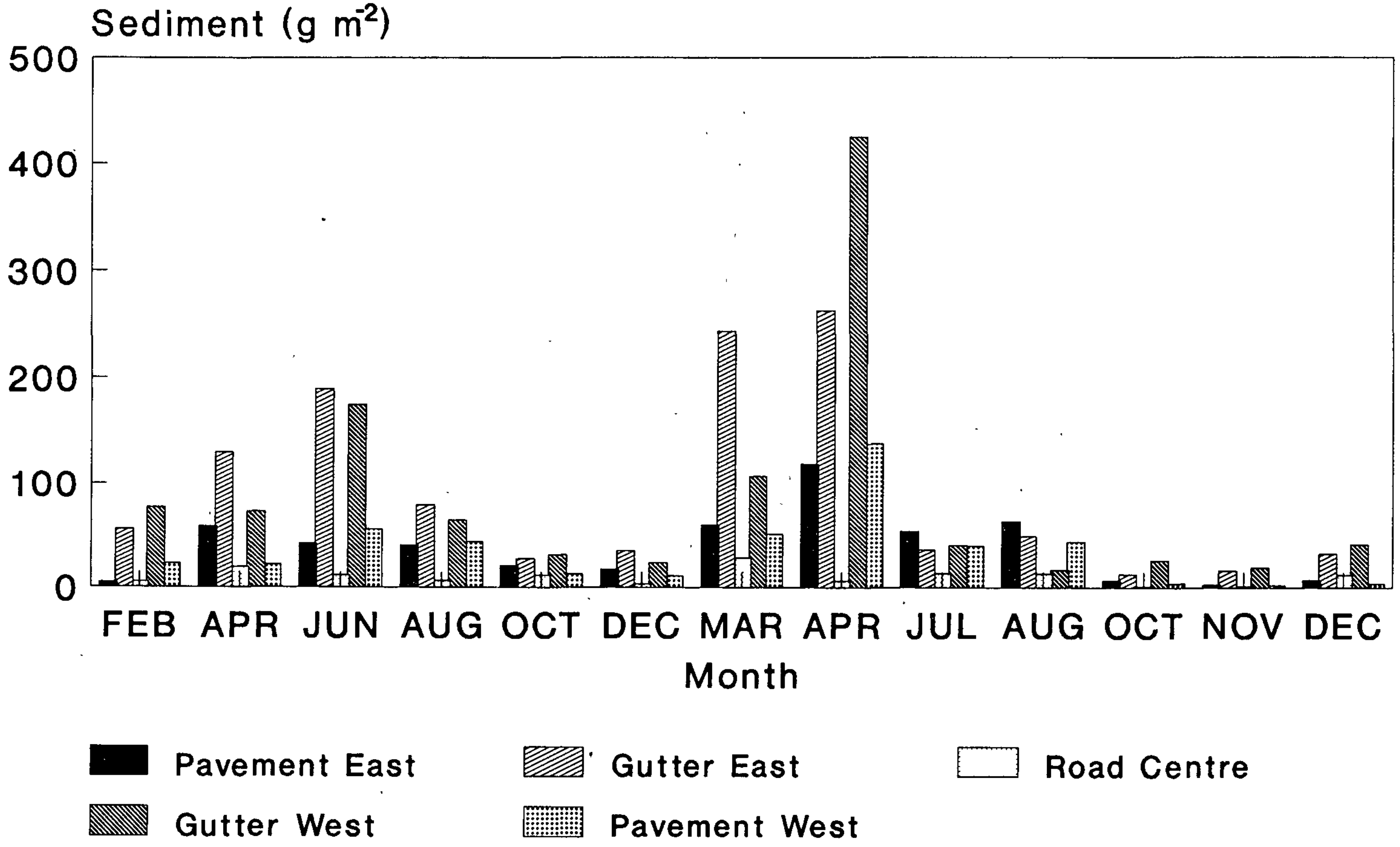


Figure 5.8 Temporal Variations in Loadings of Highway Associated Sediments.

sediments on the eastern side of the sub-catchment. Alternatively, the Cd loadings for pavement sediments on the western side of the catchment showed no distinct maxima in April of either year. Cadmium loading maxima for road centre sediments were not confined to April as a loading peak was observed in October. The loadings of road gutter sediments peaked in June of the first year, and in the second year peaked in March/April.

The temporal patterns exhibited by metal loadings indicate that during the spring their is an overall gain of sediment and associated pollutants which peaks in the summer. the sediment is then removed either by intense summer rainfall, such as thunderstorms, or the increasing frequency of rainfall at the onset of autumn, or a combination of both.

Roof loadings did not exhibit any identifiable patterns, which may be partly due to the limited sampling of this area. The *in situ* sampling, however, allows a first order approximation of the total metal loading within the Chilwell Gardens sub-catchment including contributing roof areas (Table 5.4). It was not possible to clean the entire length of

Table 5.4 Total Loadings of Heavy Metals Within the Chilwell Gardens Sub-Catchment

	Cd (mg)	Cu (mg)	Fe (g)	Pb (mg)	Mn (mg)	Zn (mg)
Roof Area	0*-57 (21)	82-863 (376)	96-1428 (550)	773-24179 (8388)	874-11524 (4999)	929-3544 (2755)
Road Area	0*-179 (23)	69-3077 (903)	33-1082 (351)	251-13478 (4148)	841-22198 (8681)	371-15438 (4299)
Total	0*-237 (44)	152-3940 (1279)	130-2510 (901)	1024-37657 (12536)	1715-33722 (13680)	1300-18983 (7054)

Mean values in parentheses

0* Zero loading resulting from being based on a range of concentrations with a minimum below the detection limits.

roof gutter feeding the sampled point. The loadings may therefore be misleadingly high as accumulated sediment lodged further along the roof gutter may have moved into the cleared area, possibly stimulated by the cleaning of the sampling section. The Pb loadings were found to be unexpectedly high compared to paved surface loadings. This reflected the high concentrations found in roof gutter sediments compared to pavement sediments which has already been discussed.

5.3 Mineral Magnetic Measurements.

5.3.1 Mineral Magnetic Characterisation of Surface Sediments.

Comparison of the concentration related magnetic parameters indicates a strong linear relationship between IRM_{300mT} and χ for all samples which accounts for 96% of the variation observed. Detailed comparison reveals that the relationship is stronger for the highway associated impermeable surface sediments alone than for all sampled sediments. The relationship is therefore apparently weakened by the inclusion of roof sediments which suggests there may be a distinct difference between the magnetic mineralogy of paved surface sediments and roof sediments.

From inspection of Table 5.5 it can be seen that the concentration related mineral magnetic parameters, IRM_{300mT} and χ, exhibit a similar pattern of distribution to those of Cu, Pb and Zn concentrations, i.e. an increase in magnitude from the pavement to the road centre (Figures 5.9 and 5.10). It therefore seems likely that the dominant source of the magnetic minerals is located in the area of the road centre and is associated with motor vehicles. The spatial variation was analysed statistically and it was found that there was no significant difference between the means of determinations made on sediments collected on the east and west sides of the sub-catchment.

Temporal variations were also similar to those of Cu, Pb and Zn with peak measurements of magnetic mineral concentration related parameters occurring in samples collected in June and July, although this was slightly more marked with IRM_{300mT} (Figures 5.9 and 5.10). As with Cu,

Table 5.5 Mineral Magnetic Parameter Ranges and Means for Sampled Bulk Sediments.

	χ (μm^3 kg^{-1})	χ_{fd} (%)	IRM_{300mT} (mA m^2 kg^{-1})	IRM_{-20mT} $/IRM_{300mT}$	$-IRM_{-40mT}$ $/IRM_{300mT}$	$-IRM_{-100mT}$ $/IRM_{300mT}$	$-IRM_{-200mT}$ $/IRM_{300mT}$	IRM_{-20mT} $/IRM_{-40mT}$
Pavement	0.86-2.87 (1.79)	0-7.67 (1.86)	9.12-25.68 (17.21)	0.03-0.219 (0.112)	0.286-0.455 (0.385)	0.779-0.889 (0.855)	0.931-0.995 (0.976)	0.067-0.706 (0.308)
Road Gutter	0.97-4.78 (2.43)	0.21-4.69 (2.42)	12.83-68.51 (30.63)	0.084-0.285 (0.215)	0.252-0.499 (0.309)	0.777-0.896 (0.823)	0.933-1.0 (0.971)	0.17-1.1 (0.741)
Road Centre	2.82-7.26 (5.17)	0-4.79 (2.04)	37.68-105.24 (68.21)	0.191-0.289 (0.265)	0.255-0.374 (0.316)	0.792-0.987 (0.841)	0.937-0.999 (0.978)	0.513-1.082 (0.853)
Roof Surface	0.53-0.95 (0.68)	0 0	3.28-8.31 (5.69)	0.323-0.38 (0.344)	0.128-0.16 (0.138)	0.703-0.752 (0.736)	0.886-0.976 (0.926)	2.074-2.881 (2.5)
Roof Gutter	0.37-1.6 (0.77)	0-1.946 (0.79)	4.21-9.47 (6.7)	0.262-0.319 (0.291)	0.175-0.277 (0.223)	0.751-0.784 (0.764)	0.909-0.944 (0.928)	1.144-1.823 (1.337)
In Pipe (Roof Drain)	0.4-0.59 (0.53)	1.18-5.05 (2.55)	4.54-8.32 (6.44)	0.161-0.278 (0.229)	0.249-0.35 (0.3)	0.796-0.837 (0.812)	0.964-0.995 (0.982)	0.461-1.113 (0.79)
Gully Pot	0.78-1.68 (1.27)	0-4.8 (1.14)	9.73-24.85 (15.21)	0.206-0.297 (0.233)	0.203-0.449 (0.291)	0.732-0.995 (0.812)	0.935-1.0 (0.96)	0.558-1.268 (0.833)
In Pipe (Gully Drain)	2.88	0	41.563	0.295	0.237	0.831	0.977	1.246
In Pipe (Combined drain)	0.93-2.06 (1.64)	1.05-2.21 (1.75)	11.53-28.19 (18.3)	0.132-0.239 (0.209)	0.271-0.378 (0.304)	0.794-0.859 (0.825)	0.943-1.0 (0.976)	0.349-0.868 (0.709)

Mean values in parentheses

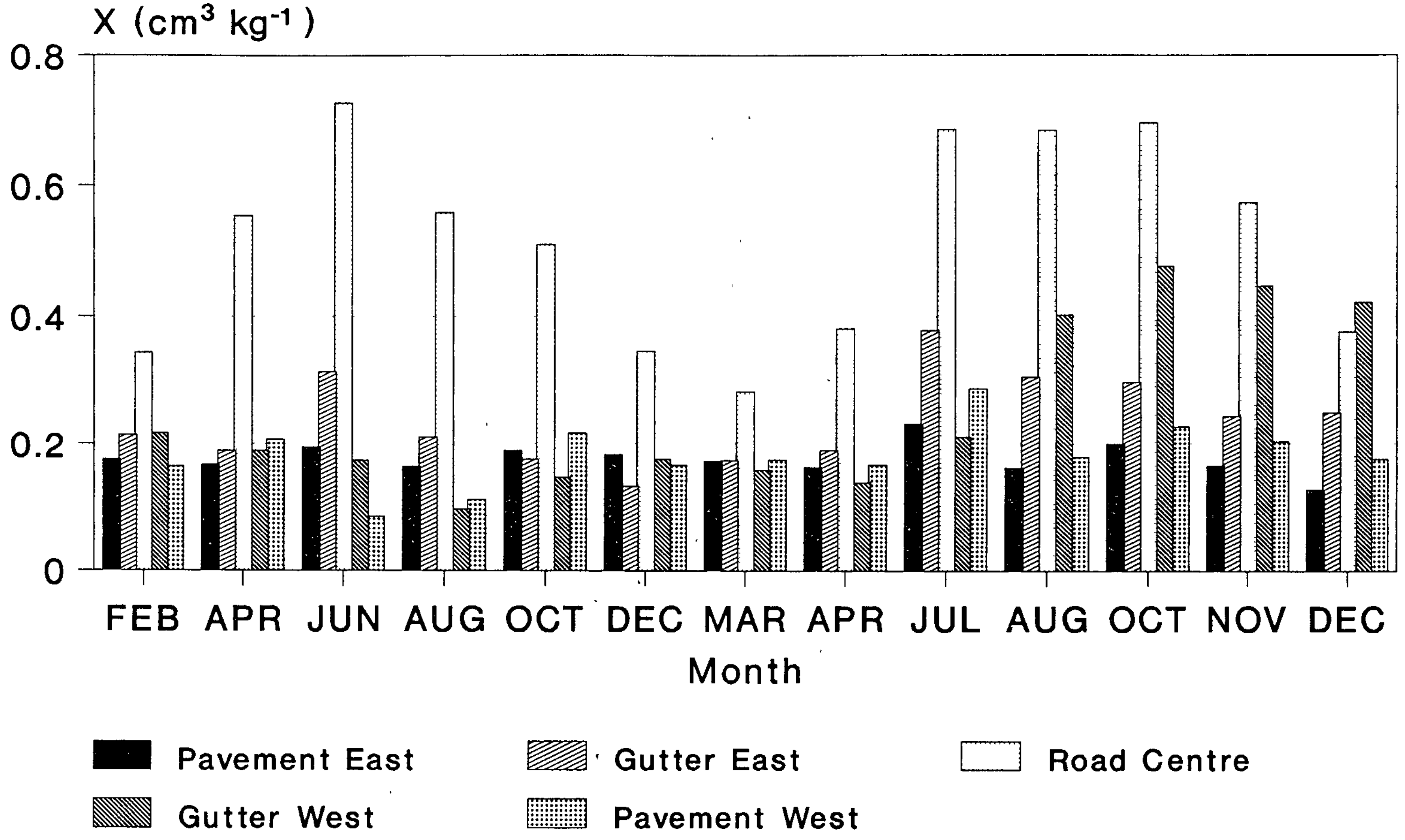


Figure 5.9 Temporal Variations in Susceptibility in Highway Associated Sediments.

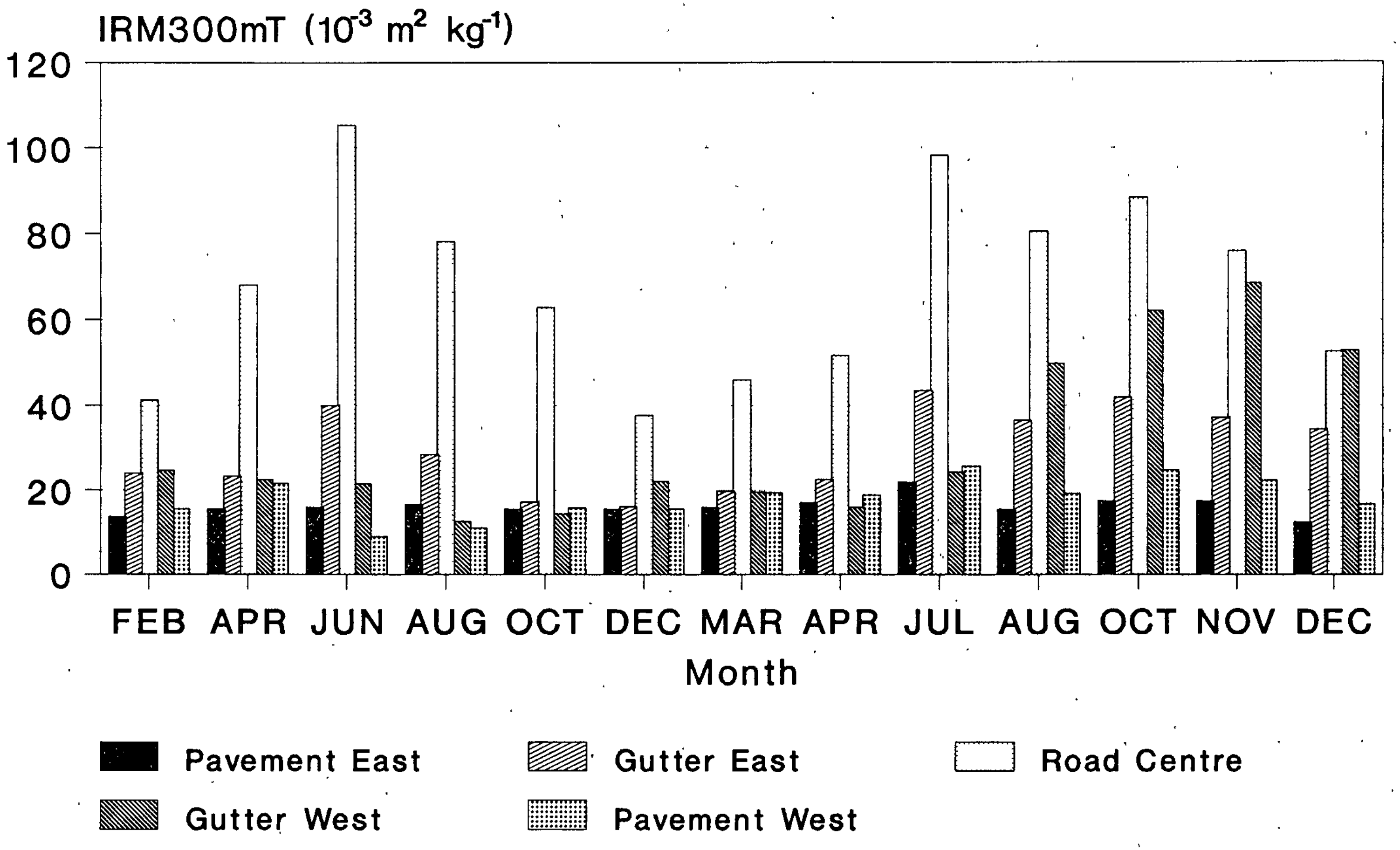


Figure 5.10 Temporal Variations in IRM300mT in Highway Associated Sediments.

Pb, Mn and Zn the means of χ and IRM_{300mT} for the road centre samples collected between April and August were significantly greater than the means of the October to March samples. This is a further indication of the co-genesis of magnetic minerals and heavy metals within the sub-catchment.

Investigation of χ_{fd} revealed that there was no distinct pattern of distribution either with time or spatial location. The backfield ratios did not exhibit any obvious pattern with time which was not unexpected as these parameters are independent of concentration. This does suggest that the source of magnetic minerals does not change throughout the year, as any seasonal change in source would be likely to be indicated by a change in mineralogy, which in turn would be highlighted by the backfield ratios.

It was anticipated that the research procedure might enable mineral magnetic measurements to distinguish between sediment types. From Table 5.5 it can be seen that for the road surface sediments the concentration parameters allow some separation of the three types. However, as might be expected with adjacent sampling areas, there is a tendency for the adjacent groups to overlap. Use of IRM_{300mT} or χ does allow the separate grouping of road centre sediments from pavement sediments. It was found that χ_{fd} did not aid discrimination of highway associated sediments. The discrimination can be further enhanced, however, by plotting χ or IRM_{300mT} against either of the first two low-field backfield ratios, $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ or $\mathrm{IRM}_{40mT}/\mathrm{IRM}_{300mT}$, or a combination of both (Figure 5.11). The two higher backfield ratios do not aid discrimination to the same degree due to a much greater overlap between the highway associated impermeable surface sediment subgroupings. The range of values for the ratio $\mathrm{IRM}_{-200mT}/\mathrm{IRM}_{300mT}$ for pavement and road gutter sediments is almost identical. The lack of discrimination of samples achieved by the higher backfield ratios suggests that the sample is easily magnetised in the reverse direction. This magnetically "softer" behaviour is indicative of samples containing predominantly ferrimagnetic minerals. This can be seen by referring back to the typical shapes of hysteresis curves of haematite and magnetite (Figures 3.5a and 3.5b). It can be noted that the haematite curve only reaches saturation at higher fields

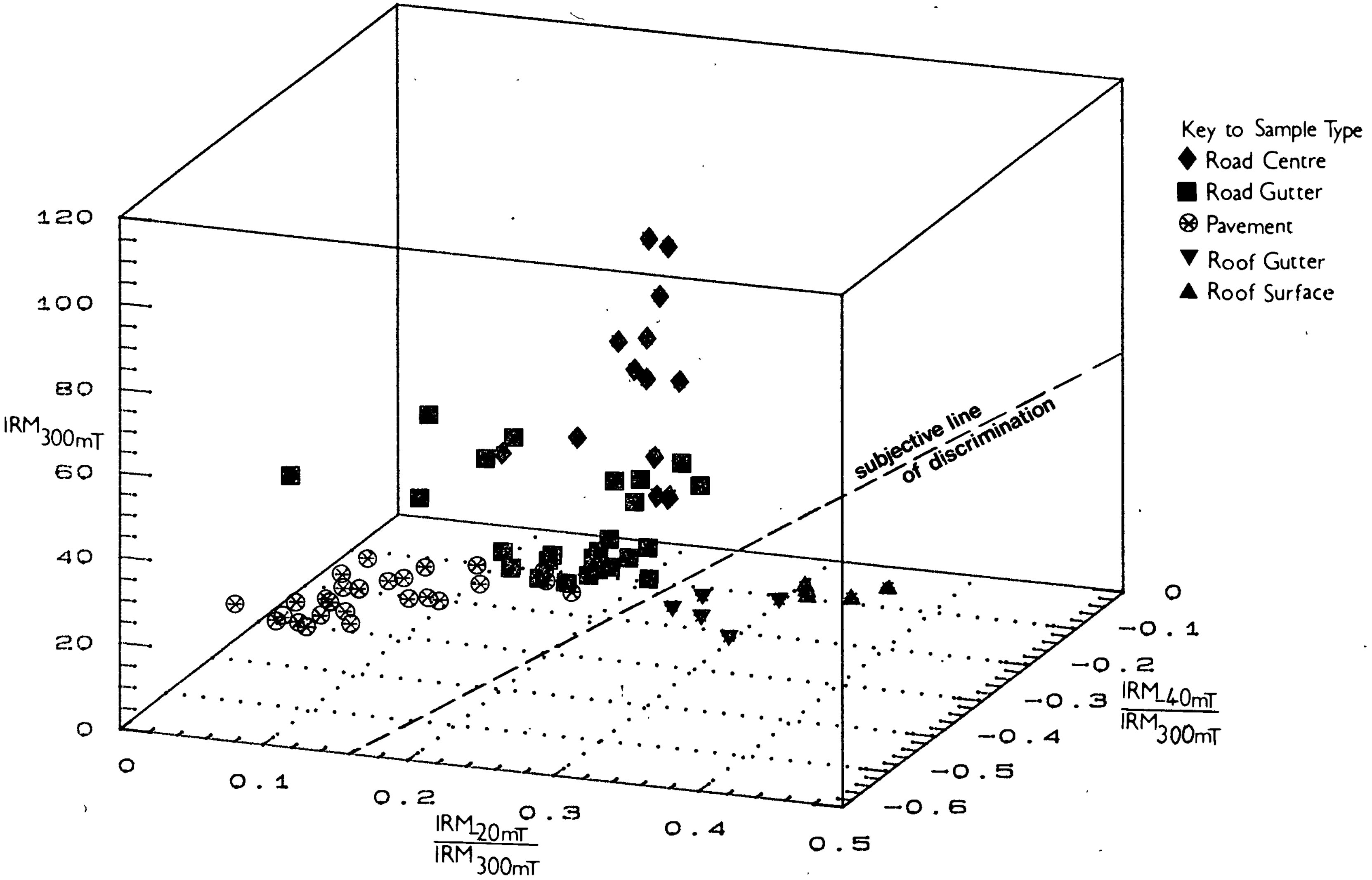


Figure 5.11 Tri-Axial Plot of IRM_{300mT}, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT} for Sediment Samples from Chilwell Gardens Sub-Catchment.

than magnetite and with a flatter curve the changes in reverse fields are greatest at high backfields rather than at lower backfields which is the case for the samples analysed here.

Investigation of the most discriminant parameters for highway associated impermeable surface sediments and roof sediments reveals that use of IRM_{300mT} and χ does allow some discrimination as roof sediments tend to have low concentrations of magnetic minerals in comparison to highway associated surface sediments. Use of IRM_{300mT} provides slightly greater discrimination than χ. The values of χ_{fd} were found to be zero for roof surfaces. This is thought to have occurred owing to the small weight of sample collected so that variations between χ at high and low frequency were too small to be detected. The roof gutter values of χ_{fd} are generally less than those of the highway associated sediments although the values fall within the range of those for highway associated sediments. From these results and the values of χ_{fd} for sub-surface sediments it can be seen that χ_{fd} does not aid discrimination of sediment sources, accordingly further investigation of this parameter was not carried out.

A significant difference which can be observed between paved surface sediments and roof sediments is the shape of the coercivity curves and this is indicated by the differences in the ranges of the backfield ratios for the source sediment types. The use of any of the three lowest backfield ratios as a secondary discriminating factor will also aid identification. The data in Table 5.5 shows that any of these backfield ratios could be used to discriminate between roof surface and highway associated impermeable surfaces. The discrimination provided by use of IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT} however, appears better than that provided by use of IRM_{-100mT}/IRM_{300mT}. There would be an overlap in these ratios if they were to be used solely in an attempt to discriminate between roof gutter and highway associated sediments. These ratios can be used with IRM_{300mT} to provide a full discrimination (Figure 5.11). In order that these can be presented in a simpler 2-dimensional format a combination of the two backfield ratios IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT}, (i.e. the former ratio divided by the latter) can be plotted against either of the concentration related parameters, χ or IRM_{300mT} (Figure 5.12). The combination of these backfield ratios achieves a discrimination between all roof sediments and highway associated sediments with each having an exclusive range of values (Table 5.5).

The use of the two backfield ratios as a secondary ratio produces a value that is useful as an indicator of the mineral magnetic characteristics for these particular samples. The ratio will decrease as the sample becomes less ferrimagnetic. This cannot be applied as a general principle as it only holds where the backfield ratios of the samples under examination are selected such that the remanent magnetisations change from the original positive magnetisation to a negative magnetisation between the two selected backfield ratios. For the samples under investigation here the premise can be applied. This is illustrated in Figure 5.13 where the section of the hysteresis curve that is indicated by the ratio is highlighted and the changes in the ratio with sample type are shown.

In Figures 5.11 and 5.12 a line delineating a plane of discrimination can be drawn subjectively and could be positioned such that it would achieve total discrimination between the two groups of samples. This would yield the result that might be expected, however, it would be based only on the samples of each group that are in closest proximity with regard to the axes used. A purely subjective line would be able to differentiate two goupings with no overlap, even if the maximum space between the two groupings was one unit on the axes. However, if one sample caused an overlap despite the space between the rest of the two groupings being 100 units on the axes a subjective line could not be drawn discriminating the two groupings. In order that a representative discrimination can be achieved the discriminating plane must be based on the whole of each two populations of samples, and to this end statistical analysis of the discriminant functions between sample groupings was carried out.

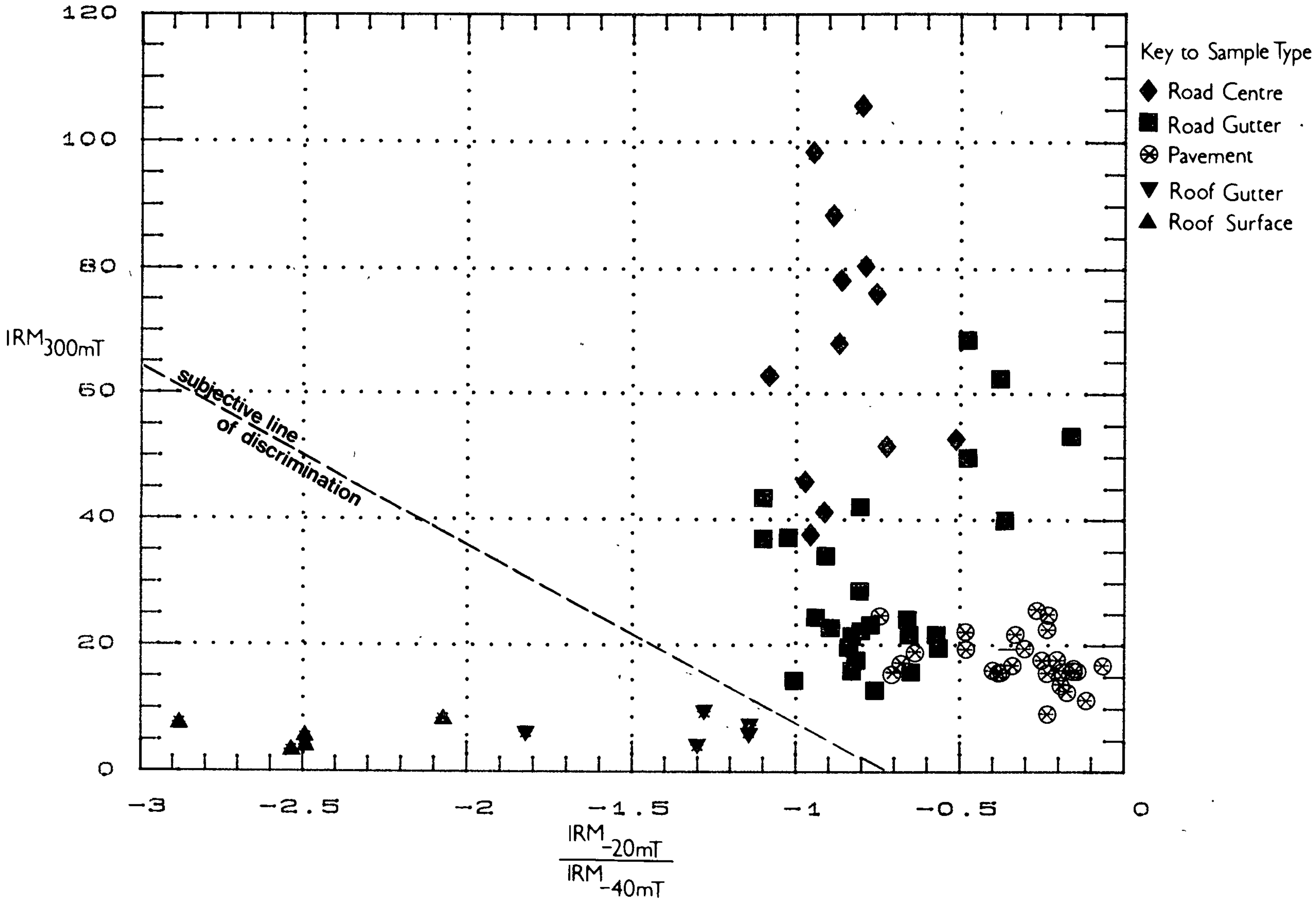


Figure 5.12 Plot of IRM$_{300mT}$ against IRM$_{-20mT}$/IRM$_{-40mT}$ for Sediment Samples from the Chilwell Gardens Sub-Catchment.

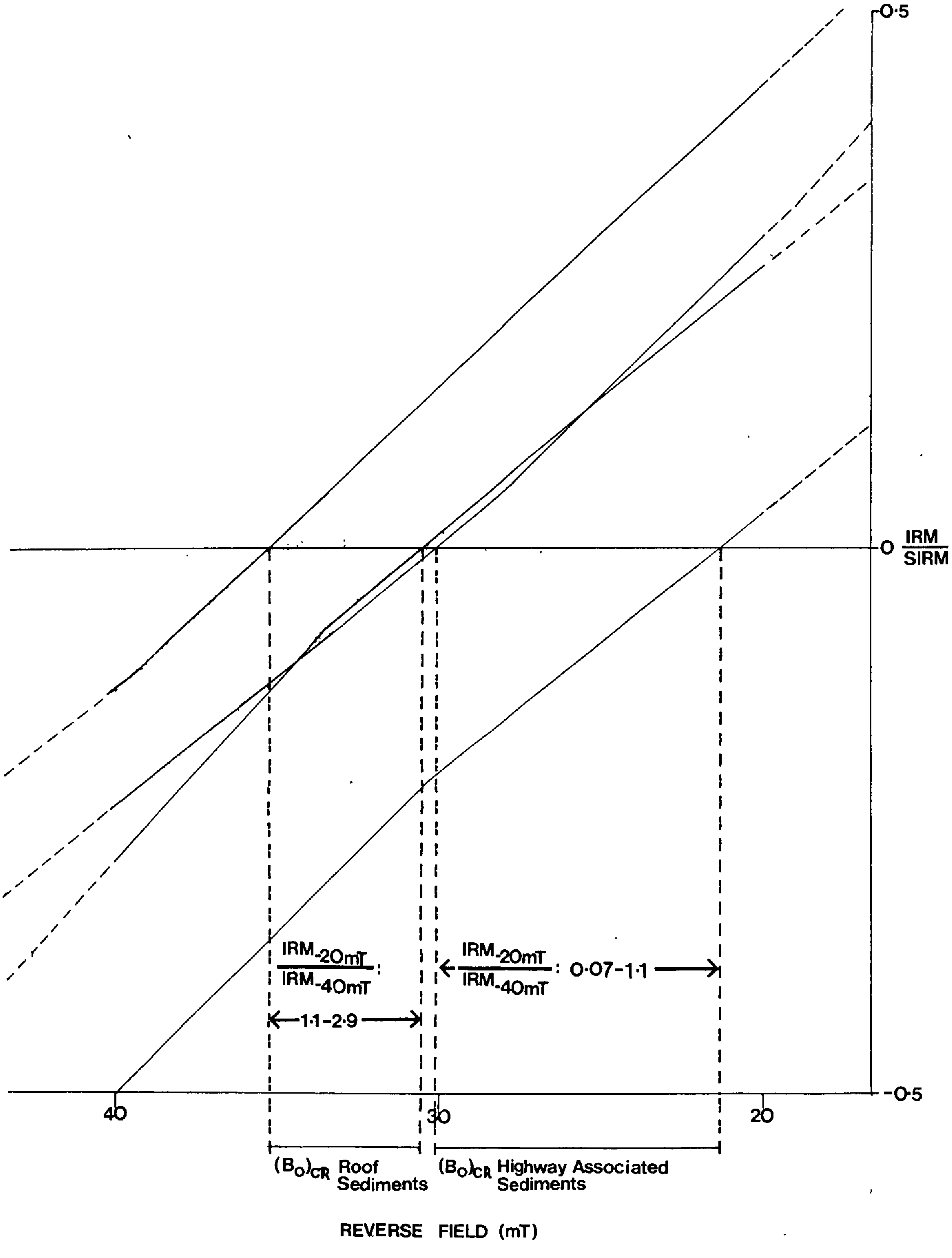


Figure 5.13 Section of Hysteresis Curves and IRM_{-20mT}/IRM_{-40mT} Ratio for Source Sediment Samples Collected within the Chilwell Gardens Sub-Catchment.

5.3.2 Statistical Analysis of Discriminant Functions.

Discriminant analysis, as provided on a statistical package of programmes SPSS$^{x\ R}$ (Statistical Packages for the Social Sciences), was applied to the data set for road, pavement and roof sediments. The results of this statistical analysis are presented in Tables 5.6-5.8.

In discriminant analysis the space occupied by the samples on the discriminating variables is defined by the canonical discriminant functions; that is they represent the axes of the discriminant space. In the case of the analysis of mineral magnetic parameters as determined on samples from highway or roof surfaces, the first discriminant function was found to be sufficient to explain 98.67% of the sample variance, with subsequent functions not contributing significantly (Tables 5.6-5.8).

It can be seen from Tables 5.6-5.8 that the parameters IRM_{300mT}, χ, IRM_{-20mT}/IRM_{300mT}, IRM_{-40mT}/IRM_{300mT} and IRM_{-20mT}/IRM_{-40mT} can all be used to achieve a similar level of discrimination. In the case of IRM_{300mT} or χ and the two backfield ratios, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT}, the single misclassified sample is from the road sediment grouping (Tables 5.6 and 5.7). In the case of IRM_{300mT} and IRM_{-20mT}/IRM_{-40mT} it is one of the roof samples which is misclassified (Table 5.8). The roof grouping consists of ten samples so that in terms of explaining the variance of the two groupings the use of IRM_{-20mT}/IRM_{-40mT} and IRM_{300mT} explains 100% of the highway sediment grouping and 90% of the variance of the roof sediment grouping. In comparison the classification using the parameters IRM_{300mT}, χ, IRM_{-20mT} and IRM_{-40mT} explains 100% of the roof sediment grouping and 98.5% of the highway sediment grouping.

In an attempt to improve the discrimination such that the misclassifed sample could be correctly classified the data for the parameter IRM_{-100mT}/IRM_{300mT} was included. The inclusion of this data did not succeed in producing an improvement, or any significant change in the discrimination of the samples. This was the case when the additional parameter was used in conjunction with all three data formats previously

Table 5.6 Discriminant Classification Results For Variables IRM_{300mT}, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT}.

SAMPLE GROUP	NUMBER OF CASES	PREDICTED GROUP MEMBERSHIP	
		1	2
Highway Surfaces	65	64	1
		98.5%	1.5%
Roof Surfaces	10	0	10
		0%	100%

Percent of "grouped" cases correctly classified: 98.67%

Table 5.7 Discriminant Classification Results For Variables χ, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT}.

SAMPLE GROUP	NUMBER OF CASES	PREDICTED GROUP MEMBERSHIP	
		1	2
Highway Surfaces	65	64	1
		98.5%	1.5%
Roof Surfaces	10	0	10
		0%	100%

Percent of "grouped" cases correctly classified: 98.67%

Table 5.8 Discriminant Classification Results For Variables IRM_{300mT}, IRM_{-20mT}/IRM_{-40mT}.

SAMPLE GROUP	NUMBER OF CASES	PREDICTED GROUP MEMBERSHIP	
		1	2
Highway Surfaces	65	65	0
		100%	0%
Roof Surfaces	10	1	9
		10%	90%

Percent of "grouped" cases correctly classified: 98.67%

used in discriminant analysis. This reinforces the previous subjective observations made with respect to Table 5.5, that the values of IRM_{-100mT}/IRM_{300mT} for each sediment grouping do not exhibit sufficiently significant variations from the other groupings to assist greatly in discrimination.

An inherent assumption in the process of discriminant analysis is that the groupings being analysed conform approximately to a normal distribution. In the case of individual sample groups such as roof surface or road gutter, where samples have been collected from the same or similar sampling sites, the distribution is found to be approximately normal. When the samples are combined to form the two mass groupings of highway sediments and roof sediments the distribution will not nescessarily remain an approximation of the normal distribution. The mean values of the roof gutter and the roof surface are generally similar, the largest difference in the means occurring in the parameter IRM_{-40mT}/IRM_{300mT} (Table 5.5). It is not surprising therefore that the combined grouping for roof sediments still approximates to the normal distribution. From Table 5.5 it can be seen that for the various highway associated surface sediments the mean values vary greatly and when these samples are combined the distribution is trimodal, approximating equally towards a normal and a logarithmic normal distribution. It is thought that the results of the discriminant analysis are such that the limitations do not compromise the analysis to such an extent that discriminant functions based on the analysis cannot be used as a first order classification of unknown samples.

In order that discriminant analysis could be carried out with groupings conforming to the normal distribution, individual sample sets for the highway sediments were analysed with the combined roof grouping. By taking individual sample sets for the highway sediments it was found that the parameters IRM_{300mT}, IRM_{-20mT}/IRM_{300mT}, IRM_{-40mT}/IRM_{300mT} can discriminate perfectly between pavement and roof sediments, road gutter and roof sediments and road centre and roof sediments (100% correct classification). In the case of IRM_{300mT} and $IRM_{-20mT}/$ IRM_{-40mT} it was found that discrimination between road centre and roof sediments was less successful with two samples being misclassified (94.4% correct classification). The discriminant functions are defined by the probability of a sample being of one population based on the distance of the sample from the group centroid. In the case of $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{-40mT}$ and IRM_{300mT} the group centroid for the road gutter samples is close to the group centroid of the roof samples and the distance that separates the two group centroids is not sufficient to achieve good discrimination. When the group centroid for $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{-40mT}$ of all highway associated impermeable surfaces is considered the population as a whole causes a shift in the group centroid location away from the group centroid roof sediments. This shift in the subgroup centroid indicates how important the whole population of samples is, rather than only the samples on the perimeter of a grouping adjoining another grouping. This analysis does not stretch the basic assumptions concerning the normal distribution of samples in each group. It would appear from the statistical analysis, therefore, that the parameters IRM_{300mT} or χ, $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$, $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$ used together achieve the most robust discrimination and and therefore the most successful classification when all the assumptions in the analysis are complied with.

The statistical package calculates a series of linear discriminant functions for each grouping. By combining these linear functions, a linear function defining the discriminating plane can be produced. The linear equations found for the analysis of the combined sample groupings and the individual highway sediment groupings are given below for the parameters IRM_{300mT}, $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ and $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$:

Highway Associated Surfaces and Roof Sediment Groupings (Eq5.1)

$$0 = (0.1633 * \mathrm{IRM})-(56.7754 * \mathrm{TR})+(4.1838 * \mathrm{FR})+12.1328$$

Pavement and Roof Sediment Groupings (Eq5.2)

$$0 = (1.2843 * \mathrm{IRM})-(120.3576 * \mathrm{TR})+(3.9057 * \mathrm{FR})+13.1745$$

Road Gutter and Roof Sediment Groupings (Eq5.3)

$$0 = (0.158 * \mathrm{IRM})-(58.3012 * \mathrm{TR})+(14.9981 * \mathrm{FR})+16.2828$$

Road Centre and Roof Sediment Groupings (Eq5.4)

$$0 = (0.2475 * \mathrm{IRM})-(69.3987 * \mathrm{TR})-(23.5263 * \mathrm{FR})-5.1664$$

where $\mathrm{IRM} = \mathrm{IRM}_{300mT}$ in $10^{-3}\mathrm{A\ m^2\ kg^{-1}}$
$\mathrm{TR} = \mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$
$\mathrm{FR} = \mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$

The equations represent planes that divide the two groupings. In each equation the plane is signified as a zero value with road sediments achieving positive values and roof groupings negative values. These equations will be an important tool in future classification of sediment samples of unknown or mixed origin. The equations resulting from discriminant analysis based on the parameters IRM_{300mT}, $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ and $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$ are presented and will be used in preference to equations based on discriminant analysis using χ and backfield ratios as it is known that χ and IRM_{300mT} have a strong linear relationship and give similar results in terms of discrimination. The relationship between χ and IRM_{300mT} has been found to be sufficiently strong in some studies that IRM_{300mT} has been used to derive surrogate values of χ where the value of the latter has been too weak to be determined (Oldfield et al, 1981a). It is known from previous studies that the weight of suspended sediments filtered from stormwater samples will not be sufficient to determine values of χ accurately and therefore the equations to be used for classifying samples will be based on parameters that can be determined in all collected samples. This will allow the classification of source particulates, source sediments and stormwater suspended sediments to be compared and any relationships identified.

5.3.3 Sub-Surface Sediments.

Sub-surface sediments appear to have low concentrations of magnetic minerals and are thus similar to pavement and the lower end of the range of values found for road gutter samples (Table 5.5). However, the backfield ratios exhibit greatest similarity to road gutter sediments. There is little difference between weir plate and gully pot samples although mean values suggest that the weir plate sediments generally have slightly greater magnetic mineral concentrations. It is not unexpected that gully pot sediments reflect the nearest source of sediment, which is the road gutter, but this implies that there may be little hope of providing a distinct differentiation between surface and sub-surface sediments. Nevertheless, it can be inferred that the road surface mineral magnetic signature is generally robust throughout the catchment. The observed overlap of gullypot sediments and road gutter sediments would indicate that, despite the strong biochemical reactivity which occurs in the gully pot, the magnetic parameters appear to remain relatively unaltered. It remains to be seen if the paved surface and subsequent gully pot sediments are present in sufficient concentrations to mask all other sediment mineral magnetic signatures within the sewer system.

The data for sub-surface sediments has been processed using equation Eq5.1. The results reveal that the gully pot samples are assigned to the highway sediments grouping with only one exception. It is not surprising that the values of parameters determined on sediments from the gully pots are grouped with those of sediments from the nearest sources. The one exception that is grouped with roof sediment would seem to be illogical and it indicates that statistical evidence must be interpreted with care. There is no source of roof sediment to the gully pots so the sample classified as belonging to the roof grouping cannot truly be a member of that grouping. Possible anomalies which may have caused this are that the sample was contaminated in some form during analysis orthat the gully pot was subject to an influx of similar material to that of the roof sediments. Alternatively, it may be that the discriminant procedure has limitations, possibly as a result of only a small discriminant space between the groupings under investigation. The actual values of the mineral magnetic parameters for the gully pot sample classified with the roof sediment grouping were 13.328, 0.297 and -0.449 for IRM_{300mT}, $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ and $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$, respectively. Comparison to the range of values for gully pot samples (Table 5.5) indicates that while the value for IRM_{300mT} is fairly typical, the values for $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ and $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$ represent the maximum values found for both parameters in gully pot sediments. The difference between these maximum readings and the next nearest reading represents 38.5% of the total range of $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ values and 34.2% of the range of $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$ values for gully pot sediments. These values can be seen as outliers and untypical for gully pot sediments. It would seem unlikely that this represents a failure in the discriminant procedure but is more likely to be an experimental error or an unexplained input of atypical magnetic minerals into the gully pot. The gully pot data was also classified using equation Eq5.3. This was thought appropriate as the nearest source of sediment would be the road gutter. It was found that the use of this equation also resulted in the classification of the previously misplaced sample as being part of the roof sediment grouping.

The results of mineral magnetic analysis of the samples of in-pipe deposition collected from behind the weir plate in the sewer pipe were also processed using equation Eq5.1. The grouping was split, with 83% being assigned to the highway group and 17% (one sample) being assigned to the roof group. The single sample classified with the roof grouping was not contemporaneous with the anomolous sample of gully pot sediment. The use of equation Eq5.3 resulted in the classification of this sample with the road gutter sediment grouping. It can be seen that unlike the gully pot sample the characteristics of this sample are close to the borderline of the two groupings, with the result that the two equations assign it to different groupings.

The sediment that collects at the weir plate is supplied from both the highway associated surfaces and roofs. It would seem logical that either source may dominate this sediment dependent on the characteristics of the flow regime occurring over the time between the samples being taken. From the statistical analysis the highway sediments would appear to dominate the mineral magnetic parameters found in this in-pipe sediment although the existence of intermediate characteristics in one sample suggests that at times the roof sediments may make a significant contribution. This inference is reliant on representative samples having been taken. Grab samples of the sub-surface sediments were taken and the nature of the sampling was such that resuspension and loss of fine particles may have occurred. This is particularly true of sampling gully pot sediments where the sample, collected in the dipper, had to be raised through the water column of the gully chamber. The sediment collected at the weir plate was dependent on the hydrological regime operating at the time of sediment deposition. The character of the deposited sediment may therefore be modified by the extended runoff from land and french drains.

For these reasons the present inferences with regard to sub-surface sediments must be tentative and further investigation is required to be able to draw more certain conclusions. More detailed investigation of the road and roof sediments is presented in the following Chapter which deals with the physical size characteristics of sediment type and the variation of metal and mineral magnetic parameters with size of contributing sediment particulates.

5.4 Relationship Between Heavy Metals and Mineral Magnetic Parameters.

In earlier sections of this chapter similarities between the distribution of the heavy metals, Cu, Pb, Zn and to a lesser degree Fe, and concentration related mineral magnetic parameters have been noted. The major similarities are most noticeable for the highway associated impermeable surfaces but do not extend to roof surfaces. This is emphasised by the fact that roof sediments are characterised by low values of mineral magnetic related parameters but have high Fe concentrations and moderately high Pb concentrations. Table 5.9 presents the results of correlation studies of heavy metals and magnetic mineral concentration related parameters.

Table 5.9 Correlation Coefficients Between Heavy Metals and Magnetic Mineral Concentration Related Parameters.

	Cd	Cu	Fe	Pb	Mn	Zn	χ
Highway Associated Sediments							
χ	-0.22	0.61	0.73	0.56	-0.19	0.62	1.0
IRM_{300mT}	-0.22	0.63	0.68	0.58	-0.23	0.62	0.98
Correlation coefficient 99%: ≥ 0.325							
All Source Sediments							
χ	-0.26	0.6	0.16	0.38	0.21	0.35	1.0
IRM_{300mT}	-0.24	0.62	0.16	0.42	0.15	0.35	0.98
Correlation coefficient 99%: ≥ 0.267							

Table 5.9 indicates that there are several reasonably strong relationships that can be identified although these become stronger when paved surface sediments are considered separately. The same relationships are not found to be significant if the sediments other than from paved surface are solely considered. The disruption of the covariation of Fe, Pb and Zn with magnetic mineral concentration related parameters resulting from inclusion of values for roof sediment parameters, can be seen (Table 5.9). Correlation of Cu does not exhibit the same disruption which reinforces the suggestion of only one source of Cu in the sub-catchment, that being vehicular in origin, while other sources such as atmospheric deposition and attrition of structural materials contribute significant quantities of Fe, Pb and Zn.

The strongest relationship, as has been mentioned earlier, is between χ and IRM$_{300mT}$. This is not unexpected as the two parameters relate approximately to magnetic mineral concentrations within a sample. Unlike other relationships this remains constant when either all the samples or only those from paved surfaces, are considered (Table 5.9).

There is a strong correlation between Fe and magnetic mineral concentration related parameters in highway associated impermeable surface sediments. The postulated linear relationship providing approximately 50% explanation of the covariance. The covariation of Cu, Pb and Zn with IRM$_{300mT}$ and χ also exhibit linear relationships, the proportion of variation explained by the linear relationships ranging from 31% to 40%. The strength of the linear relationships between Cu, Fe, Pb, Zn and magnetic mineral concentration related parameters in highway associated sediments tends to confirm the hypothesis that the motor vehicle is the major source of both metals and magnetic minerals in these sediments.

CHAPTER 6 HEAVY METAL LEVELS AND MINERAL MAGNETIC PARAMETERS FOR SIZE FRACTIONATED SEDIMENTS FROM THE CHILWELL GARDENS SUB-CATCHMENT.

6.1 Introduction.

In the previous chapter it was noted that the metal concentrations and mineral magnetic parameters of the collected bulk sediment samples exhibited certain spatial variations enabling inferences regarding the sources of metals and magnetic minerals to be drawn. It is well established that heavy metal concentrations tend to increase with decreasing particle size (Section 2.2.4.2) and it would therefore seem appropriate to investigate variations in this trend with differing sampling locations in order that transportation mechanisms and sources of heavy metals can be more precisely identified.

Other studies have investigated the variation of metal concentrations with particle size in highway sediments (Rameau, 1972; Duggan and Williams, 1977; Ferguson and Ryan, 1984; Hamilton et al, 1984; Sartor and Gaboury, 1984; Rapsomanikis and Donard, 1985), but only Ellis and Revitt (1982) studied the spatial variation of heavy metal concentrations with particle size. Their results indicate that there is a greater concentration of the metals Cu, Mn and Zn in the less than 250 μm fraction of sediments adjacent to the gully pot than is found in the same size fraction of sediment midway between the two gully pots on the same stretch of motorway. Lead levels exhibit an inverse distribution. The levels of Pb, Mn and Zn in the greater than 250 μm fraction for the sediment collected midway between the gully pots were found to be less than those for the same size fraction adjacent to the gully pot. The limited number of analysed samples mean that any inferences can only be tentative but the results suggest that Mn and Zn associated particulates are more readily transported to the vicinity of the gully pot for all size ranges, while with the Cu associated particulates only the finer fractions exhibit this trend. The pattern of Pb concentrations may have resulted from the finer Pb associated particulates having been dispersed by wind and the movement of passing traffic or by the agglomeration of the smaller particles. Whilst such inferences are indicative of possible processes and not conclusive in themselves they do suggest investigation of spatial distributions of heavy metals with particle size might aid the identification of possible transportation pathways.

Assessment of heavy metal concentrations and mineral magnetic parameters in a series of size fractions will also highlight the dominant size ranges controlling the characteristics of these parameters in the bulk sediments. Stormwater particulates do not have the same particle size range as roadside or roof sediments but are made up of particulates predominantly in the 0.45 μm-230 μm size range (Ellis, 1977; Roberts et al, 1988). It is, therefore, important to ascertain whether the observed mineral magnetic characteristics found in bulk sediments are representative of the size fractions found in stormwater so that the characteristics can be used to type stormwater sediments.

Size fractionation was carried out on the bulk sediment samples for the first four sampling periods. As described in the previous two chapters the bulk samples were collected from five sites forming points on a transect across the Chilwell Gardens pavement and road surfaces. Additionally, samples were collected directly from the roof gutter. Bulk sediments collected from the roof surface could not be fractionated owing to the small mass of the collected sample. The roof gutter and highway associated sediments were separated into size fractions by passing the dried bulk sediment through a series of stainless steel sieves of 500 μm, 250 μm, 125 μm, 63 μm and 38 μm aperture (Section 4.5.1). The sediments were analysed as described previously (Sections 4.5.2. and 4.5.3).

6.2. Variations of Heavy Metals with Respect to Particle Size in Sediments Collected within the Chilwell Gardens Sub-Catchment.

The results of heavy metal determinations for Cd, Cu, Fe, Pb, Mn and Zn in highway associated impermeable surface sediments for the six different size fractions are presented in Table 6.1 and Figures 6.1-6.6. The data in Tables 6.1a-f shows that for all metals the concentration

Table 6.1a Cadmium Concentration Ranges and Means ($\mu g\ g^{-1}$) for Fractionated Highway Associated Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	0-1.48 (0.48)	0-1.73 (0.78)	0.14-2.0 (0.94)	0-5.36 (1.79)	0.87-33.73 (6.02)	0-52.24 (12.74)
Gutter	0-1.35 (0.35)	0-1.05 (0.62)	0.19-1.24 (0.89)	0-7.91 (2.02)	0.19-9.91 (3.61)	0-3.44 (1.77)
Surface	0-0.49 (0.31)	0.36-1.44 (0.79)	0.77-1.26 (1.0)	0-2.04 (1.12)	1.34-59.6 (16.5)	2.23-250 (64)

Mean values in parentheses

Table 6.1b Copper Concentration Ranges and Means ($\mu g\ g^{-1}$) for Fractionated Highway Associated Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	17.2-64 (33.1)	30.5-64 (40.1)	27.4-66.3 (42.0)	32.5-174 (77.4)	27.9-118.6 (63.6)	44.4-221.9 (107.3)
Gutter	28.6-53.6 (38.7)	22.2-56.1 (36.6)	32.1-124.4 (64.1)	37.3-219.1 (95.3)	47.7-255.3 (127.5)	36.1-181.3 (108.8)
Surface	20.1-79.3 (50.1)	32.8-133.1 (75.6)	98.9-582.0 (322.5)	107.7-560.7 (337.2)	131.3-462.2 (249.1)	100.0-387.6 (176.4)

Mean values in parentheses

Table 6.1c Iron Concentration Ranges and Means ($mg\ g^{-1}$) for Fractionated Highway Associated Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	16.6-35.0 (25.5)	15.7-32.4 (24.6)	18.1-28.6 (22.8)	21.2-34.0 (26.8)	19.9-31.3 (25.3)	26.1-49.3 (35.8)
Gutter	14.1-31.8 (22.9)	11.3-28.4 (21.2)	17.2-29.7 (22.3)	22.3-33.7 (26.0)	17.4-42.4 (25.8)	20.8-35.0 (29.6)
Surface	25.0-29.6 (27.6)	22.5-34.7 (29.5)	22.5-46.2 (36.5)	42.8-135.9 (68.6)	34.1-37.3 (35.1)	28.8-237.2 (84.1)

Mean values in parentheses

Table 6.1d Lead Concentration Ranges and Means ($\mu g\ g^{-1}$) for Fractionated Bulk Highway Associated Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	23.0-269.0 (95.4)	38.5-169.3 (88.2)	79.3-284.9 (151.9)	124.2-511.7 (314.0)	44.9-1057.6 (405.4)	257.5-2211.9 (843.0)
Gutter	90.8-438.5 (166.8)	143.1-420.0 (248.8)	302.1-531.6 (415.9)	629.7-1003.8 (825.5)	657.0-1520.2 (1045.3)	691.7-3034.0 (1334.0)
Surface	132.2-1182.7 (525)	418.2-2404.5 (989.5)	529.7-3469.4 (1855.0)	2543.5-4530.9 (3483.2)	1817.9-4333.8 (2818.0)	454.4-4113.8 (2416.7)

Mean values in parentheses

Table 6.1e Manganese Concentration Ranges and Means ($\mu g\ g^{-1}$) for Fractionated Bulk Highway Associated Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	569.3-828.1 (724.8)	282.3-709.8 (611.2)	381.0-758.2 (631.4)	581.1-1170.5 (833.5)	527.1-821.6 (663.6)	521.0-832.6 (700.9)
Gutter	350.2-509.6 (441.7)	345.6-605.5 (460.8)	436.1-681.4 (522.4)	472.8-1221.6 (779.7)	710.5-1493.7 (941.6)	717.0-1462.4 (918.2)
Surface	386.3-447.5 (433.7)	318.7-761.3 (505.7)	449.4-476.8 (466.5)	553.1-1072.9 (765.1)	385.6-951.9 (729.0)	290.8-866.8 (547.2)

Mean values in parentheses

Table 6.1f Zinc Concentration Ranges and Means ($\mu g\ g^{-1}$) for Fractionated Bulk Highway Associated Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	85.0-156.6 (107.2)	116.7-379.6 (181.0)	129.6-332.4 (219.1)	289.2-451.2 (352.5)	318.7-707.6 (416.8)	344.2-1360.7 (587.6)
Gutter	104.6-343.7 (205.1)	133.6-384.6 (230.2)	210.9-511.3 (334.4)	367.5-880.8 (521.3)	258.6-2406.0 (776.0)	131.5-4036.3 (979.5)
Surface	130.0-453.6 (250.6)	266.8-445.9 (362.9)	225.4-779.9 (524.8)	774.8-966.2 (915.2)	663.2-1094.3 (848.5)	460.8-2050.0 (1012.4)

Mean values in parentheses

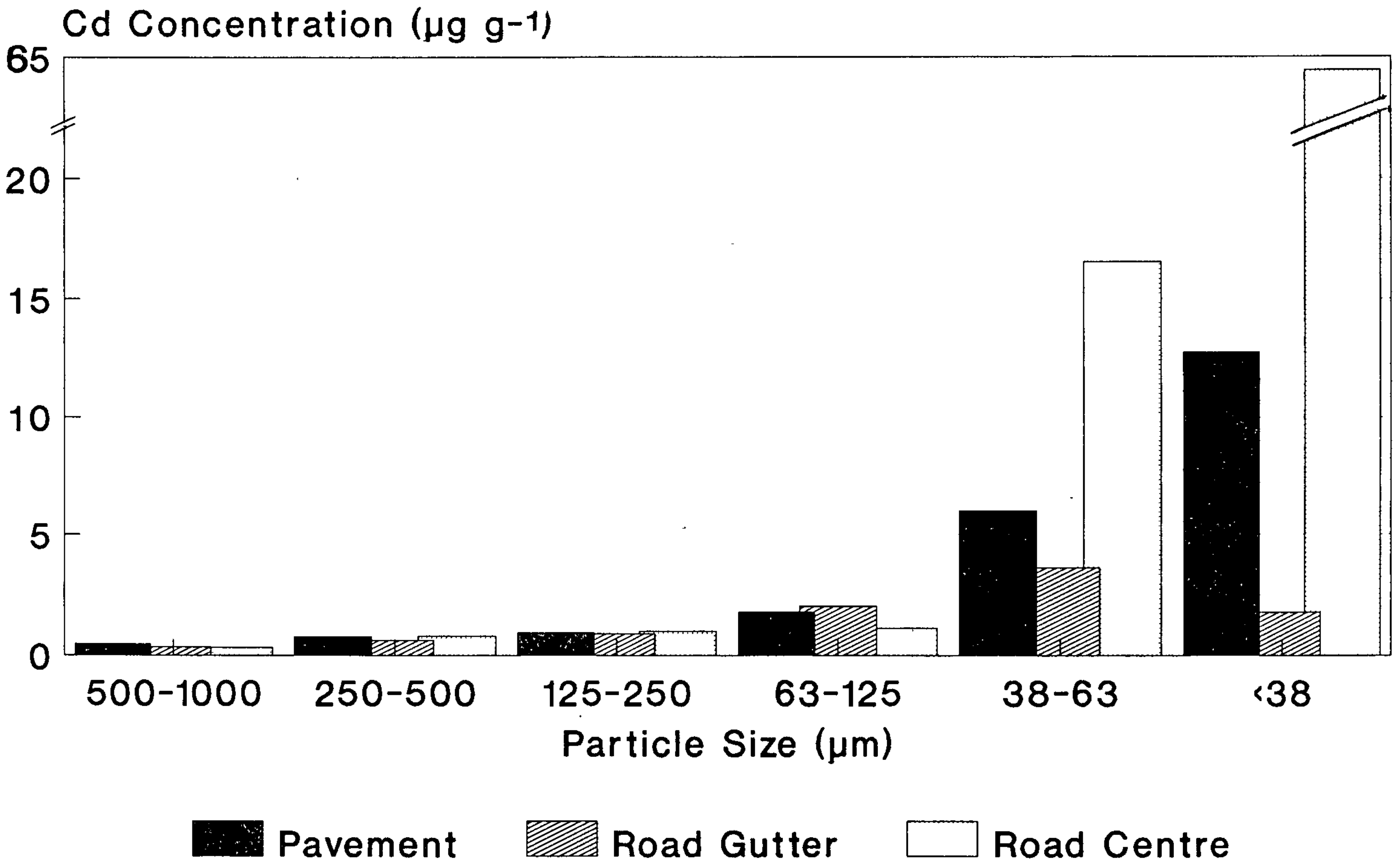


Figure 6.1 Mean Cadmium Concentration with Respect to Particle Size.

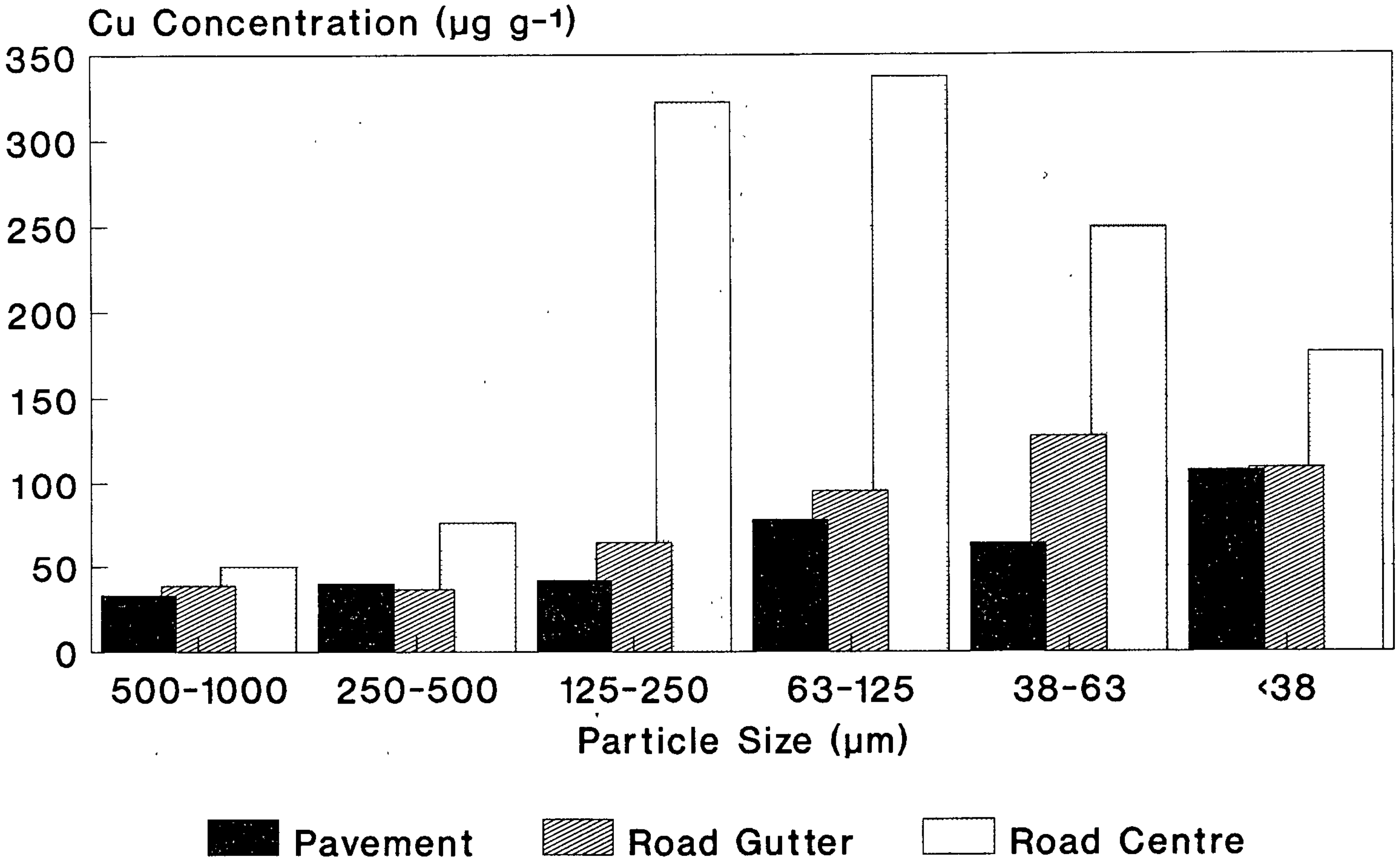


Figure 6.2 Mean Copper Concentration
with Respect to Particle Size.

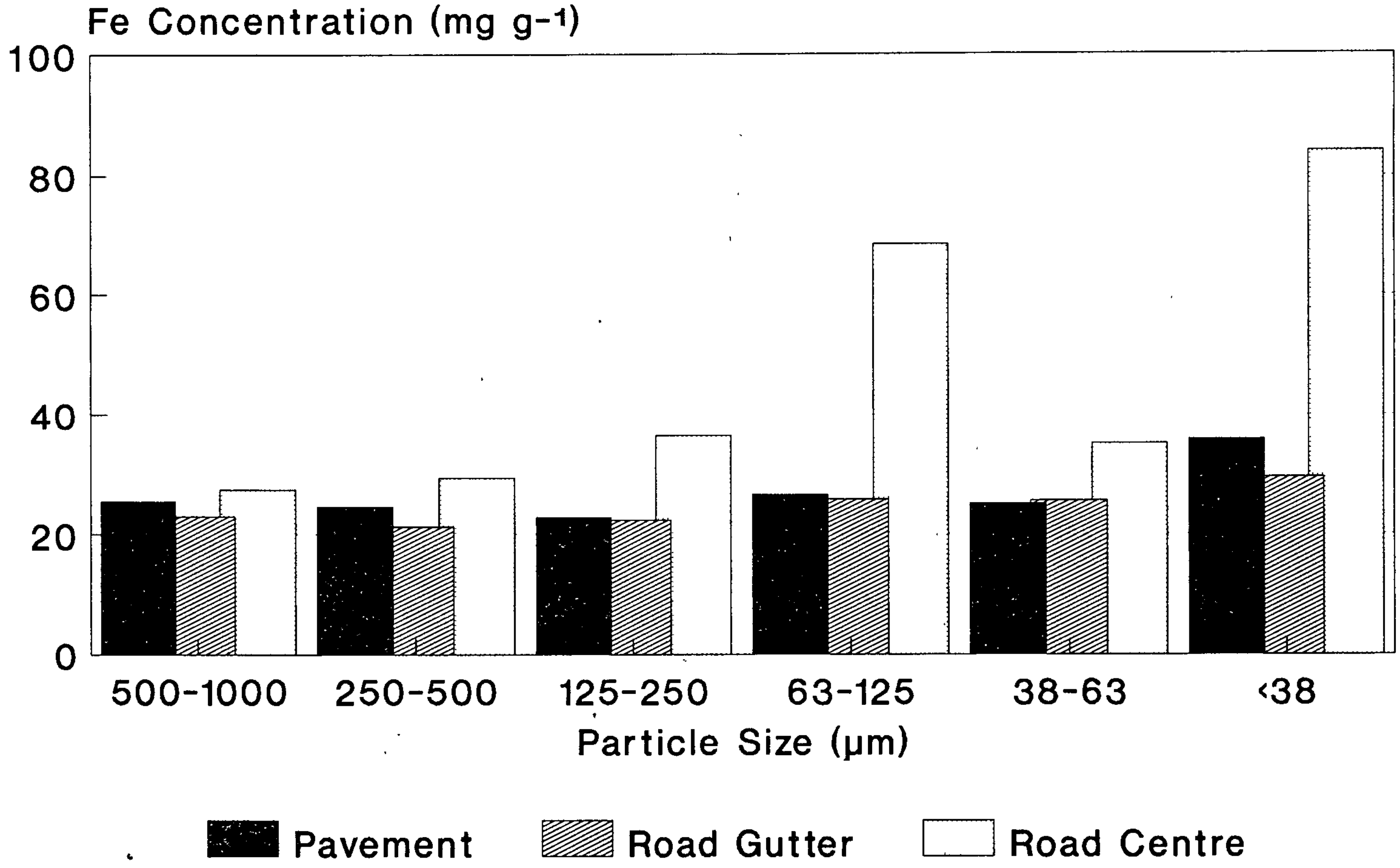


Figure 6.3 Mean Iron Concentration with Respect to Particle Size.

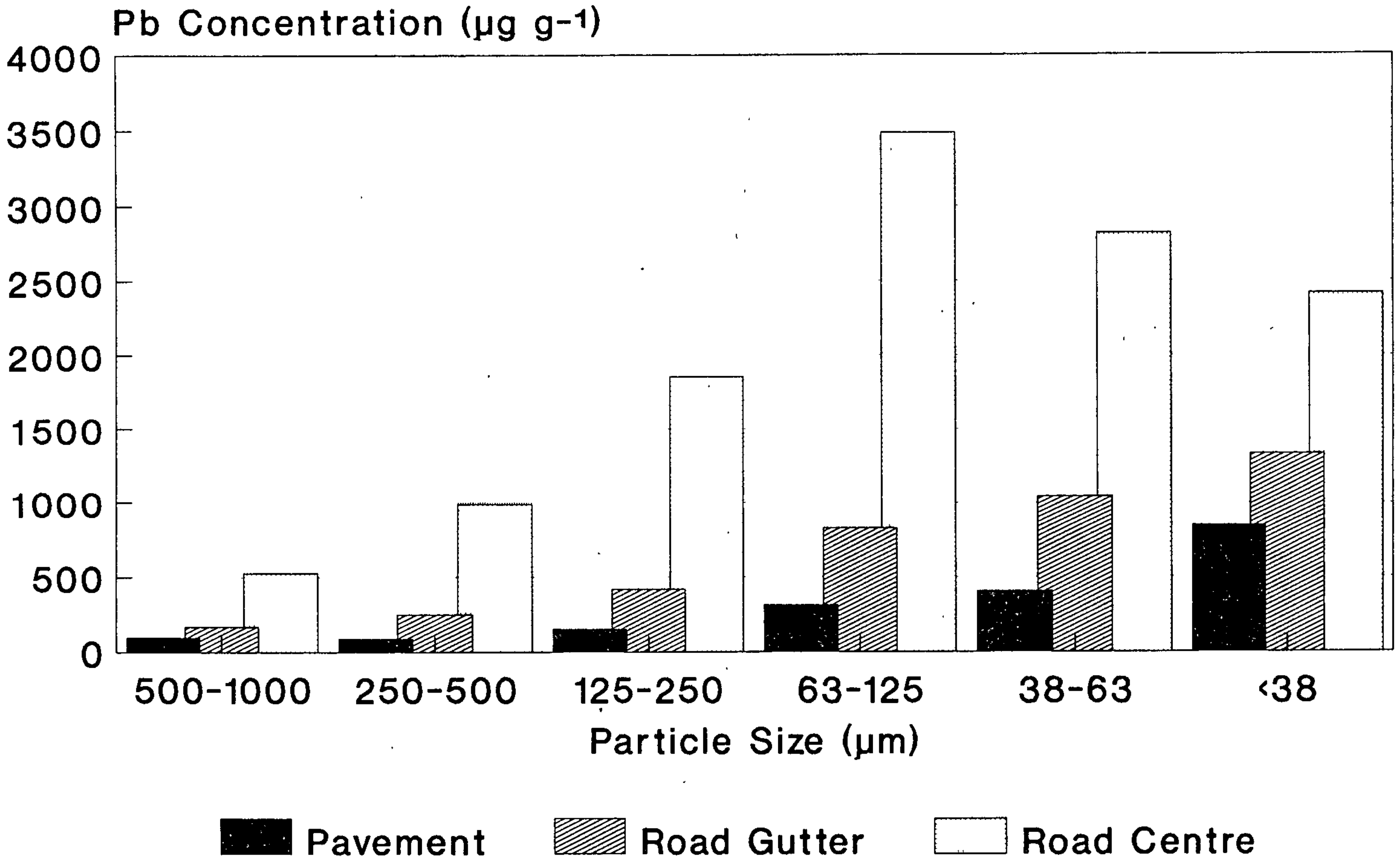


Figure 6.4 Mean Lead Concentration with Respect to Particle Size.

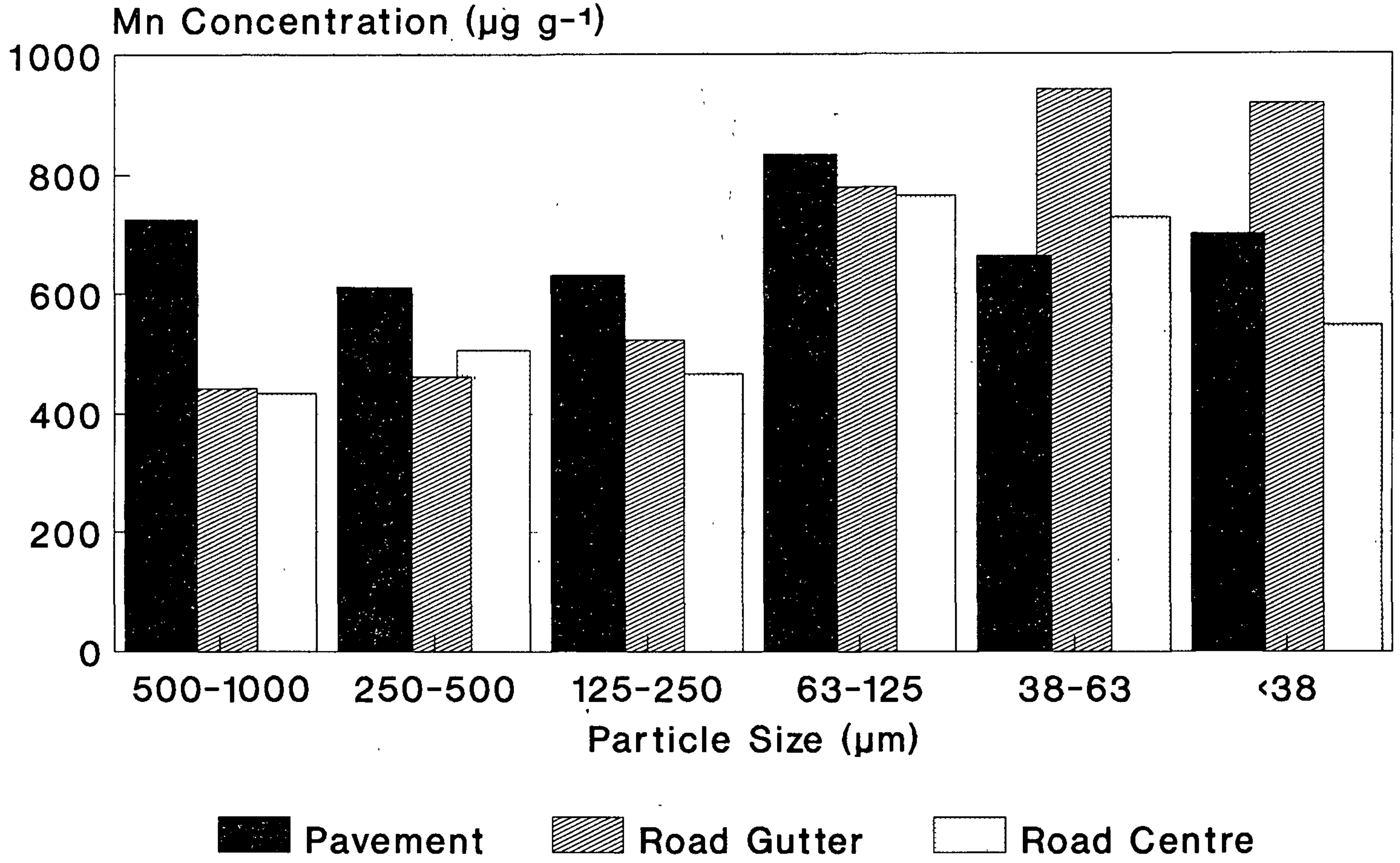


Figure 6.5 Mean Manganese Concentration with Respect to Particle Size.

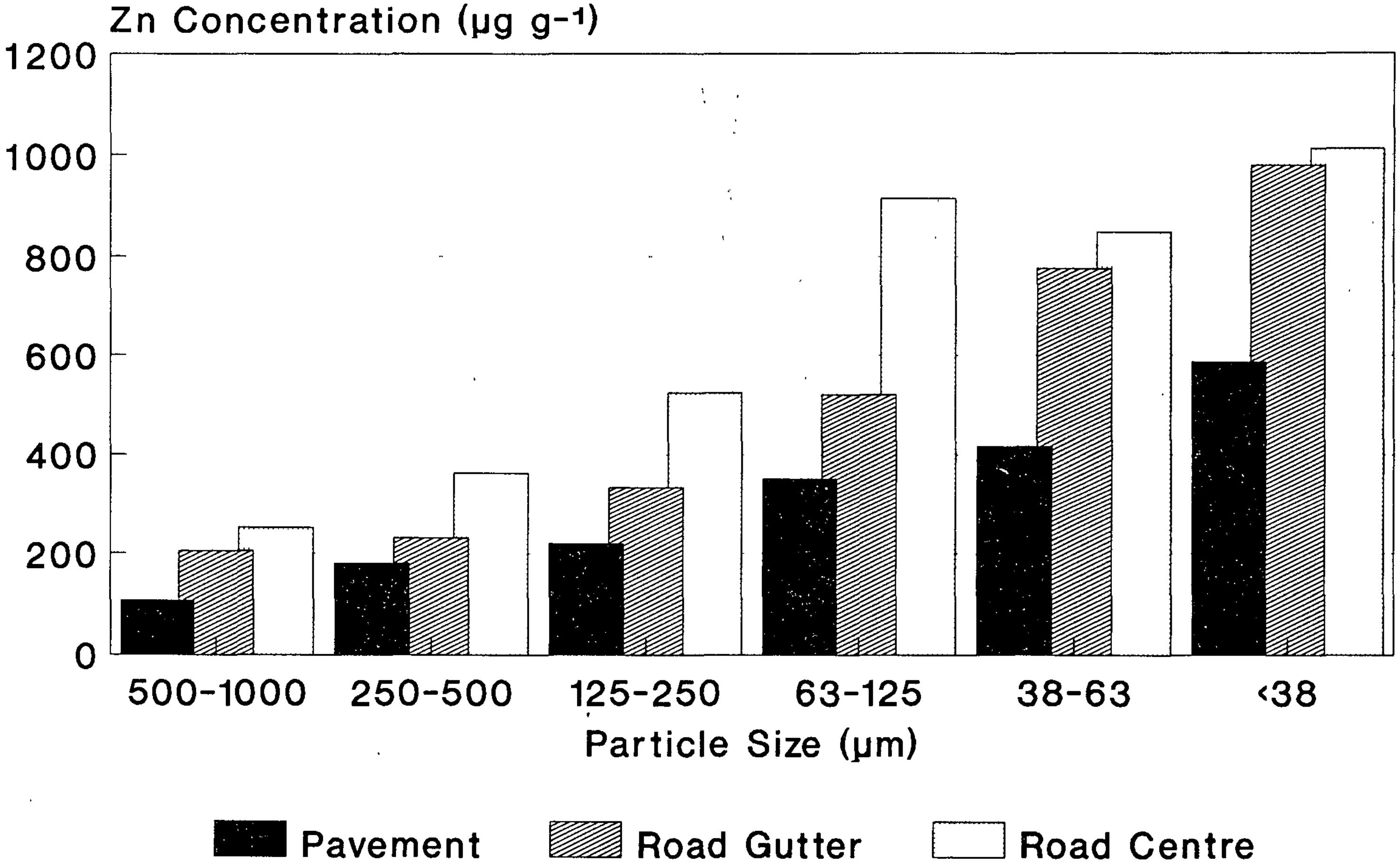


Figure 6.6 Mean Zinc Concentration with Respect to Particle Size.

generally increases with decreasing particle size. The concentrations found in the finer particle size fractions (less than 125 μm) are consistently higher than those found in the coarser particle size fractions (greater than 125 μm).

Temporal variations were not evaluated as it was felt that four samples collected at each location over eight months did not represent a sufficient data base for such variation to be assessed.

Cadmium does not exhibit spatial variations similar to those found in the examination of the bulk samples (Section 5.2.1). The tendency of Cd concentrations in bulk sediments to decrease towards the road centre is very weak and only becomes apparent in terms of the mean concentrations of many sets of samples. It could be that an insufficient number of samples were analysed with regard to particle size for the weak distribution patterns to appear and any spatial variation was obscured by the inherent variations caused by working close to the detection limits of the analytical equipment.

The spatial distribution of Cu, Pb and Zn is similar to that found in the bulk samples. There is an increase in concentration from pavement samples to road centre samples for the mean concentrations of all size fractions with the exception of Cu in the 250 μm-500 μm (Figures 6.2, 6.4, 6.6). The mean concentration of Pb in all fractions of the road surface sediment samples is greater than that of Zn except for the 500 μm-1000 μm fraction of the road gutter sediments where Zn is greater than Pb. In contrast the mean Zn concentrations are consistently greater than those of Pb in all size fractions of the pavement sediments except in the less than 38 μm fraction. This suggests that there is a greater input of particulates with higher associated Zn concentrations than Pb in the vicinity of the pavement.

Iron concentrations also exhibit similarities to the spatial distribution of concentrations found in bulk sediments with the lowest concentrations occurring consistently in the road gutter samples. The distribution of Mn concentrations with respect to location is seen to be generally similar to the bulk samples in the size fractions

63 μm-1000 μm. The greatest concentration values were observed in the pavement samples, with a decrease towards the road centre as was generally found in bulk sediments. In the 250 μm-500 μm fraction, the mean Mn concentration in the road gutter samples was slightly less than that of the road centre but both were considerably less than the mean value of the pavement sediments. The finest fractions (<63 μm) exhibit greatest mean concentrations in the road gutter samples unlike the bulk samples. This suggests that for Mn the size fractions dominating the concentrations observed in the bulk samples are those greater than 63 μm.

6.2.1 Road centre Sediments.

The road centre sediments show a tendency to have peak concentrations in the particles of size range 63 μm-125 μm. This tendency is apparent for Cu, Pb, Mn, Zn and to a lesser extent for Fe (Table 6.1; Figure 6.1-6.6). This suggests that the distribution of metal concentrations in surface road dusts is not solely a function of increased surface area with respect to diameter of a particle as this would result in an exponential increase in metal concentration throughout the particle size range.

The Cd concentrations are unique in that they generally increase with decreasing particle size (Table 6.1a; Figure 6.1). Although the mean values reflect perfectly this pattern of distribution, it should be noted that when each individual set of values of Cd concentrations in the six size fractions of the separate size fractionated bulk samples is considered, the distribution is not as obvious. An increase in Cd concentration with decreasing particle size is observed in only one set of values, there being at least one aberrant value in each of the other three sets.

Copper and Pb concentrations in the size fractions of road centre sediments were found to increase with decreasing particle size, from the 500 μm-1000 μm size fraction to the 63 μm-125 μm size fraction (Table 6.1b and 6.1d; Figures 6.2 and 6.4) followed by a decrease through the two finer size fractions. The distribution as exemplified by the mean values was observed in three of the four size fractionated samples for Cu and in all four for Pb. An increase in Cu values to the 38 μm-63 μm size fraction and a subsequent decrease in the less than 38 μm size fraction was observed in the one set of Cu values that did not conform to the distribution exhibited by the mean values.

The distribution of Zn concentrations with respect to particle size in road centre sediments was generally similar to that of Cu and Pb (Table 6.1f; Figure 6.6). The less than 38 μm size fraction of the first sample collected, however, was found to have a concentration of 2050 μg g^{-1} which resulted in a mean value indicative of a secondary peak for this finest fraction. Excluding this extreme value the mean value of Zn concentration of the less than 38 μm size fraction would be 666.6 μg g^{-1} which would result in similar distributions of mean Cu, Pb and Zn concentrations with respect to particle size.

The Fe concentrations were found to be distributed in a similar manner to that of Zn. In general, individual concentrations show that a peak concentration occurs in the 63 μm-125 μm size range, although the mean values suggest a secondary peak in the less than 38 μm size fraction. This secondary peak is due to one unusually high Fe concentration value (237.2 mg g^{-1}) in the less than 38 μm fraction of the first sample collected. This value corresponds to the high Zn value found in the less than 38 μm fraction of the same sample. If the high concentration value is excluded the mean Fe concentration in the less than 38 μm size fraction would be 23.3 mg g^{-1} and the distribution of mean concentrations would be similar to that of Cu and Pb.

Figure 6.5 shows that the distribution of Mn with particle size is generally similar to that of Cu and Pb. There is a general increase in concentration from the 500 μm-1000 μm size fraction to peak concentration values occuring in the 63 μm-125 μm size fraction, although elevated values in the 250 μm-500 μm size fraction slightly disrupt the trend compared with the distribution pattern of Cu and Pb.

There are several possible explanations for the occurrence of peak concentrations in the 63 μm-125 μm size range:

a) All source particulates with elevated Cu, Fe, Pb and Zn concentrations have nominal diameters larger than 38 μm, and probably larger than 63 μm.

b) Source particulates with elevated Cu, Fe, Pb and Zn concentrations but less than 63 μm nominal diameter are removed efficiently from the road centre by deflation and resuspension processes and/or washoff processes.

c) Source particulates with elevated Cu, Fe, Pb and Zn concentrations but less than 63 μm nominal diameter do not settle in the road centre but remain suspended in the air column by deflation processes and air turbulence.

d) Source particulates with elevated Cu, Fe, Pb and Zn concentrations but less than 63 μm nominal diameter are subject to coagulation processes resulting in the finer particulates becoming part of larger particulates.

e) Source particulates with elevated Cu, Fe, Pb and Zn concentrations but less than 63 μm nominal diameter are leached by acidic deposition even when deposition is of too low an intensity to mobilise sediment particles themselves.

g) A combination of one or more of (a) to (f).

The major source of Pb in the highway environment is known to be exhaust particulates from automobiles, the majority of which are generally less than 50 μm in diameter (Habibi, 1973). It is therefore unlikely that the observed variation of Pb concentration with particle size is due to the absence of Pb associated particulates in the less than 63 μm size range. In view of the predominant size range of exhaust particulates it might be expected that the 38 μm-63 μm and the less than 38 μm size fractions of highway sediments, nearest to the source, represented by the road centre samples, would exhibit consistently higher Pb concentrations. Hence the existence of peak Pb concentrations in the 63 μm-125 μm size range would appear to support the theory that a certain proportion of the finer Pb associated particulates are adsorbed onto larger particulates present on the road surface or that they coagulate to form larger particulates as suggested by Ellis and Revitt (1982).

Copper is likely to be derived from the abrasion of brakes. The size of particles is not well documented, however the airborne fraction makes up 4-81% of the total weight of particulates resulting from brake wear (Jacko and DuCharme, 1973; Malmqvist, 1983) and the average diameter of the airborne fraction is 3 μm (Malmqvist, 1983). It is therefore likely that particulates of less than 63 μm are deposited onto the road surface as a result of brake emissions.

It is more difficult to predict the size of Zn associated particulates as they may arise from a variety of sources, such as the wear of plated surfaces, exhaust pipes and tyres. The particulates from tyre wear have been found to range in size from 0.01 μm to 30 μm with the larger particulates dominating the total mass (Cadle and Williams, 1978). These particulates would be of a similar size range to exhaust particulates. The particulates from the mechanical failure of exhaust pipes and the 'flaking-off' of galvanised surfaces from the exhaust pipes are liable to be much larger than those of brake and tyre particulates which result from abrasion. The Zn associated particulates found on the road surface may therefore occur in a variety of size ranges. The nature of tyre particulates may make them more adhesive to the road surface as would be expected of rubberised particulates. This may also mean that the particulates make an important contribution to the agglomeration of Zn and other metal associated particulates. Noll et al (1987) have observed that rubber particulates collected from the road surface have limestone embedded in them, thought to be from wear of road surfaces. This suggests that the particulates are partial agglomerations at the time of deposition.

It would appear that agglomeration and coagulation processes are implicated as a cause of the observed Cu, Pb and Zn distribution with particle size. Several sub-samples from the size fractionated road centre sediments were subjected to Scanning Electron Microscopy. The micrographs are presented in Plates 6.1-6.3. It can be seen that there is some evidence of coagulation and agglomeration of particulates. Similar agglomerations have been observed in car park dusts (Ahmed, 1985) and street dusts (Biggins and Harrison, 1980). It cannot be determined as to whether this is agglomeration of naturally occurring

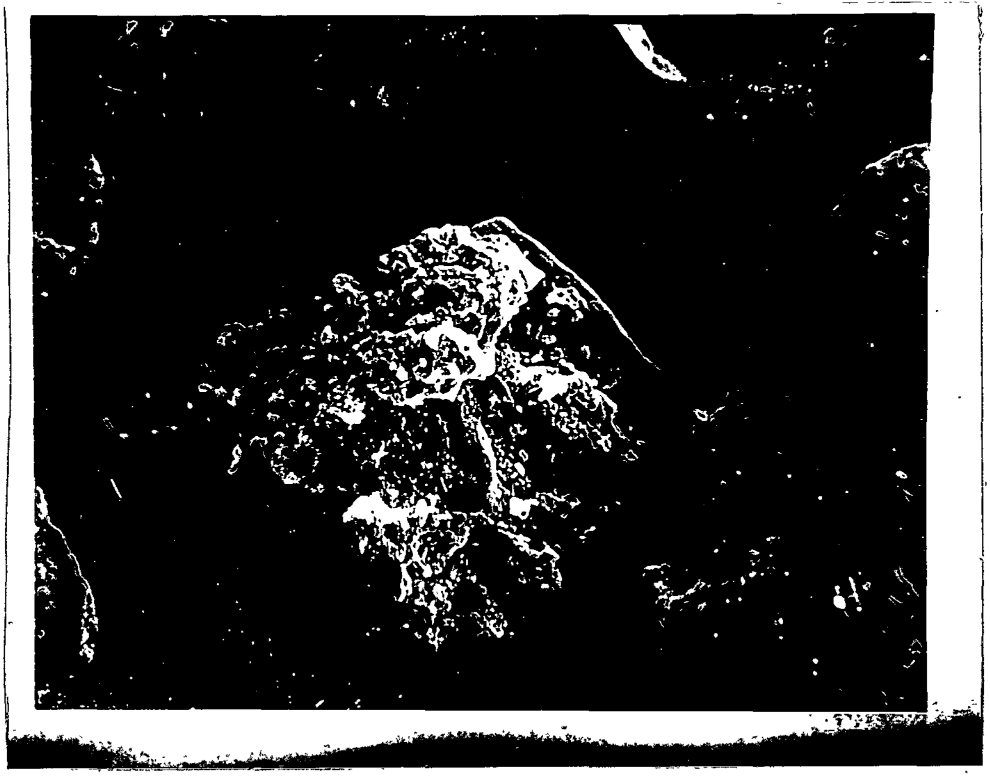


Plate 6.1 Scanning Electron Micrograph at a Magnification of 200 of Particles in the 125 µm-250 µm Size Fraction of a Road Centre Sediment Sample from the Chilwell Gardens Sub-Catchment (Note surface encrustation and satellite particles).

Plate 6.2 Scanning Electron Micrograph at a Magnification of 400 of Particles in the 63 µm-125 µm Size Fraction of Road Centre Sediment Sample from the Chilwell Gardens Sub-Catchment (Note surface encrustation and satellite particles).

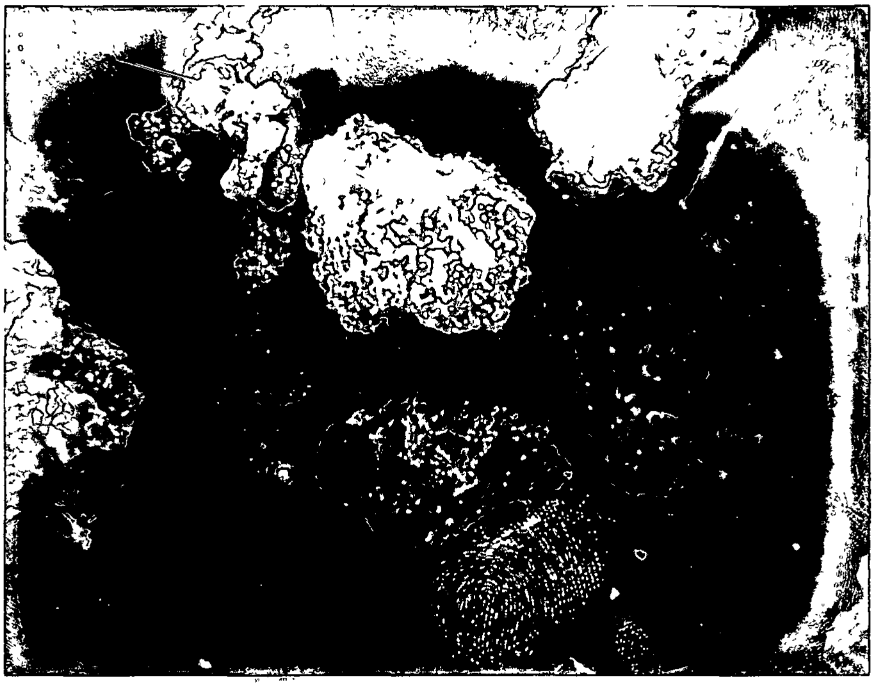


Plate 6.3 Scanning Electron Micrograph at a Magnification of 400 of Particles in the 38 μm-63 μm Size Fraction of a Road Centre Sediment Sample from the Chilwell Gardens Sub-Catchment (Note agglomerated particle in the top left hand corner of micrograph).

particulates or of small particulates with high metal concentrations. It was hoped that the nature of the particulates could be assessed by the use of dispersive X-ray fluorescence analysis in conjunction with scanning electron microscopy. Unfortunately mechanical difficulties with the equipment meant that this aspect of the work could not be followed up.

From subjective evidence it is known that particulates are re-suspended from the road surface by the passage of cars and, dependent on wind conditions, the particulates may be redistributed away from the road surface. Owing to their physical size and mass the finer particulates will remain airborne longer and will be dispersed further and therefore may not settle onto the road surface. The main argument against the removal of metal associated particulates of vehicular origin by re-suspension and deflation processes is that the spatial metal concentration gradients indicate a source in the road centre and these are dependent on increased deposition near to that source to form the gradient.

The possibility of metals in sediment on the road surface being leached by a low intensity acidic rainfall event has been suggested by Morrison et al (1988). This would certainly assist in the creation of the situation observed, although whether such conditions occur regularly enough to cause the consistency of the distribution patterns would require further investigation.

It would appear likely that Cu, Fe, Pb and Zn associated particulates finer than 63 µm are diminished in road centre sediments due to a combination of explanations (b), (d) and (e) above.

6.2.2 Road Gutter Sediments.

The distribution of metals with particle size in samples of road gutter sediments does not show the consistent patterns found in sediments from the road centre sediments. The mean Cd concentrations of the size fractionated bulk samples exhibit an increase with decreasing particle size, peaking in the 38 µm-63 µm size fraction (Figure 6.1). Of the eight bulk samples of road gutter sediments which were size fractionated only three exhibited the complete distribution of concentration with particle size as exhibited by the mean concnetrations.

The Cu concentrations in fractionated road gutter sediment samples exhibit a general increase with decreasing particle size (Figure 6.2). The levels are generally lower than those found in the road centre sediments. The mean peak gutter sediment concentration occurs in the 38 µm-63µm size range, although of the individual samples two did not conform to this distribution and exhibited a concentration increase throughout all the decreasing particle size ranges. There is an increase in Pb concentrations with decreasing particle size across all size fractions (Figure 6.4). The distribution of mean Zn concentration is similar to that of Cu and Pb with Zn concentrations increasing throughout all decreasing size fractions in six of the fractionated bulk samples (Figure 6.6). The Zn concentrations in the other two fractionated samples exhibited peak values in the 38 µm-63 µm size fraction which is similar to the mean Cu distribution. The distribution of particulates would appear to be dominated by the same processes although the nature of the particulates does exert some influence on the distribution. Atypical results were found for Zn in one sample on the western side of the road. High concentrations of 4036, 2406 and 881 μg g^{-1} were found in the less than 38 μm, the 38 μm-63 μm and 63 μm-125 μm size ranges, respectively. It is thought that these values are likely to be a consequence of vehicle maintenance practices on one of the parked cars that are normally found at this location. The exclusion of these atypical values does not change the concentration distribution pattern. However, the mean values for the less than 38 μm, 38 μm-63 μm and 63 μm-125 μm size ranges become reduced to 470.0, 533.2 and 542.8 μg g^{-1}, respectively.

Manganese concentrations generally increase from the 500 μm-1000 μm to the 38 μm-63 μm size fraction, and in three of the samples analysed the increase continued in the less than 38 μm size fraction. This would appear to be similar to the distribution of Cu, Pb and Zn, however, road gutter concentrations are generally greater than those of the road centre suggesting Mn associated particulates are not derived from the same source although they may be undergoing the same physical processes.The Fe concentration distribution with particle size in road gutter sediments is generally constant. The only variation that can be observed is a tendency for slightly higher concentrations to occur in the size fractions less than 125 μm than in those size fractions greater than 125 μm.

Unlike road centre sediments, the concentration maxima for Cu, Fe, Pb and Zn in the road gutter sediments occur in the 38 μm-63 μm or less than 38 μm size ranges. It is thought that this occurs as a result of airborne particulates of less than 63 μm being more readily trapped by the raised edge of the road gutter. The process is most probably exponential during the initial stages, such that the greater the bulk of material which collects the more readily are particulates trapped. This is particularly true in autumn when leaf litter forms a successive number of layers covering particulates and thus preventing resuspension. As materials collect, the sheltered area in the lee of the kerb becomes smaller until a balance between further deposits of material and removal by deflation occurs. This is similar to the conceptual view of the pollutant accumulation relationship adopted by computer-based urban runoff models such as the Storage, Treatment, and Overflow Runoff Model, STORM (US Army Corps of Engineers, 1974) and the Stormwater Management Model, SWMM (Lager et al, 1971).

An alternative and additional explanation is that the coagulated particulates proposed as a partial explanation for the absence of highest metal concentrations in the finest particulates in the road centre are broken down into their finer constituents as they are transported across the road surface. The effect of low intensity acidic rainfall events would also account for the preferential movement of fine particulates from the road centre and a reduction in concentration of metals associated with these particulates.

6.2.3 Pavement Sediments.

The trend for metal concentrations to increase throughout all decreasing particle sizes occurs in the pavement samples, except in the case of Mn. The difference between the concentration in the finest and coarsest fractions is generally less in the pavement sediments than that observed in the road gutter and road centre sediments.

Cadmium concentrations as represented by the mean values in (Table 6.1a; Figure 6.1) increase over the whole range of decreasing particle sizes. The distribution has greater similarity to that of the road centre sediments than those of the road gutter.

Copper concentrations generally increase with decreasing particle size in the pavement sediments, although only two samples exhibited a full increase throughout all the size ranges. The concentration distribution pattern is not clearly defined. Peak concentration values are found in the less than 38 μm size range in five out of the eight fractionated bulk samples. In the other three samples peak concentrations occur in the 38 μm-63 μm and the 63 μm-125 μm size ranges. Generally Cu concentrations in pavement sediments are less than those in road gutter or road centre sediment samples in similar size fractions. This suggests a lesser presence of Cu associated particulates than in the road gutter or road centre with a greater proportion of the particulates being in the less than 38 µm size range indicating that the major input of Cu is from airborne dispersion.

The mean concentrations of Pb increase with decreasing particle size in the pavement sediments, although two of the sieved bulk samples did not exhibit an increase throughout all decreasing particle size fractions. The concentrations are less than those in the equivalent particle size fraction of the road gutter or road centre. The peak Pb concentrations, however, consistently occur in the less than 38 µm size fraction. It is likely that the Pb asssociated particulates in the pavement sediments occur predominantly as a result of deposition of fine particulates. The Pb concentrations in the pavement sediments were found to show a bias towards one side of the road with generally higher concentrations on the east side. This was especially marked in the finer fractions (<125 µm) and increased from the 63 µm-125 µm size range to the less than 38 µm size range. The effect of cars being parked on the western side is that they would shelter the adjacent pavement from some of the dispersed fine particulates thus lowering the concentration.

The Mn concentrations in pavement sediments are greater than those of the road gutter and road centre in the size fractions greater than 63 µm. There is no definite distribution with particle size and individual samples exhibit peak concentrations in the 63 µm-125 µm, 125 µm-250 µm and 500 µm-1000 µm size ranges. It would appear from the concentration gradient that there is an indication of an input of Mn from the vicinity of the pavement. Similar levels of Mn have been cited as reflecting their derivation from soil (Harrop et al, 1983). It is possible that soil particulates are being blown onto pavement surfaces and then to road surfaces from surrounding gardens. Washoff of soil from gardens is not possible owing to the position of the gardens which slope away from the pavement. Additionally soil particulates may be carried to the pavement adhered to the shoes of pedestrians.

Zinc concentrations in the pavement sediments are distributed in a similar manner to those of Cu and Pb. Thus a more even concentration gradient, with occassional reversals is observed, with an overall lower concentration than the corresponding road gutter samples. Atypical values, corresponding to those found in one fractionated road gutter sample, are also observed. In the case of the pavement, the aberration was restricted to the less than 38 µm and 38 µm-63 µm size ranges. This reinforces the idea of an isolated pollution event resulting from vehicle maintenance activities. Consequently the explanation that the bias of elevated Cu and Zn concentrations found on the western side of the road for bulk samples (Section 5.1.1) occurs as a result of maintenance practices appears to be correct.

The metal gradients are not exponential and occur over a lesser range than those for the road gutter and road centre. This suggests that surface area dependent uptake is not the dominant process controlling metal concentrations in pavement sediments. The decreased concentration range also suggests an input of particulates with low metal concentrations, which is thought to include organic debris from trees surrounding the sub-catchment, as well as the possible input of soil.

6.2.4 Roof Gutter Sediments.

The metal concentrations and ranges in fractionated bulk roof gutter sediments are presented in Table 6.2 and show that the mean concentrations of all metals increase with decreasing particle size. The only deviations from this trend are for Cd and Mn which show slight decreases in going from the 38 µm-63 µm size range to the less than 38 µm size range and for Fe where there is an intermediate peak in the 250 µm-500 µm size fraction.

Comparison of Tables 6.1 and 6.2 reveals that the Cd concentrations found in roof gutter sediments are generally less than those found in highway associated sediments. The Cu, Pb, and Zn concentrations in roof gutter sediments are similar to those of the pavement or road gutter sediments, although less than the road centre sediments. The major

Table 6.2 Metal Concentration Ranges and Mean for Fractionated Roof Gutter Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Cd	0-0.64 (0.34)	0.82-1.04 (1.06)	1.13-2.24 (1.72)	3.44-5.6 (4.2)	4.61-9.05 (6.86)	4.27-6.9 (6.01)
Cu	16.2-19.1 (18.1)	21.4-28.3 (25.4)	30.3-54.3 (45.5)	65.6-92.4 (79.7)	68.7-134.2 (98.8)	65.8-170.5 (119.4)
Fe	26.5-32.4 (30.5)	37.0-38.0 (37.6)	20.1-46.7 (35.0)	52.8-67.9 (58.4)	50.1-85.7 (71.2)	54.4-112.7 (91.3)
Pb	145.0-177.4 (159.4)	171.2-294.2 (216.7)	376.9-421.7 (392.2)	1102.4-1113.4 (1107.3)	1069.6-1319.1 (1227.8)	1399.0-1791.6 (1560.7)
Mn	185.7-290.9 (235.9)	184.8-393.9 (307.40	203.4-419.7 (325.0)	401.3-861.1 (648.3)	602.4-765.2 (702.3)	608.8-791.8 (700.3)
Zn	146.9-199.2 (165.9)	200.9-206.2 (203.2)	294.0-532.4 (430.7)	745.1-932.2 (843.0)	901.1-1005.8 (943.6)	873.2-1032.3 (964.5)

Mean values in parentheses

differences in metal concentrations between the highway associated surface sediments and the roof gutter sediments are exhibited by Fe and Mn concentrations. The Mn concentrations are generally less than those of highway associated sediments and exhibit a distinct increase throughout all decreasing particle sizes. The construction material of the roof gutter is reflected by high Fe concentrations which generally increase with decreasing particle size.

The consistent trend of increasing metal concentrations with decreasing particle size suggests that the roof gutter sediment is not affected by resuspension and deflation processes in the same way as highway associated sediments and consequently, the concentration distribution is mainly a function of surface adsorption. It also suggests that runoff/washoff processes are efficient for all size ranges, which considering the design and purpose of roof surfaces and guttering would seem appropriate.

6.2.5 Sub-Surface Sediments.

Samples of gully pot sediments and in-pipe deposits were analysed for metals with respect to particle size (Tables 6.3 and 6.4). Generally metal concentrations increase with decreasing particle size, although the in-pipe sediments sampled from below the confluence of the roof and road drains are least consistent in exhibiting this trend.

By comparing Tables 6.1, 6.2, 6.3 and 6.4 the variation of the distribution of metal with particle size throughout the drainage system from surface source to the exit from the sub-catchment can be investigated. In the case of Cd there are no obvious patterns although it was noted that the concentrations in the gully pots are generally greater than those of the road gutter sediments and for sediments of particle size greater than 63 µm the gully pot sediment Cd concentrations are greater than those of the equivalent particle size range in road centre or pavement sediments (Figure 6.1 and 6.7). This would appear to substantiate the suggestion in Section 5.2.3 that the increase in concentration of sediments in the gully pot compared to

Table 6.3 Metal Concentration Ranges and Mean for Fractionated Gully Pot Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Cd	0-3.38 (1.56)	0-3,4 (2.38)	2.28-4.41 (3.36)	0.96-4.8 (2.72)	2.86-3.76 (3.47)	1.54-5.28 (4.04)
Cu	31.9-88.4 (62.2)	18.0-75.0 (57.9)	43.8-240.0 (119.6)	76.7-109.9 (90.0)	94.1-125.3 (102.1)	105.2-186.7 (136.3)
Fe	16.2-29.5 (20.4)	15.3-24.4 (19.1)	19.9-37.3 (28.1)	21.2-43.1 (28.7)	22.5-50.1 (40.2)	24.2-60.4 (40.7)
Pb	146.3-923.2 (409.7)	203.1-678.5 (406.4)	502.1-1523.6 (806.3)	626.6-1036.4 (778.3)	731.8-1004.7 (845.1)	745.4-2190.4 (1182.2)
Mn	276.4-587.4 (434.9)	192.3-419.6 (351.4)	339.2-829.5 (604.0)	402.9-566.1 (453.5)	393.7-568.4 (465.9)	412.7-765.9 (526.1)
Zn	254.0-454.8 (386.0)	225.0-483.9 (376.4)	447.3-1004.8 (662.1)	427.9-912.2 (607.8)	561.8-937.2 (695.9)	641.6-1750.6 (966.6)

Mean values in parentheses
All values in μg g^{-1} except for Fe in mg g^{-1}

Table 6.4 Metal Concentration Ranges and Means for Fractionated In-Pipe Deposited Sediments.

		Particle Size (μm)					
		500-1000	250-500	125-250	63-125	38-63	<38
Cd	(a)	0.83,0.87	0.7,1.12	0.56,1.77	0.18,5.18	2.18,2.55	0,1.72
	(b)	0.21	0.86	1.3	3.98	4.66	8.43
Cu	(a)	23.1,44.9	18.7,21.2	38.8,88.1	68.7,98.5	72.5,87.3	66.2,98.1
	(b)	18.8	26.4	36.7	51.7	89.1	130.9
Fe	(a)	36.5,53.9	22.5,45.5	39.7,60.4	39.1,43.6	47.4,57.8	39.4,57.2
	(b)	28.5	32.6	35.5	46.2	63.8	100.3
Pb	(a)	152.2,236.3	149.7,258.5	379.3,415.7	649.2,692.2	767.1,777.6	688.6,725.4
	(b)	104.3	188.7	383.0	982.6	1277.7	1460.7
Mn	(a)	295.5,341.6	182.4,243.7	317.6,388.8	669.4,725.2	688.4,706.3	618.2,633.9
	(b)	319.4	302.8	295.4	626.7	568.4	549.7
Zn	(a)	218.6,282.6	205.1,232.7	325.7,431.6	618.6,677.9	744.0,801.0	732.4,734.8
	(b)	112.6	166.2	326.5	873.2	1003.9	1001.2

All values in μg g^{-1} except for Fe in mg g^{-1}
a) In-pipe sediment below confluence of roof and road drains.
b) In-pipe sediment in roof drain only.

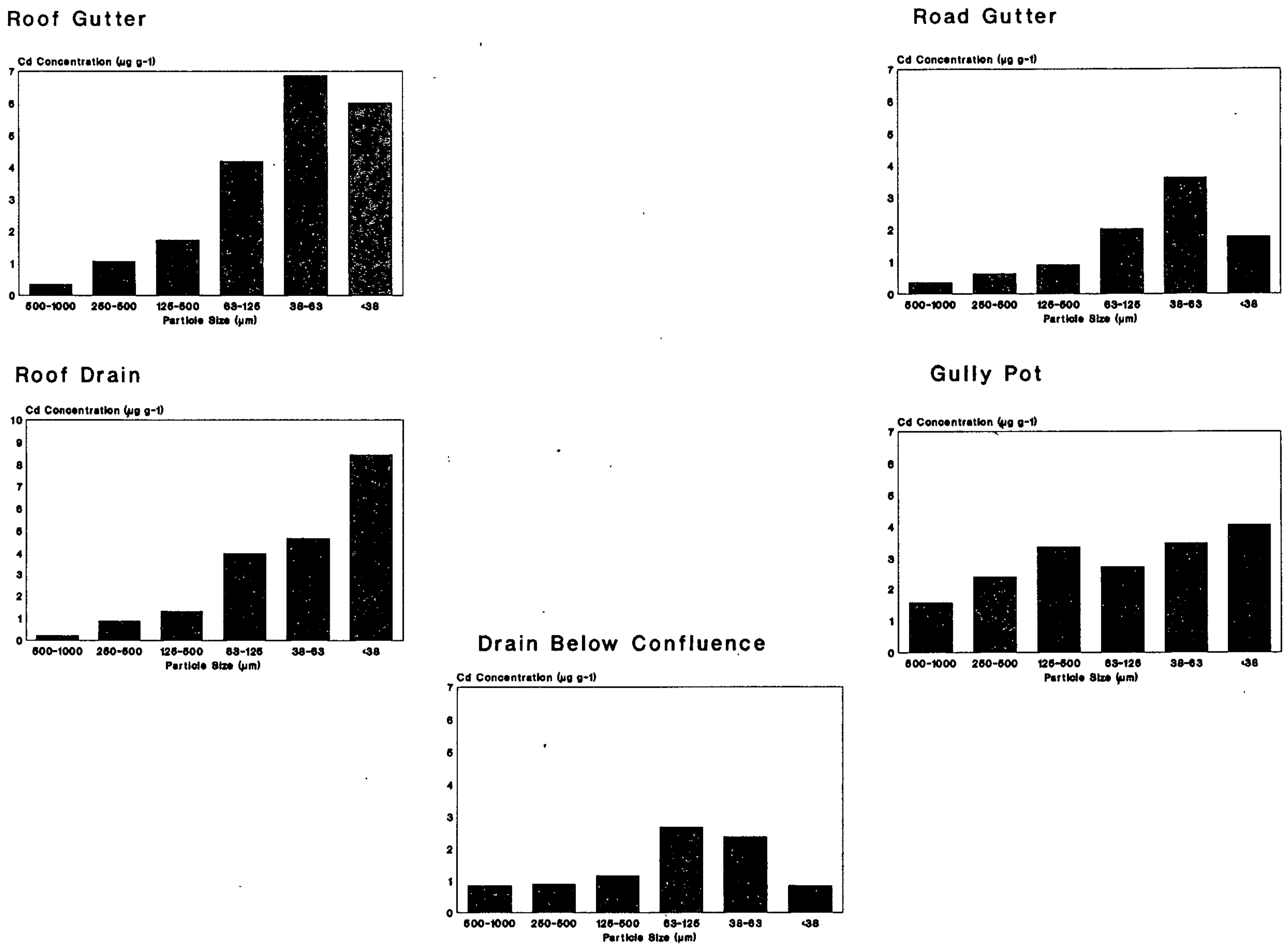


Figure 6.7 Mean Cd Concentrations (µg g-1) with Respect to Particle Size in Surface and Sub-Surface Source Sediments.

those of the road gutter are not a function of preferential washoff of fine particles from the road centre sediments but result from the physical and biochemical reactions within the gully pot itself. The in-pipe deposits below the confluence exhibit generally lower concentrations of Cd than all size fractions of gully pot sediments and the roof gutter sediment finer than 250 µm. This may arise as a result of sediment dilution by inputs from undefined sources such as soil from French drains, or more probably it indicates the chemical solubilisation of Cd from the sediment which at the sampling point below the confluence has had the longest residence time within the sub-surface system. Morrison et al (1988) indicated that acid rain may solubilise the exchangeable metal which is weakly adsorbed on the surface of road dusts. With an increased exposure time metals may also be solubilised from the carbonate and hydrous oxide phases.

Investigation of the variation of Cu, Fe, Pb and Zn concentrations with particle size indicates that generally gully pot sediment concentrations are elevated compared to road gutter sediments (Tables 6.1b, 6.1d, 6.1f and 6.3; Figures 6.8-6.10 and 6.12). The exceptions to this are Pb concentrations in the size range less than 125 µm, and Zn concentrations in the size range less than 63 µm. The Cu, Fe, Pb and Zn concentrations in the in-pipe deposits in the roof drain are similar to those of the roof gutter (Tables 6.2 and 6.4; Figures 6.8-6.10 and 6.12). There appears to be limited transformation of roof derived sediments upon entry to the drainage system. The sediment samples from below the confluence indicate the mixing of the roof and road derived sediments to produce sediments with intermediate characteristics of the surface source sediments (Figures 6.8-6.10 and 6.12). The sub-surface Fe concentrations exhibit the mixing of sediments with the high roof derived sediment concentrations being diluted by the road derived sediments. The concentrations in the finer size ranges are less than the immediate source sediments. In a similar manner to Cd, there is possible dilution or solubilisation of Cu, Fe, Pb and Zn concentrations, but it is restricted to the finer fractions. This suggests that a surface area influenced process such as chemical solubilisation is the cause.

The distribution of Mn does not exhibit any distinct patterns. The

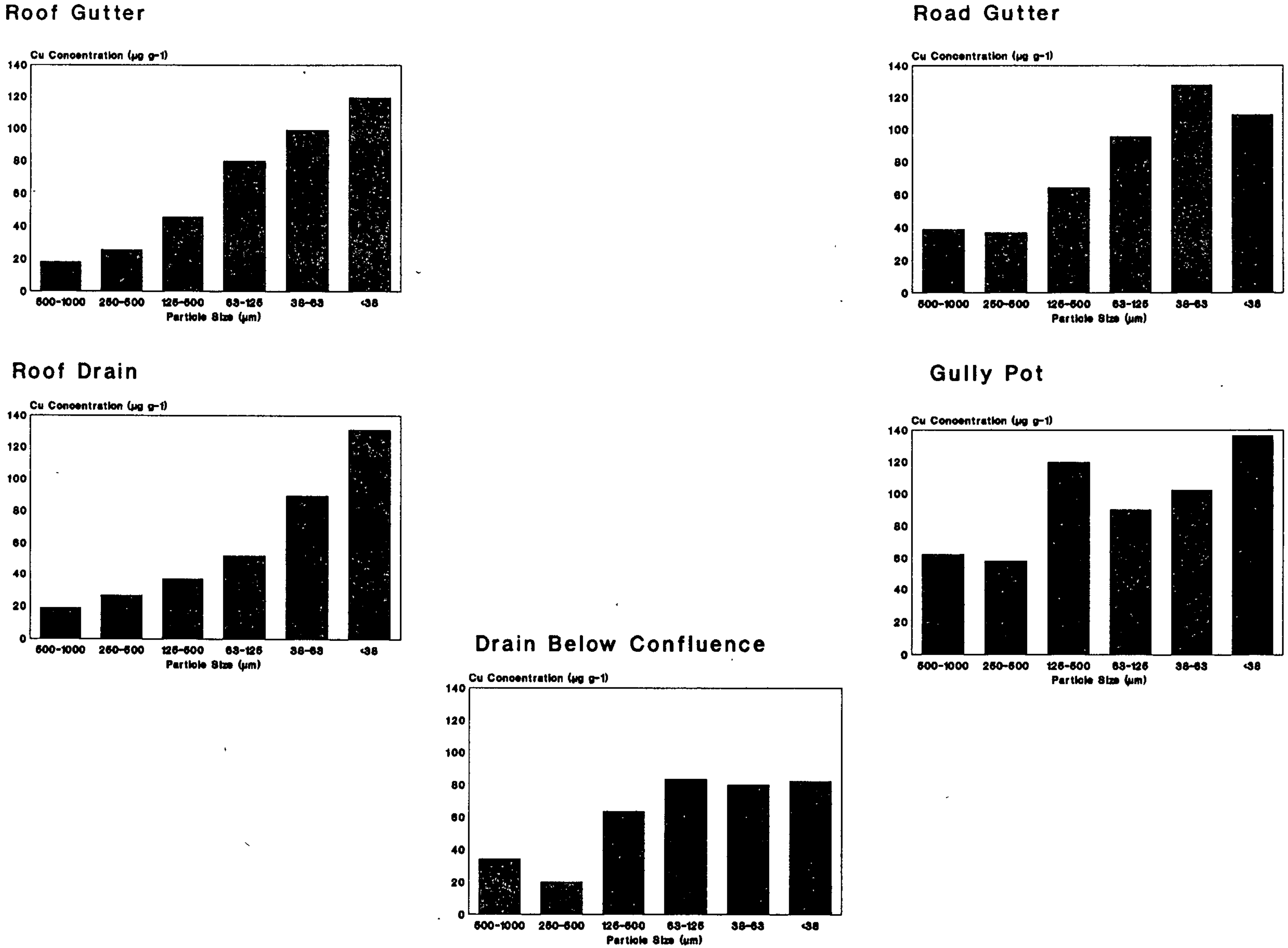


Figure 6.8 Mean Cu Concentrations (µg g-1) with Respect to Particle Size in Surface and Sub-Surface Source Sediments.

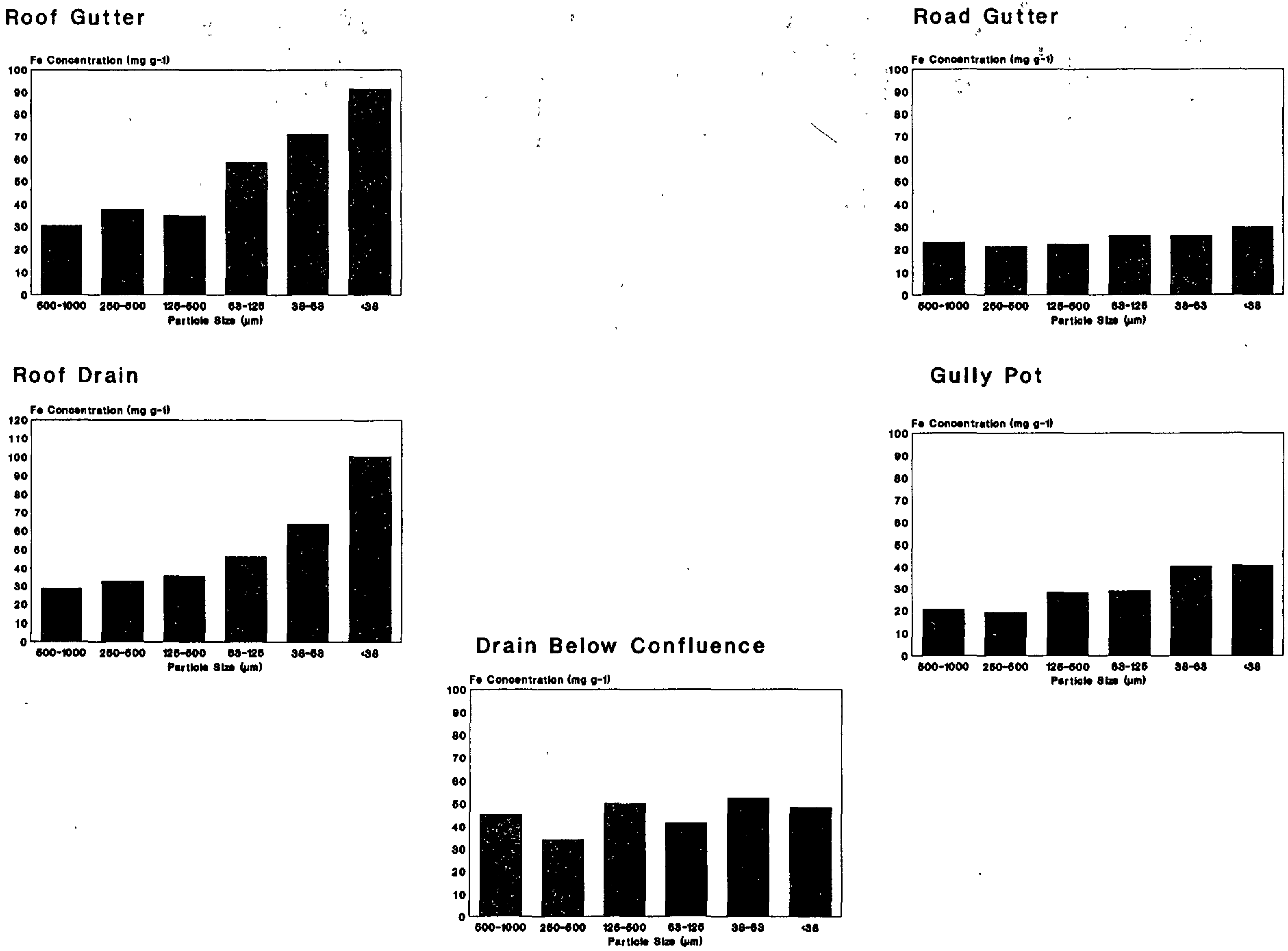


Figure 6.9 Mean Fe Concentrations (mg g-1) with Respect to Particle Size in Surface and Sub-Surface Source Sediments.

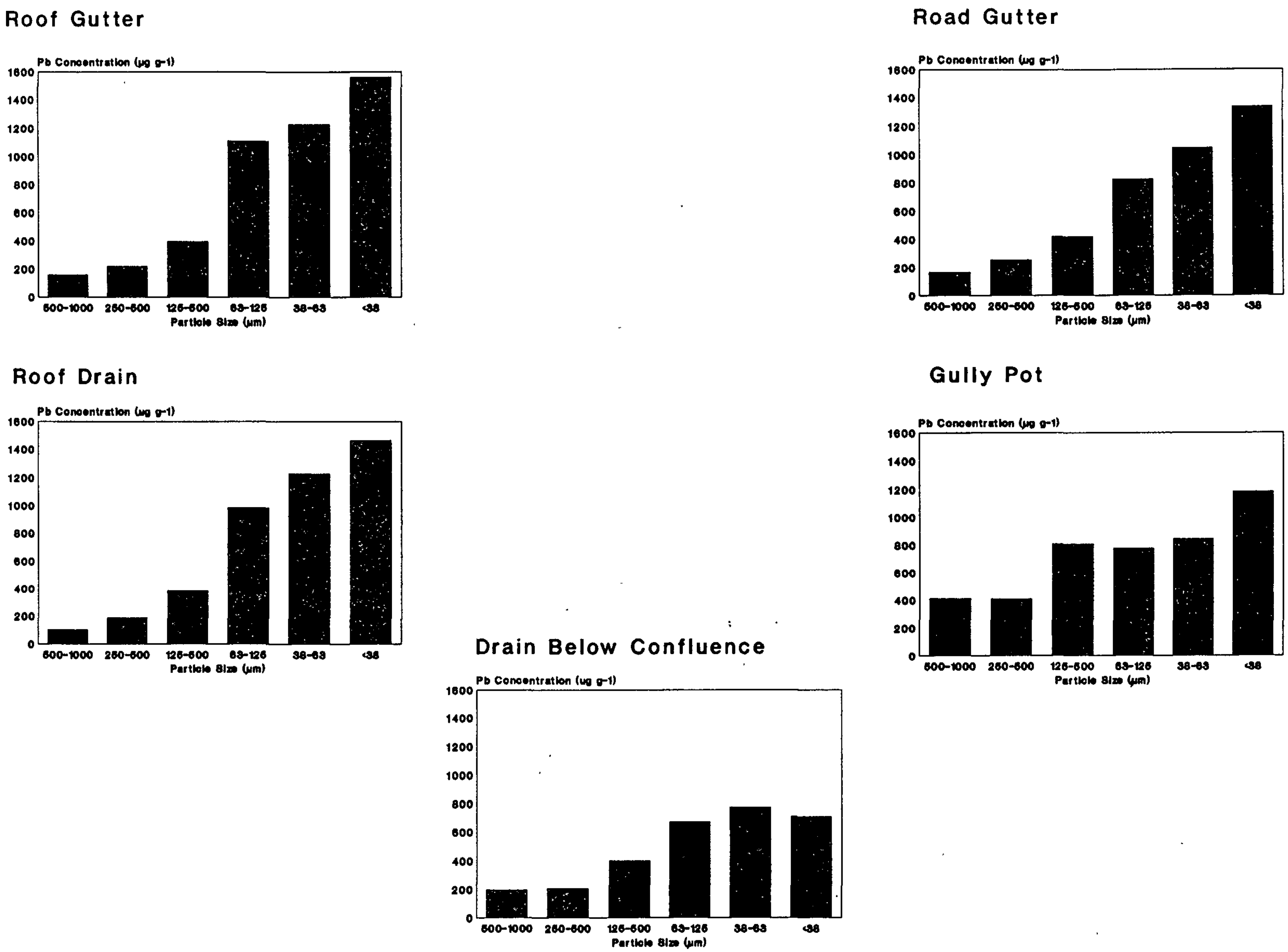
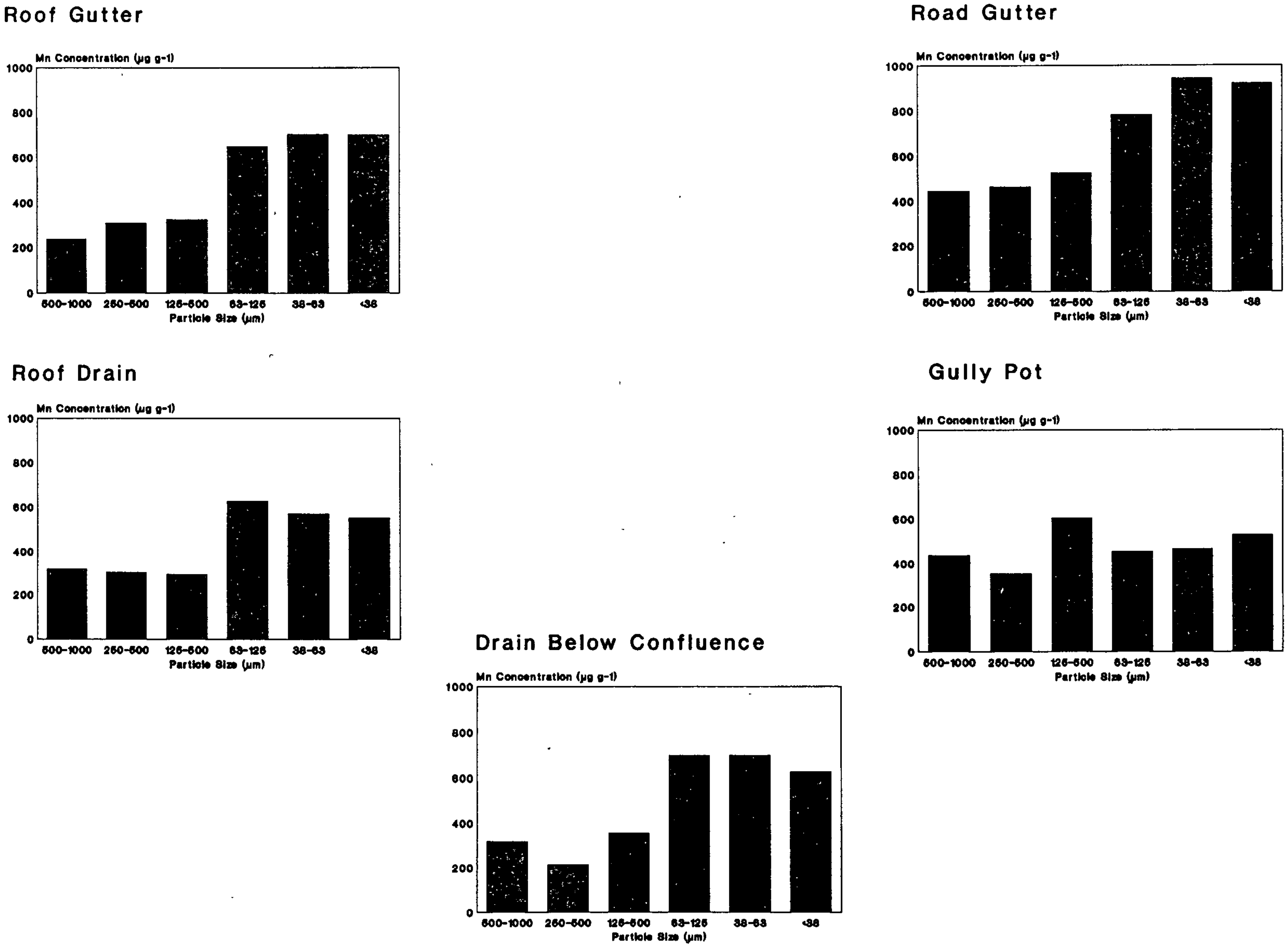


Figure 6.10 Mean Pb Concentrations (µg g-1) with Respect to Particle Size in Surface and Sub-Surface Source Sediments.



Roof Gutter

Road Gutter

Roof Drain

Gully Pot

Drain Below Confluence

Figure 6.11 Mean Mn Concentration (µg g-1) with Respect to Particle Size in Surface and Sub-Surface Source Sediments.

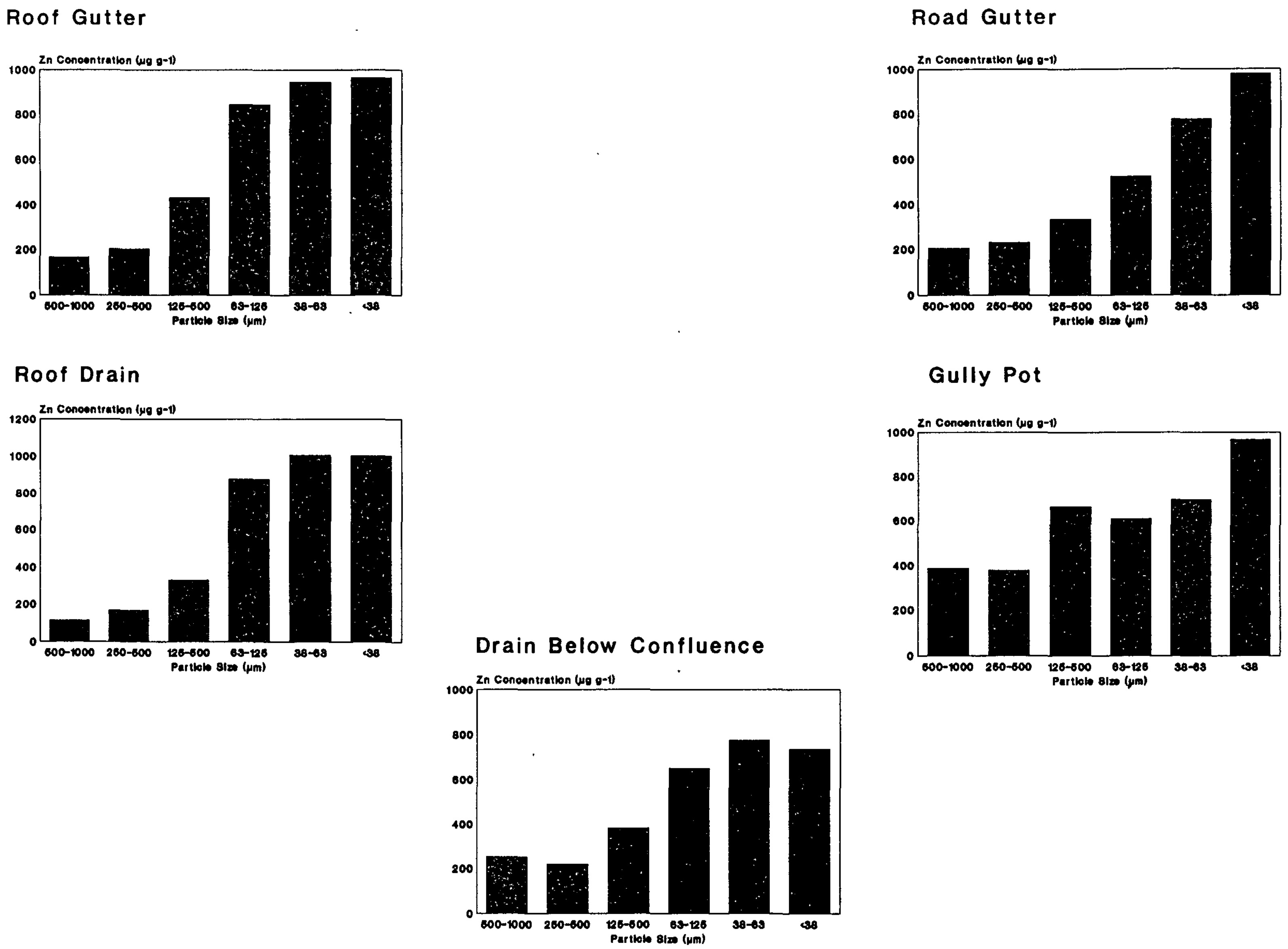


Figure 6.12 Mean Zn Concentrations (µg g-1) with Respect to Particle Size in Surface and Sub-Surface Source Sediments.

concentrations in the size fractions greater than 125 μm are generally of greater magnitude than those of size fractions less than 125 μm (Figure 6.11). The Mn concentrations in the sub-surface sediments are generally slightly less than those of the surface sediments. Unlike Cu, Fe, Pb and Zn, the Mn concentrations in the finer fractions of the in-pipe deposits below the drainage confluence are greater than the Mn concentrations in equivalent size fractions of gully pot sediments or in-pipe deposits within the roof drain (Figure 6.11). This cannot be taken to refute the suggestion of dilution of sediments by soil particulates as unpolluted subsoil normally posseses relativley high Mn concentrations (Webb, 1978).

6.3 Sediment and Heavy Metal Loadings with Respect to Particle Size.

Heavy metal concentrations have been seen in the preceding sections to vary with particle size, generally increasing with decreasing particle size. It has been indicated that the metals associated with fine particle sizes are most liable to be accidentally ingested by children (Duggan, 1983), inhaled (Rameau, 1972; Chamberlain et al, 1978; Laxen et al, 1985) and preferentially removed by runoff (Revitt et al, 1982; Harrison and Wilson, 1983). Investigations of street sweeping have shown that this efficiently reduces the mass of particulates greater than 2000 μm (Section 2.3.5). The efficiency of street sweeping decreases with decreasing particle size and therefore the distribution of metal loadings with particle size is important when assessing the use of street sweeping as a control mechanism in areas similar to Chilwell Gardens.

6.3.1 Sediment Loadings.

The data for the size fractionated sediments shows that the road gutter samples, as was found in the case of bulk samples, are responsible for the greatest sediment loadings (Table 6.5). This emphasises the ability of the raised kerb edge to trap particulates. The sediment loadings for

Table 6.5 Sediment Loadings (g m^{-2}) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	1,7-22,79 (10,68)	1,35-25,64 (11,67)	1,21-14,28 (9,38)	0,18-5,14 (3,17)	0,04-2,21 (1,36)	0,06-1,17 (0,51)
Road Gutter	14,62-45,5 (32,18)	15,95-54,35 (33,1)	3,9-53,68 (24,55)	0,42-19,21 (7,77)	0,27-8,34 (3,07)	0,11-4,15 (1,53)
Road Centre	3,4-9,04 (5,37)	2,18-7,12 (4,02)	0,58-4,37 (1,19)	0,14-0,69 (0,31)	0,08-0,34 (0,16)	0,01-0,19 (0,07)

Mean values in parentheses

each size fraction show that the road gutter normally carries three times the loading of the pavement sediment in each size fraction, and six to twenty times that of the road centre depending on the particle size fraction concerned.

The road centre sediments are found to be depleted in the less than 250 µm size ranges compared to the road gutter and pavement. The dominant size fraction with regard to sediment loadings in the road centre sediments is seen in Figure 6.13 with the 250 µm-1000 µm particulate size fractions making up 84.4% of the total loadings. This compares to less than 66% of the total loading being made up by these fractions in road gutter and pavement sediments. This suggests that there is efficient removal of the particulates finer than 250 µm from the road centre by resuspension, deflation and washoff.

6.3.2 Heavy Metal Loadings.

6.3.2.1 Highway Associated Surfaces.

The heavy metal loadings for each size fraction are presented in Tables 6.6a-f. A total loading was calculated from the sum of the individual

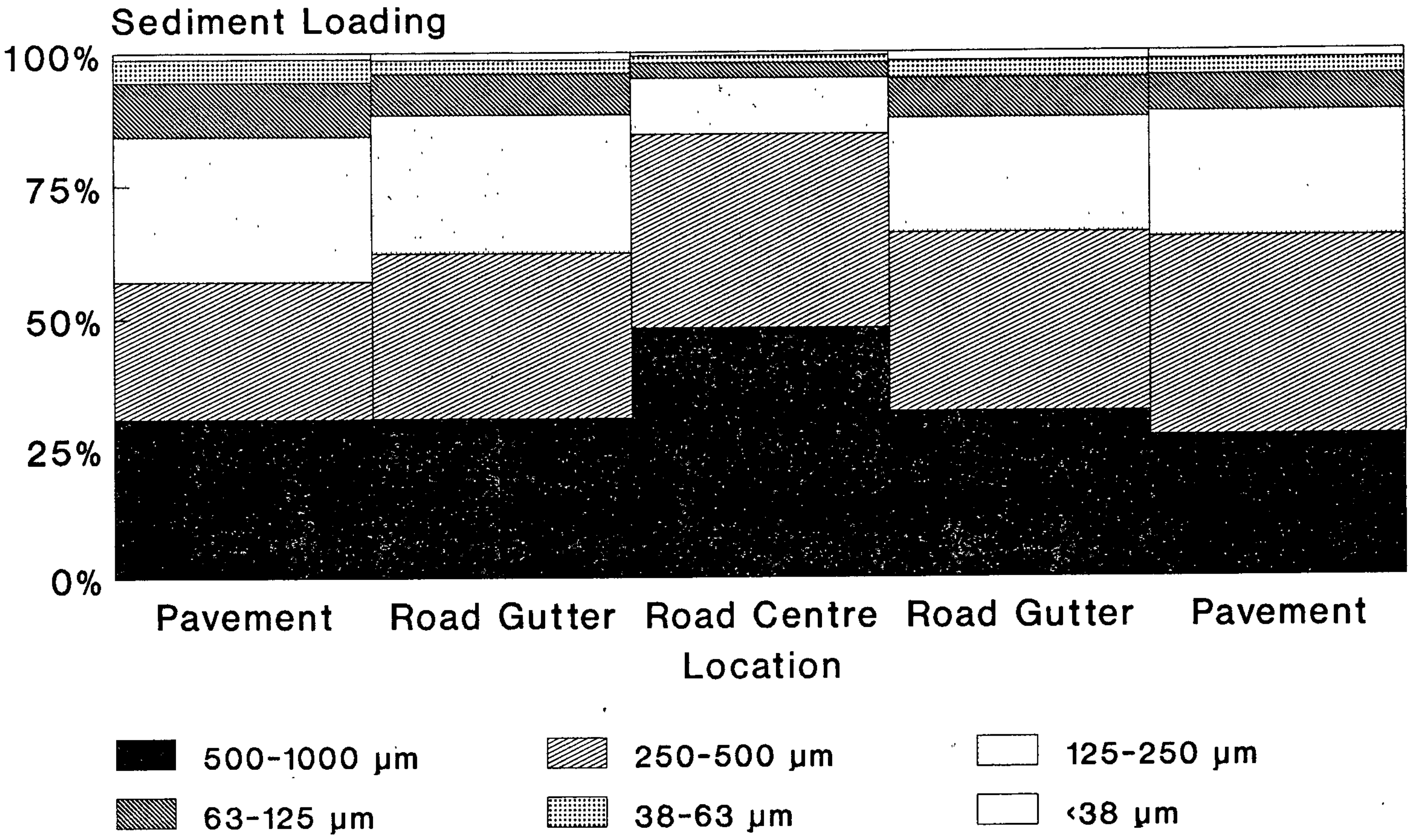


Figure 6.13 Sediment Loadings with Respect to Particle Size.

Table 6.6a Cadmium Loadings (µg m^{-2}) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	udl-15.9 (4.7)	udl-14.8 (6.7)	1.2-20.6 (8.5)	0-9.3 (3.5)	0.6-3.8 (2.2)	0-4.7 (2.1)
Road Gutter	udl-47.7 (12.9)	udl-46.8 (20.4)	4.7-45.1 (19.4)	udl-31.6 (9.4)	0.8-11.2 (4.1)	udl-9.5 (3.0)
Road Centre	udl-4.3 (1.81)	1.0-10.2 (3.61)	0.4-2.8 (1.28)	udl-0.8 (0.35)	0.2-1.0 (0.42)	0.03-2.5 (0.81)

Mean values in parentheses udl = Under detection limits

Table 6.6b Copper Loadings (µg m^{-2}) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	109-562 (310)	70-782 (437)	43-801 (402)	9-848 (294)	3-150 (86)	4-130 (50)
Road Gutter	426-1878 (1242)	453-2379 (1274)	330-6677 (1754)	37-1996 (654)	13-1066 (395)	4-444 (168)
Road Centre	60-610 (280)	57-719 (310)	46-739 (423)	3-169 (85)	1-45 (27)	1-19 (8)

Mean values in parentheses

Table 6.6c Iron Loadings (mg m^{-2}) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	59-600 (265)	44-399 (254)	28-305 (102)	6-168 (81)	1-60 (35)	3-31 (16)
Road Gutter	372-1034 (710)	336-1118 (660)	82-1127 (556)	10-510 (205)	3-186 (77)	3-145 (50)
Road Centre	74-267 (146)	39-235 (120)	10-103 (47)	4-34 (13)	0-12 (5)	1-6 (3)

Mean values in parentheses

Table 6.6d Lead Loadings ($\mu g\ m^{-2}$) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	205-2226 (780)	86-1287 (872)	291-2004 (1155)	91-2009 (907)	40-918 (476)	48-979 (327)
Road Gutter	1711-15447 (5443)	2282-22831 (8973)	1177-24948 (10457)	288-17952 (6331)	168-7060 (2795)	155-4216 (1611)
Road Centre	3911-5043 (2790)	729-5779 (3307)	245-3967 (2166)	95-1747 (800)	19-624 (307)	17-336 (111)

Mean values in parentheses

Table 6.6e Manganese Loadings ($\mu g\ m^{-2}$) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	1406-17843 (7704)	960-10619 (6385)	686-9707 (5792)	108-7003 (2664)	25.6-1511 (864)	41-853 (344)
Road Gutter	6005-20297 (14415)	8169-26757 (14899)	2656-27702 (12452)	512-15670 (5323)	277-6100 (2483)	79-3580 (1350)
Road Centre	1142-3820 (2247)	556-4424 (2271)	220-1040 (542)	30-380 (166)	6-132 (72)	6-56 (25)

Mean values in parentheses

Table 6.6f Zinc Loadings ($\mu g\ m^{-2}$) in Size Fractions of Highway Associated Surface Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	166-2044 (1121)	176-2906 (1839)	306-3351 (1839)	51-2308 (1138)	14-897 (523)	21-510 (253)
Road Gutter	3629-12109 (6429)	2209-19383 (7788)	961-22177 (8430)	168-9955 (4117)	70-4796 (2157)	14-2402 (1102)
Road Centre	698-1341 (1053)	465-2740 (1457)	104-1144 (610)	27-532 (224)	5-228 (105)	13-116 (42)

Mean values in parentheses

loadings in each size fraction. Comparison of these loadings to those calculated from the bulk sediment metal concentrations and weights for the relevant samples indicate an agreement of ±10%. Cadmium values were an exception, and this is almost certainly due to the fact that if the concentration of the bulk sample is below the detection limits then the resultant loading is zero even though concentrations may be detected in the size fractionated sediment giving a positive loading to the totalled bulk value.

The metal loadings are similar to the bulk sediment loadings in that the road gutter loadings in each size fraction dominate compared to other sampling locations (Table 6.6). Greater metal loadings occur in the coarser than 125 µm size ranges despite metal concentrations exhibiting higher values in the less than 125 µm size ranges (Tables 6.5 and 6.6; Figures 6.14-6.19). Sediment, Cd, Fe, Pb, Mn and Zn loadings for the road centre are dominated by the particulates coarser than 250 µm (Figures 6.13-6.19).

Unlike bulk sediments the metal loadings were not completely dominated by sediment loadings for all the fractionated sediments. The influence of the metal concentrations on the metal loadings is greatest with regard to the 125 µm-250 µm size fraction where the metals show significant differences from the sediment distribution. The sediment loading in this size fraction in the road centre sediments is 11.7% whereas for Cd, Cu, Fe, Pb, Mn and Zn it is 15.5, 37.4, 14, 22.8, 10.2 and 17.5%, respectively (Figures 6.14-6.19). It can be seen that Mn concentrations have little influence on the loadings while Cu, Pb and Zn have the greatest influence. This again accentuates the similarities between Cu, Pb and Zn loading distributions.

Cadmium loadings exhibit a greater percentage loading in the less than 38 µm size fraction of the road centre sediments than the pavement or road gutter sediments. This would seem to refute the suggestion that particulates are dispersed or removed from the road centre. However, inspection of the data reveals that this loading is a result of extremely high Cd concentrations being found in this size fraction and in terms of weight, the mean Cd loadings in this size fraction in the

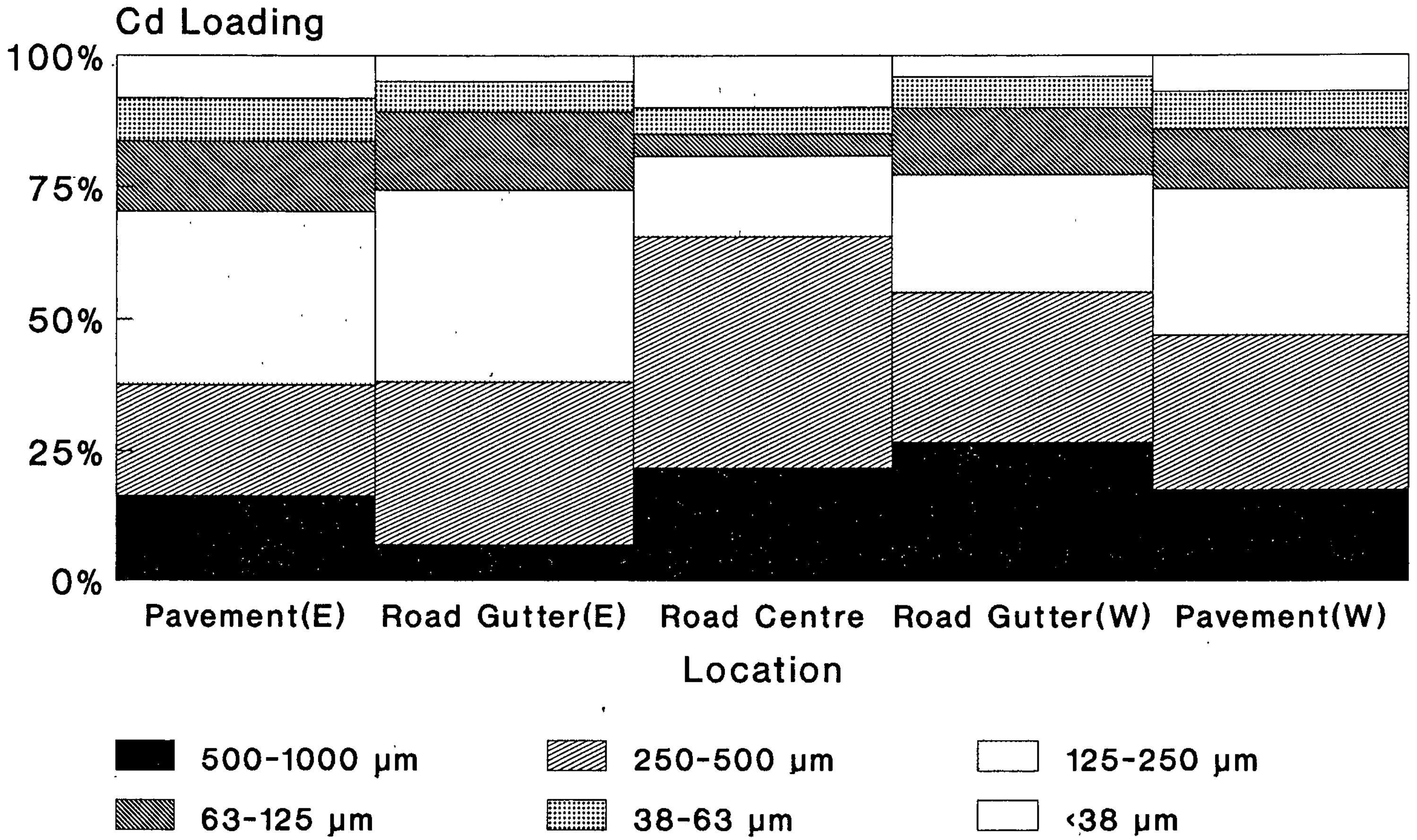


Figure 6.14 Cadmium Loadings with Respect to Particle Size.

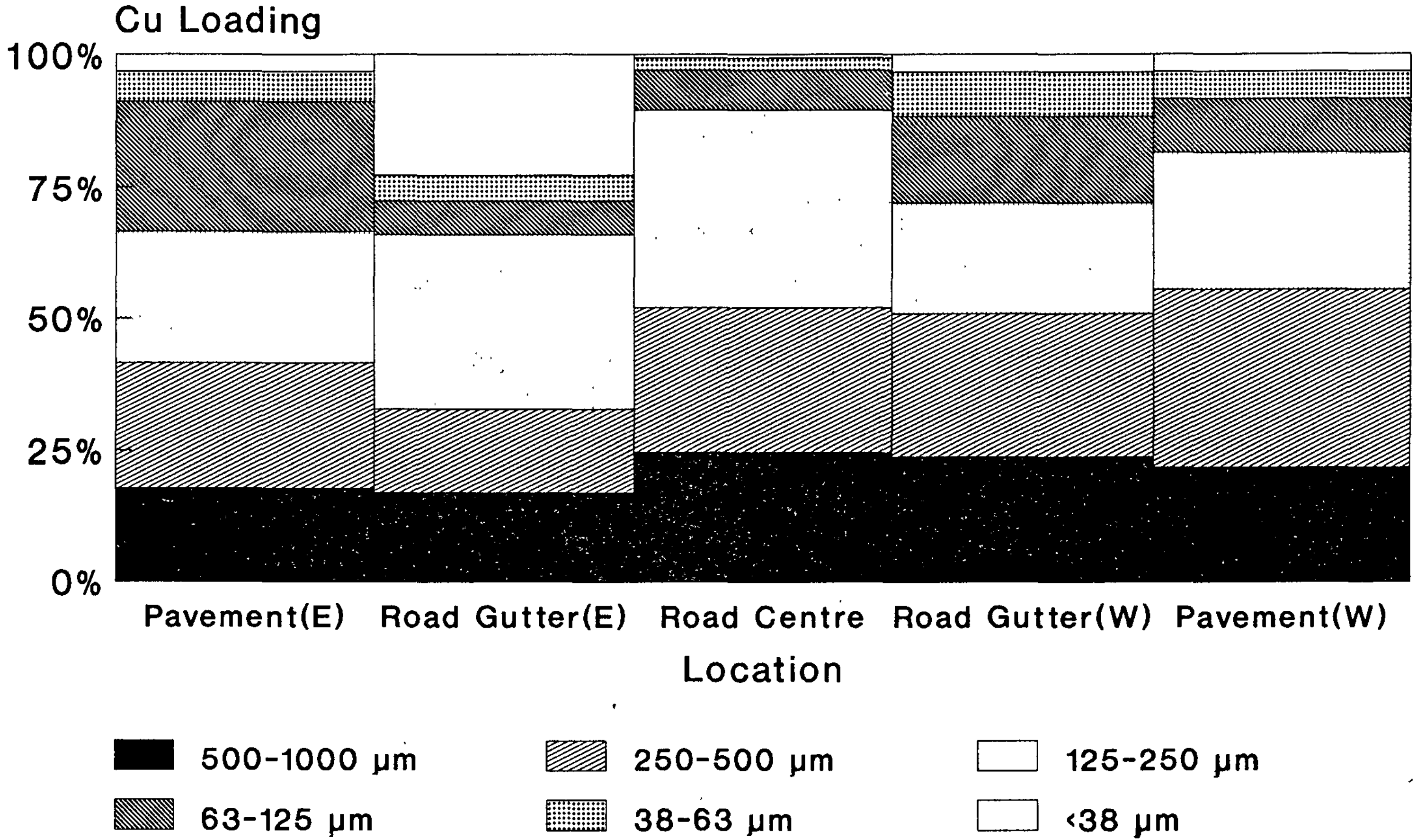


Figure 6.15 Copper Loadings with Respect to Particle Size.

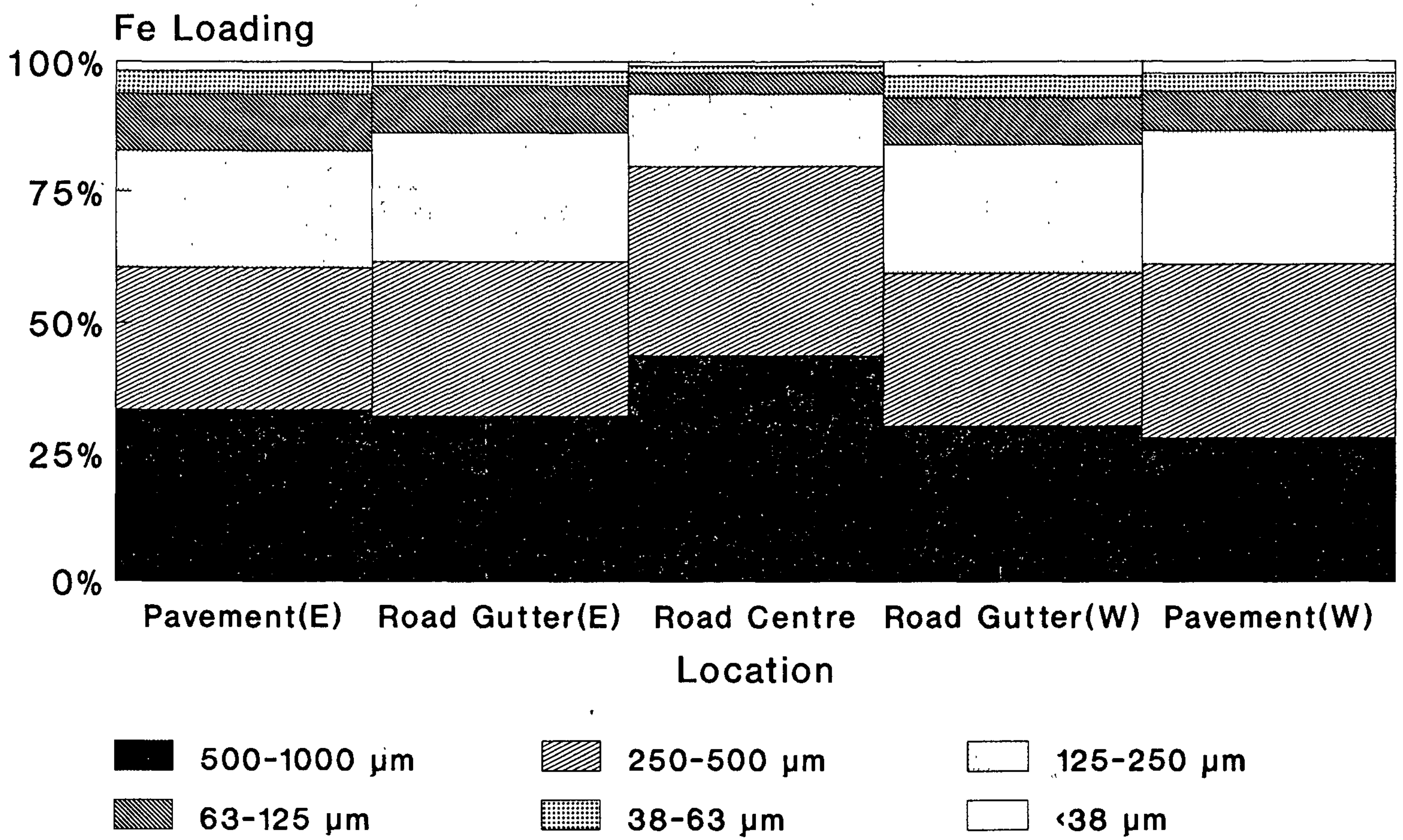


Figure 6.16 Iron Loadings with Respect to Particle Size.

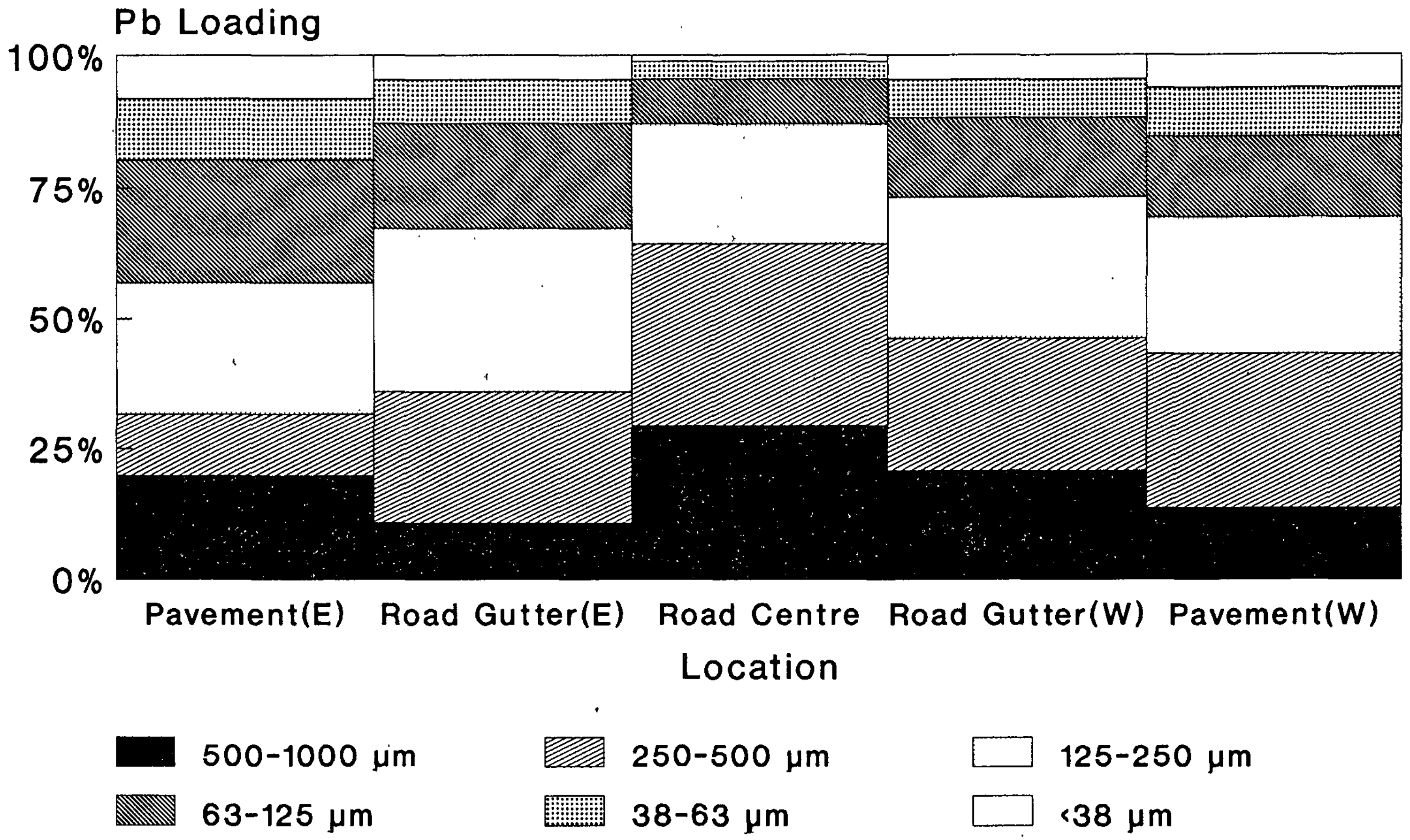


Figure 6.17 Lead Loadings with Respect to Particle Size.

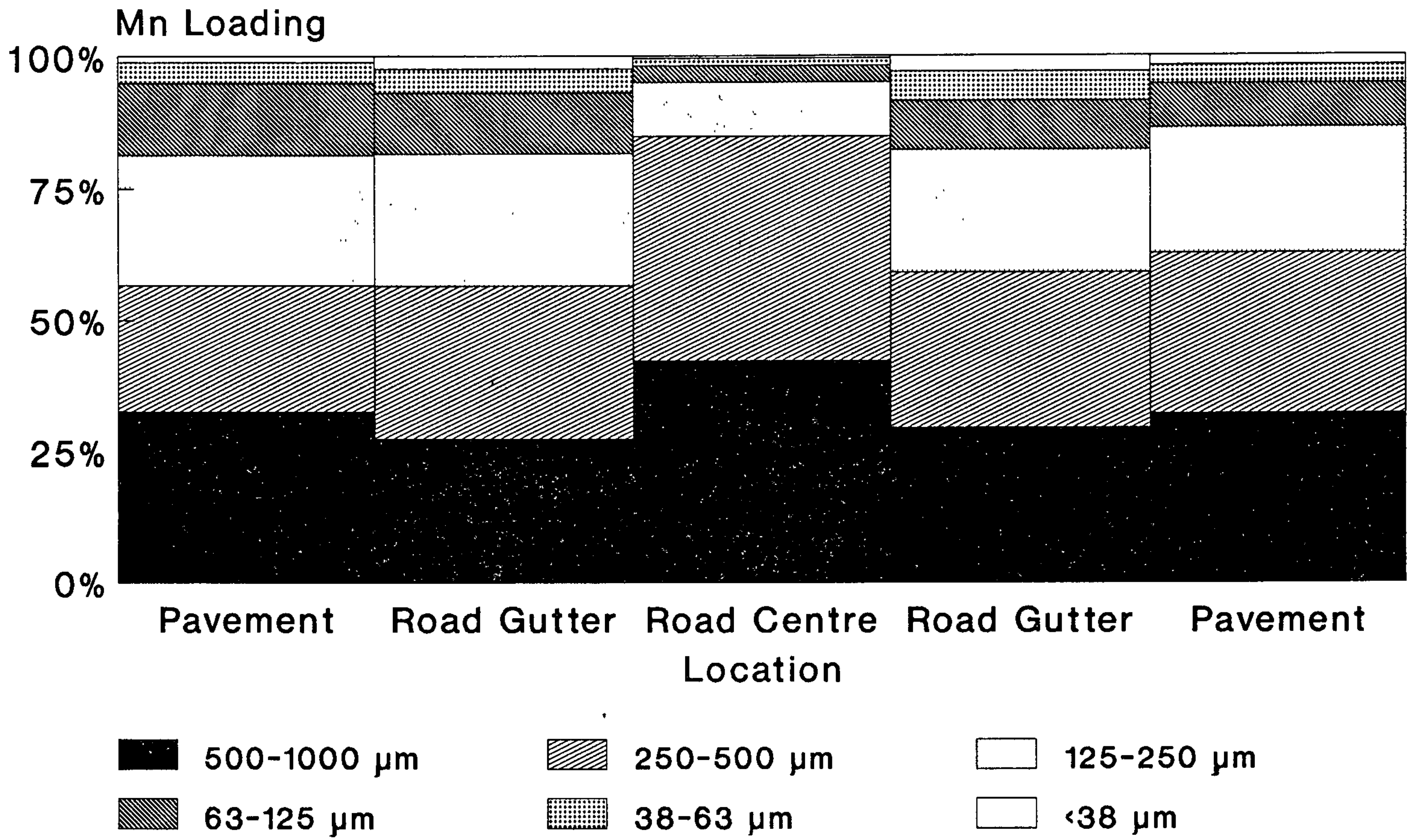


Figure 6.18 Manganese Loadings with Respect to Particle Size.

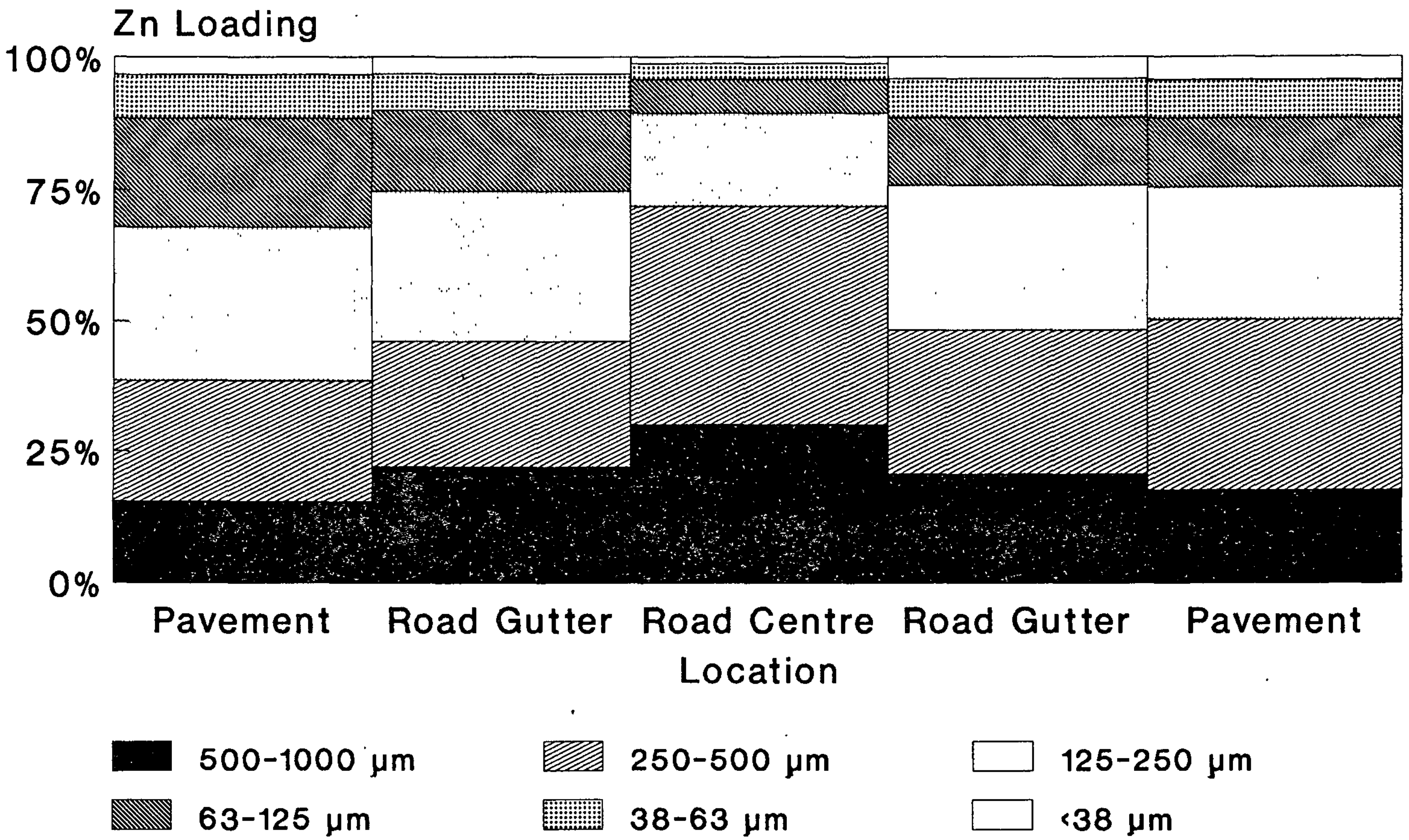


Figure 6.19 Zinc Loadings with Respect Particle Size.

road gutter and pavement sediments are 2.5 to 3.5 times greater.

The loadings of the five other metals at each site generally exhibit the smallest value in the less than 38 μm size fraction, followed by the 38 μm-63 μm size fraction. Of the three types of sampling site the road centre has the smallest percentage of the total loadings in these size fractions which supports the idea of dispersion and/or agglomeration taking place and reducing the finest fraction in the road centre.

The percentage of the total loadings of the metals Cu, Pb and Zn in both the 38 μm-63 μm and the 63 μm-125 μm size fractions are much greater than those of Fe and Mn, which would suggest that the source or sources of Cu, Pb and Zn contribute to the finer fractions to a much greater extent than do the sources of Fe and Mn.

The major outcome of looking at loadings is that whilst it has been seen that the finer size fractions have the greatest concentration of metals, in terms of the total loading they are relatively unimportant. In all cases, less than 20% of the metal loading is present in the less than 63 μm size fraction. The particulates greater than 250 μm account for approximately 70-85% of the metal loadings.

The road sweeper efficiencies for the removal of sediment vary with particle size (Sartor and Gaboury, 1984; Beckwith et al, 1985; Warren, 1987). The sweeping efficiencies given in Table 6.7 were used to calculate the effects of street sweeping on the total metal loadings on the road surface of the Chilwell Gardens sub-catchment.

In the calculation it was assumed that concentrations in the greater than 1000 μm size fraction were the same as those of the 500 μm-1000 μm size fraction and loadings were calculated accordingly. It was also assumed that the road centre loadings were typical for the road surface other than the 0.3 m strip forming the road gutter area. The results are presented in Table 6.8.

The use of road sweeping as a control measure would significantly reduce the total metal loading although it may not reduce the finer and more

Table 6.7 Removal Efficiencies (%) for Municipal Street Sweeping with Particle Size.

Particle Size (μm)	Sartor and Gaboury (1984)	Warren (*pers comm*)
>2000	79	78
1000-2000		65
840-2000	66	
500-1000		57
246-840	60	
250-500		48
125-250 (104-246*)	48	29
63-125		47
43-104	20	
38-63		85
<38 (<43*)	15	61

* Size range given by Sartor and Gaboury (1984) taken to be equivalent of size range given by Warren (*pers comm*).

Table 6.8 Potential Reductions of Total Road Surface Metal Loadings at Chilwell Gardens as a Result of Street Sweeping.

	Cd (μg)	Cu (μg)	Fe (mg)	Pb (μg)	Mn (μg)	Zn (μg)
Pre-Sweeping	4,9	361	130	3042	2469	1590
Mass Removed	1,9-2,7	165-181	63,2-71,7	1450-1518	1206-1330	771-811
% Reduction	39-55	46-50	49-55	48-50	49-54.	49-51

and more toxic particulates. The high removal efficiencies for fractions less than 63 μm given by Warren (*pers comm*) were thought to be due to the resuspension of fine particulates or coagulation of particulates (Warren, 1987). It has been observed that some areas of roads were cleaner prior to sweeping than after (Ellis, 1979). The use of street sweeping while reducing the total mass of metal on the road surface may aid redistribution of fine toxic sediments to pavements and gardens lining the road where the particulates are more likely to come into contact with children. There is a need therefore to investigate the fate of fine particulates on road surfaces after road sweeping.

6.3.2.2 Roof Gutter Sediments.

The roof gutter sediment levels indicate that for all metals the loadings were dominated by the 250 µm-500 µm size fraction (Table 6.9; Figure 6.20). The percentage of the total loading made up by this fraction ranged from 32% for Zn, to 47% for Fe (Figure 6.20). This conforms to the sediment loadings for which this fraction accounts for 45% of the total loading. All metals exhibit similar distributions with the metal loadings in the 500 µm-1000 µm size fraction accounting for a lesser percentage of the total metal loading than the percentage of the total sediment loading accounted for by this fraction (Figure 6.20). In the size fractions finer than 250 µm the reverse is true with metal loadings in each fraction (expresed as a percentage of the total metal loading) being greater than the corresponding percentage sediment loading. This confirms the observations made in relation to the concentrations found in size fractions of roof gutter sediments, i.e. that all size fractions of the sediment are affected by washoff/runoff processes and there is little or no evidence of a preferential accumulation of one metal or size range of particulates.

6.4 Variation of Mineral Magnetic Parameters with Respect to Particle Size in Source Sediments within the Chilwell Gardens Sub-Catchment.

The results obtained from an investigation of the variation inmineral magnetic parameters with particle size are presented in Table 6.10-6.13 and Figures 6.21-6.23.

Table 6.9 Sediment and Metal Loadings in Size Fractions of Roof Gutter Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Sediment (g m_{RG}^{-1})	4.7-24.4 (13.8)	6.6-32.5 (19.6)	2.6-13.3 (7.2)	0.9-3.7 (2.1)	0.4-2.1 (0.9)	0.2-1.0 (0.5)
Cd (μg m_{RG}^{-1})	0-15.6 (5.8)	8.7-33.8 (19.6)	5.8-23.7 (12.0)	6.4-20.8 (10.9)	1.6-14.8 (6.4)	0.1-6.7 (2.8)
Cu (μg m_{RG}^{-1})	90.397 (239)	176-920 (505)	135-403 (281)	75-244 (154)	50-112 (73)	28-310 (134)
Fe (mg m_{RG}^{-1})	152-792 (422)	251-1204 (733)	122-268 (201)	63-202 (116)	32-82 (54)	20-53 (33)
Pb (μg m_{RG}^{-1})	682-3803 (2213)	1789-9573 (5000)	981-5040 (2798)	1019-4142 (2294)	493-1743 (1013)	319-1447 (700)
Mn (μg m_{RG}^{-1})	874-7104 (3594)	2268-12813 (6238)	915-5595 (2552)	626-3203 (1486)	276-1247 (632)	131-768 (346)
Zn (μg m_{RG}^{-1})	937-3588 (2122)	1326-6592 (3991)	1212-7096 (3321)	687-3467 (1827)	376-1469 (806)	193-847 (422)

m_{RG} - metre of roof guttering, serving approximately 5.2 m^2 of roof surface.
Mean values in parentheses

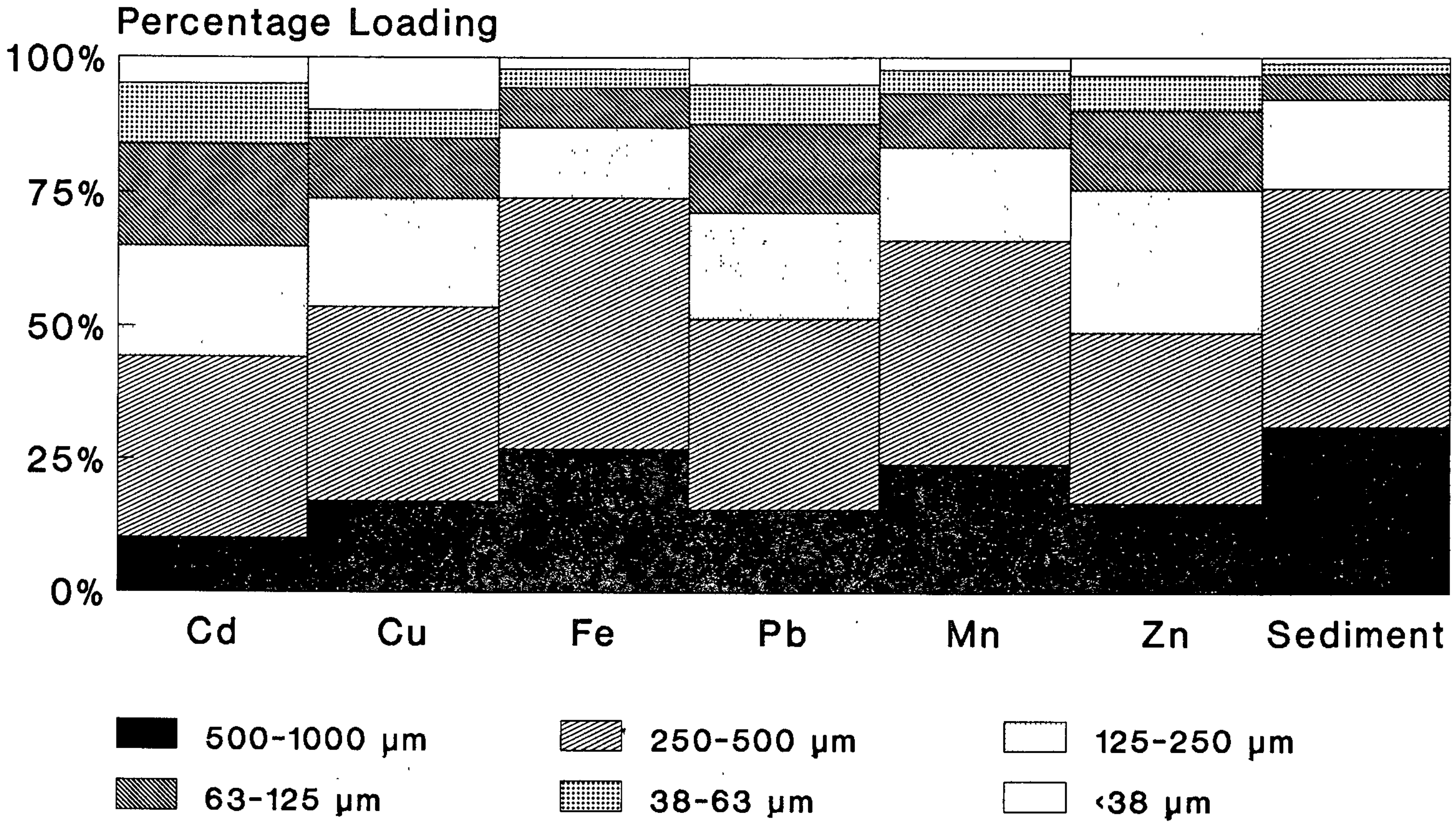


Figure 6.20 Sediment and Metal Loadings with Respect to Particle Size in Roof Gutter Sediments.

Table 6.10 Variation of Magnetic Susceptibility (cm^3 kg^{-1}) with Regard to Particle Size.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	0.98-2.5 (1.71)	0.6-1.98 (1.44)	0.99-1.87 (1.51)	1.59-2.77 (2.07)	1.38-2.7 (1.84)	0.57-3.08 (1.81)
Road Gutter	1.09-3.4 (2.128)	0.76-2.44 (1.69)	1.11-2.8 (1.75)	1.55-4.12 (2.28)	0.97-2.81 (1.88)	0.61-3.91 (2.24)
Road Centre	3.48-8.68 (5.78)	3.2-6.66 (4.97)	2.67-8.95 (6.22)	3.79-11.67 (7.35)	3.45-7.13 (4.71)	3.39-8.75 (4.98)

Mean values in parentheses

Table 6.11 Variation of IRM$_{300mT}$ (10^{-3} A m^2 kg^{-1}) with Regard to Particle Size.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	10.6-17.6 (15.56)	5.78-21.0 (14.84)	11.0-21.2 (15.68)	11.0-26.7 (17.86)	9.0-26.5 (17.29)	9.7-21.1 (16.18)
Road Gutter	13.1-40.5 (27.09)	9.6-31.7 (22.09)	13.9-30.1 (21.2)	14.9-44.2 (25.97)	9.8-45.2 (22.71)	6.7-34.7 (18.76)
Road Centre	40.8-141.5 (87.50)	28.2-88.2 (63.11)	21.1-91.0 (60.23)	5.0-75.2 (48.94)	24.0-50.5 (34.55)	26.8-48.9 (39.87)

Mean values in parentheses

Table 6.12 Variation of IRM_{-20mT}/IRM_{300mT} with Regard to Particle Size.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	0.065-0.233 (0.119)	0.47-0.153 (0.117)	0.108-0.166 (0.138)	0.041-0.247 (0.165)	0.05-0.304 (0.207)	0.152-0.35 (0.266)
Road Gutter	0.137-0.414 (0.227)	0.114-0.258 (0.217)	0.222-0.289 (0.264)	0.024-0.332 (0.268)	0.027-0.985 (0.35)	0.106-0.361 (0.297)
Road Centre	0.241-0.324 (0.284)	0.215-0.298 (0.255)	0.163-0.286 (0.237)	0.071-0.276 (0.169)	0.055-0.28 (0.169)	0.003-0.266 (0.142)

Mean values in parentheses

Table 6.13 Variation of $-IRM_{-40mT}/IRM_{300mT}$ with Regard to Particle Size.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
Pavement	0.368-0.507 (0.421)	0.331-0.456 (0.397)	0.32-0.412 (0.368)	0.255-0.398 (0.323)	0.212-0.536 (0.302)	0.133-0.333 (0.215)
Road Gutter	0.27-0.488 (0.336)	0.276-0.5 (0.334)	0.221-0.293 (0.254)	0.166-0.251 (0.202)	0.136-0.299 (0.2)	0.125-0.362 (0.185)
Road Centre	0.269-0.333 (0.299)	0.292-0.367 (0.326)	0.267-0.334 (0.302)	0.191-0.42 (0.211)	0.215-0.425 (0.323)	0.19-0.333 (0.293)

Mean values in parentheses

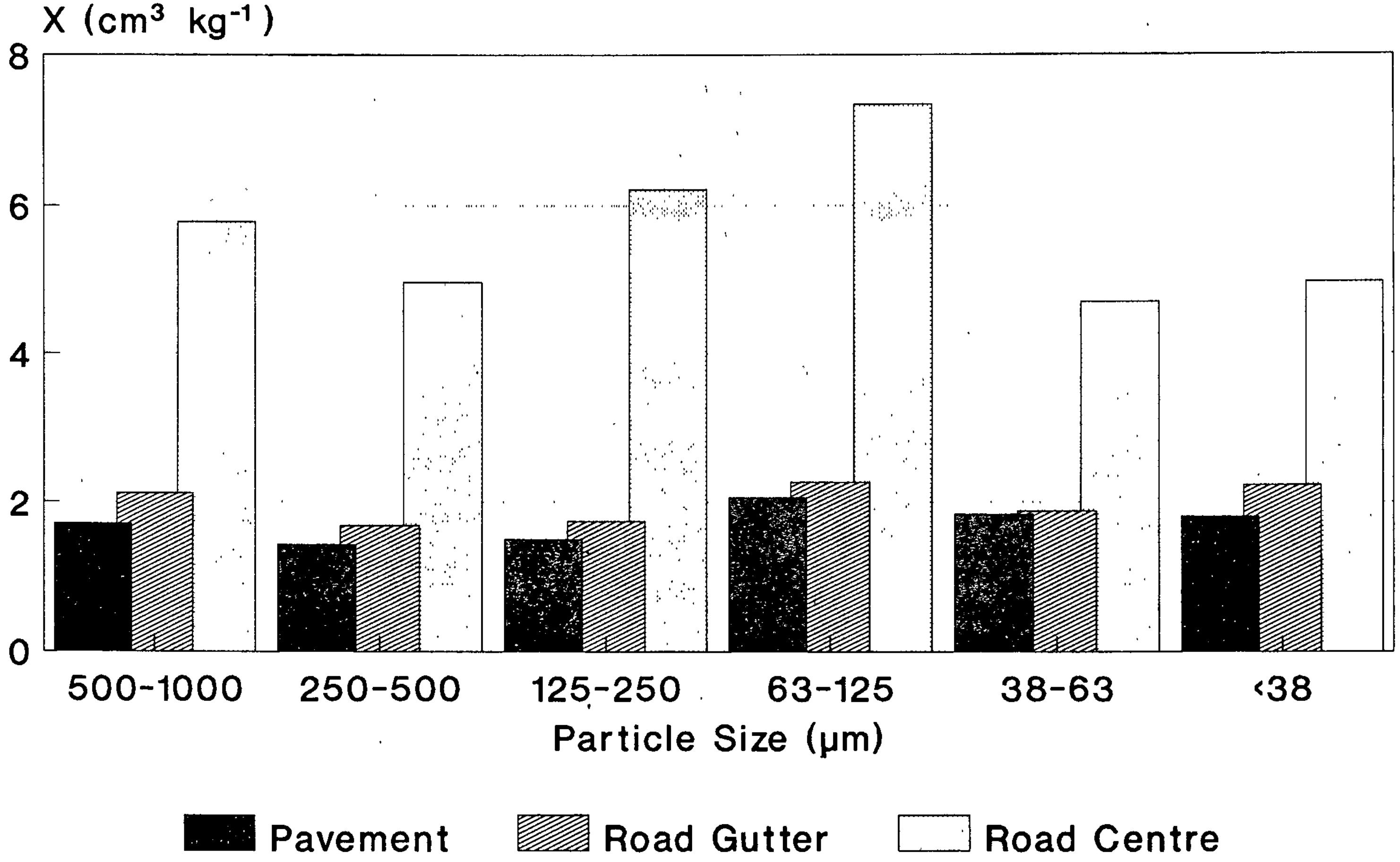


Figure 6.21 Mean Magnetic Susceptibility with Respect to Particle Size.

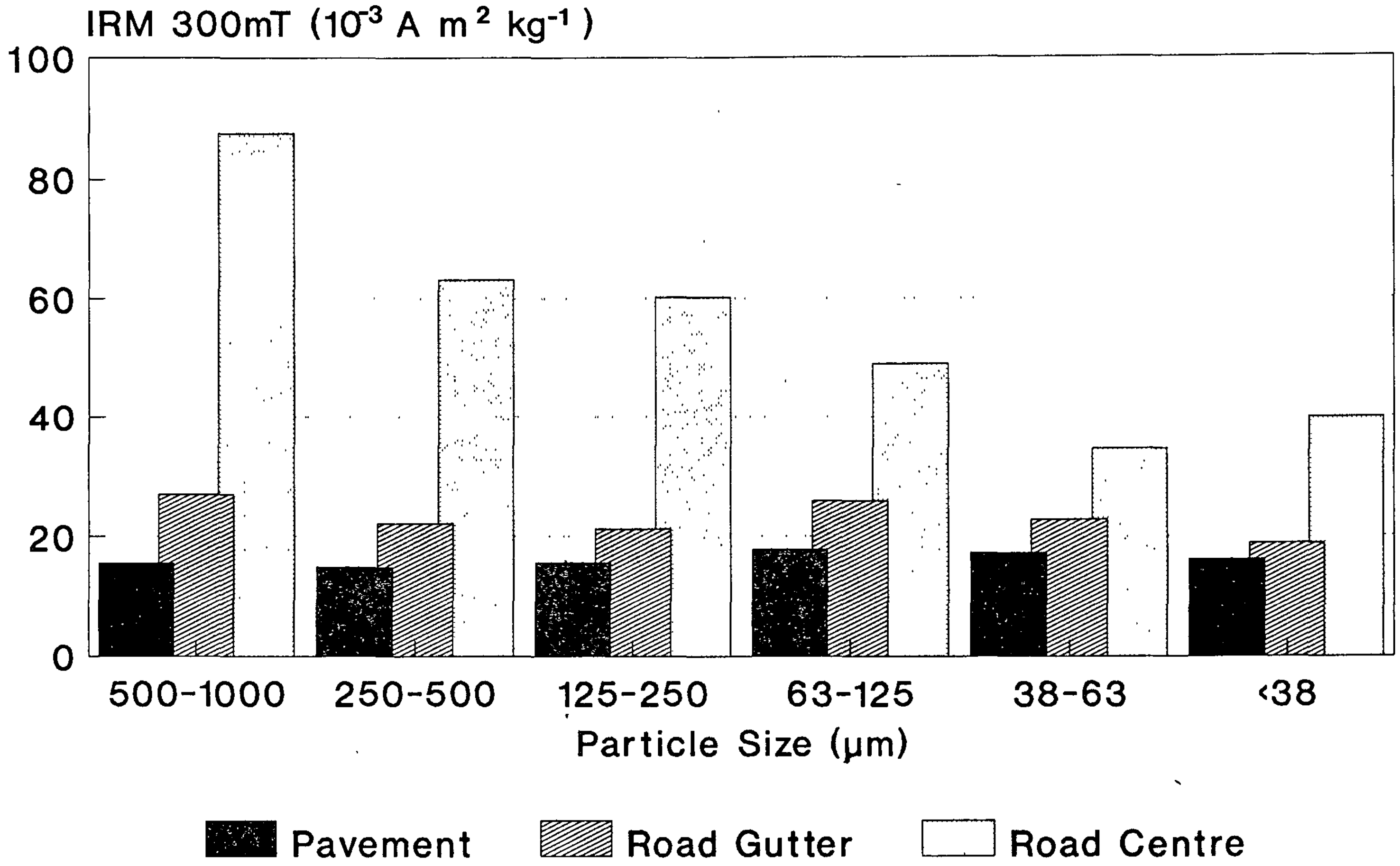


Figure 6.22 Mean IRM 300mT with Respect to Particle Size.

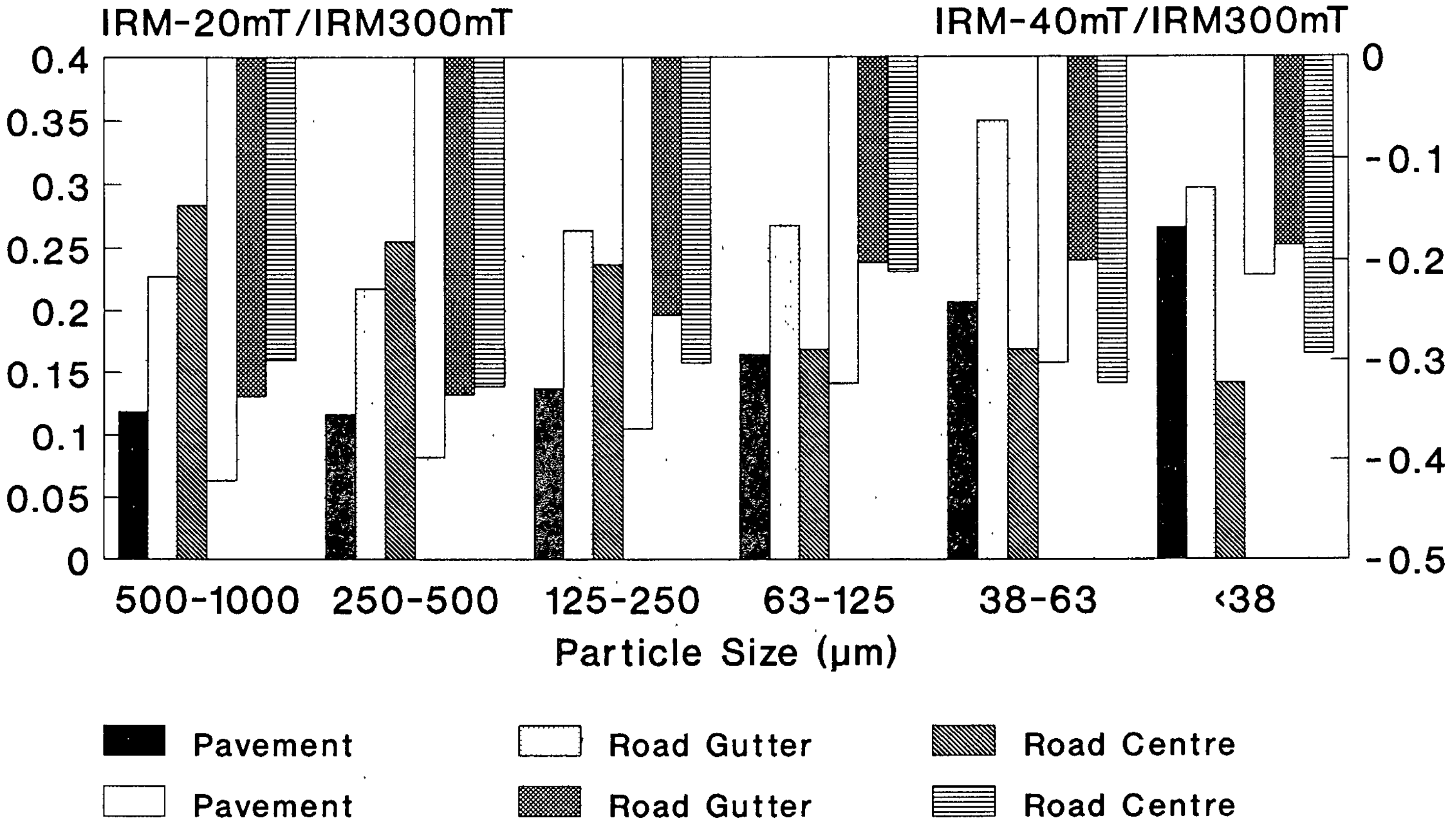


Figure 6.23 Mean IRM-20mT/IRM300mT and IRM-40mT/IRM300mT with Respect to Particle Size.

6.4.1 Highway Associated Sediments.

The mineral magnetic concentration related parameters do not consistently increase with decreasing particle size (Tables 6.10 and 6.11; Figures 6.21 and 6.22). Generally, the peak values for χ and IRM_{300mT} were observed in the 63 µm-125 µm or the 500 µm-1000 µm size ranges. These peaks were not consistent at all sampling periods. This is contrary to expectations as the major source postulated in the previous chapter was fine particulates derived from motor vehicles. The road centre sediments exhibit a decrease in IRM_{300mT} with decreasing particle size (Figure 6.22). The one consistent pattern that is, however, present in the mineral magnetic parameters is that values increase in all size fractions in the order;

pavement samples < road gutter samples < road centre samples.

This suggests that the motor vehicle is the main source of magnetic minerals although the particulates are either agglomerating or are being redistributed by other processes. There is also the possibility that other sources are contributing a proportion of the magnetic minerals giving rise to the values observed.The overall agreement in patterns between χ and IRM_{300mT} does appear to be weaker in size fractionated sediments than bulk sediments although there is still a strong linear relationship with a correlation coefficient of 0.852 (n = 120).

There is a significant relationship between the two backfield ratios, IRM_{-20mT}/IRM_{300mT} and $-IRM_{-40mT}/IRM_{300mT}$, which demostrates a negative correlation coefficient of -0.65. This inverse relationship would be expected as these ratios relate to opposite points about the inflexion on the coercivity curve. A poor relationship between these parameters would indicate that more than one magnetic mineral type is present in the sample set and the ratio of the two magnetic mineraltypes is not constant in all samples.

Generally IRM_{-20mT}/IRM_{300mT} ratio values increase with decreasing particle size in pavement sediments, and to some extent in road gutter sediments. The ratio values for road centre sediments decrease with decreasing particle size (Figure 6.23). The ratio $-IRM_{-40mT}/IRM_{300mT}$ exhibits the opposite pattern although this is not well defined for road centre sediments (Figure 6.23; Table 6.13). From these ratio values it would appear that the 'softest' or most magnetitic samples are the road centre fractions of less than 125 μm and the pavement fractions of greater than 63 μm. This distribution would suggest that either there is an input of 'harder' material affecting the road gutter and preferentially dissipating to the coarse fractions of the road centre and the fine sediments of the pavement sediments, or that two sources of 'softer' material are contributing particulates with differing size characteristics to the highway associated sediments. The latter is viewed as more probable with the source of particulates possibly being soil particulates, either windblown or entrained by pedestrians. The observed values may be a result of differences in the surface construction materials of the pavement and road surfaces.

Typing of the possible sources, including soil and construction materials would help in gaining a better understanding of the magnetic mineral characteristics of sediments in the sub-catchment and this is discussed in the next chapter.

6.4.2 Roof Sediments.

The roof sediment values (Table 6.14) are more characteristic of 'harder' magnetic minerals than the highway associated sediments. Unlike the highway associated sediments the parameters related to the concentration of magnetic minerals generally increase with decreasing particle size. This may be due to the predominating process controlling concentration being surface adsorption as suggested in Section 6.2.4. The mineral magnetic character of a particle is inherent therefore such a surface adsorption phenomena would have to be based on the adhesion of small particulates of high magnetic mineral concentration onto the surface of larger particulates.

Table 6.14 Variation of Mineral Magnetic Parameters in Size Fractionated Roof Gutter Sediments.

	Particle Size (μm)					
	500-1000	250-500	125-250	63-125	38-63	<38
χ	0.26-0.67 (0.48)	0.2-0.81 (0.49)	0.9-2.56 (1.64)	2.06-4.48 (3.02)	2.48-5.67 (3.67)	3.05-7.76 (4.7)
IRM_{300mT}	2.75-6.08 (4.91)	2.41-5.83 (3.926)	10.04-18.72 (13.32)	15.85-29.98 (24.23)	20.7-25.72 (23.76)	25.3-28.19 (26.92)
IRM_{-20mT} $/IRM_{300mT}$	0.204-0.29 (0.24)	0.295-0.323 (0.306)	0.317-0.378 (0.344)	0.279-0.393 (0.334)	0.296-0.346 (0.317)	0.288-0.363 (0.318)
$-IRM_{-40mT}$ $/IRM_{300mT}$	0.286-0.362 (0.321)	0.179-0.284 (0.228)	0.14-0.211 (0.1738)	0.185-0.195 (0.1915)	0.18-0.23 (0.208)	0.159-0.21 (0.192)

Mean values in parentheses
χ values in cm^3 kg^{-1}
IRM_{300mT} values in 10^{-3} A m^2 kg^{-1}

6.4.3 Discriminant Analysis of Size Fractionated Sediments.

Statistical analysis of the mineral magnetic parameter data for the size fractionated sediments has been carried out using specifically IRM_{300mT}, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT}. The data was analysed directly by attributing each sample to its appropriate grouping. Additionally, the size fractionated samples were classified using the equations established for the bulk samples.

Analysis of the fractionated samples achieved 73.2% correct classification when all samples and size fractions were considered. One roof sample and 36 highway associated sediment samples were misclassified. This reinforces the view that where the equation derived from discriminant analysis defines unknown samples as derived from the highway associated surfaces it is likely to be correct, however where it defines a sample as derived from the roof surface the reliability of the source definition is less robust.

The equation of the discriminating plane was found to be;

$$0 = (0.0316 * IRM)-(5.3223 * TR)-(5.9562 * FR)-0.8014 \qquad (Eq6.1)$$

where $IRM = IRM_{300mT}$ $(10^{-3}\ A\ m^{2}\ kg^{-1})$
$TR = IRM_{-20mT}/IRM_{300mT}$
$FR = IRM_{-40mT}/IRM_{300mT}$

The definition achieved by Eq6.1 (73.2% correct classification) is similar to that achieved by the application of Eq5.1 (72.5% correct classification) and Eq5.4 (70.1%) to the size fractionated sediment data.

In an attempt to improve the classification and investigate the sediments that are most likely to contribute to stormwater sediments, discriminant analysis was carried out on the less than 63 μm size fractions. It was also thought that this would aid the statistical analysis in that these smaller groupings are more likely to approximate to normal distributions than larger groupings including all fractions. The percentage of samples correctly classified was 63.8% which increases the concern that tracing by mineral magnetic parameters may not be possible.

The analysis of those size fractions less than 63 μm revealed the misclassified samples to be 22 out of the 60 highway associated surface sediment samples and only one roof sample which was in the 38 μm-63 μm size fraction. This consistency in achieving a generally correct classification of roof sediments was also seen when equations Eq5.1 and Eq5.4 were applied to the fractionated sediments. For sediments less than 125 μm only one roof sample was misclassified while 27 out 80 highway associated sediments were misclassified.

Further attempts to achieve an improved basis of discrimination involved the analysis of the chosen magnetic parameters for the less than 63 μm fractions of the prime source sediments, i.e. road centre and roof gutter sediment. The classification improved to an overall correct classification of 85.7% with 100% of the roof sediments correctly classified.

The linear equation defining the discriminating plane was found to be:

Road Centre and Roof Gutter Sediment Groupings

$$0 = (0.1082 * \mathrm{IRM}) - (32.8786 * \mathrm{TR}) + (10.5892 * \mathrm{FR}) + 6.8304 \quad \text{(Eq6.2)}$$

Use of Eq5.1 in conjunction with this data revealed that the classification of highway sediments was 100% correct and that misclassification of only one roof sample occurred.

This analysis indicates that there are likely to be limitations to the potential typing of stormwater particulates by mineral magnetic parameters. On balance it would appear that the tendency is for all sediments to be classified as roof sediments rather than as highway associated sediments. The discrimination process is still viewed as partially viable in that when the equations produced by the analysis of both bulk and size fractionated sediments are applied to stormwater samples, any sediments classified as highway associated sediment will be from that source. If samples are designated as roof sediments there will be some doubt as to the origin of the dominant sediments in the sample. This will not allow the degree of typing and identification of sequencing in stormwater that it was hoped to achieve but even this limited information may be important in understanding the processes occurring during runoff.

6.4.4 Sub-Surface Sediments

The mineral magnetic characteristics of the sub-surface sediments did not exhibit well defined trends. In terms of concentration related parameters there was some indication that the sub-surface sediments were generally similar to those of the immediate sources i.e. the in-pipe deposits in the roof drain were similar to the roof gutter (Tables 6.10-6.16). The gully pot sediments were found to reflect the levels found on the pavement rather than those of the road gutter or road centre (Tables 6.10-6.13 and 6.15). The reason for this is not immediately clear, although, it may indicate that particulates from the road surfaces are directly routed through the gully pot and do not settle out. High metal concentrations were observed in the gully pots compared to road surfaces which would appear to contradict this proposition, however, these could be due to the surface adsorption of soluble metals onto gully pot particulates. The soluble metals being derived from the leaching of road surface sediments by low intensity acidic rainfall.

In order to test the equations derived in the previous section the various size fractions of the sub-surface sediment samples were classified using Eq6.1 and Eq6.2. It was found that the roof drain in-pipe deposition was classified as roof derived by both equations. Eq6.1 appeared to be the most discriminating of the equations as Eq6.2 classified all but one of the gully pot samples with the roof grouping. This is not surprising as the equation is based on the road centre and roof gutter groupings and the gullypot sediments exhibit the greatest similarity to the pavement sediments which are intermediate between the

Table 6.15 Variation of Mineral Magnetic Parameters in Size Fractionated Gully Pot Sediments.

	Particle Size (µm)					
	500-1000	250-500	125-250	63-125	38-63	<38
χ	0.99-2.48	0.84-1.29	0.99-1.59	0.87-2.27	1.31-1.75	1.46-2.0
	(1.42)	(1.05)	(1.21)	(1.48)	(1.47)	(1.73)
IRM_{300mT}	10.56-38.26	11.86-19.22	12.08-16.48	12.72-19.11	10.21-20.09	11.73-23.12
	(18.34)	(14.39)	(13.71)	(15.63)	(14.11)	(16.22)
IRM_{-20mT}	0.192-0.283	0.23-0.276	0.211-0.296	0.191-0.316	0.149-0.234	0.177-0.289
$/IRM_{300mT}$	(0.254)	(0.257)	(0.246)	(0.283)	(0.205)	(0.246)
$-IRM_{-40mT}$	0.2-0.364	0.214-0.33	0.1292-0.33	0.271-0.329	0.247-0.413	0.248-0.349
$/IRM_{300mT}$	(0.256)	(0.261)	(0.26)	(0.29)	(0.306)	(0.291)

Mean values in parentheses
χ values in cm^3 kg^{-1}
IRM_{300mT} values in 10^{-3} A m^2 kg^{-1})

Table 6.16 Variation of Mineral Magnetic Parameters in Size Fractionated In-pipe Deposited Sediments.

		Particle Size (µm)					
		500-1000	250-500	125-250	63-125	38-63	<38
χ	(a)	1.43, 2.47	0.97, 1.47	1.49, 1.58	2.93, 3.3	2.78, 3.05	2.67, 3.05
	(b)	0.51	0.47	1.55	2.57	3.28	4.72
IRM_{300mT}	(a)	8.95,35.67	6.06,14.49	15.88,21.42	30.56,38.77	26.67,31.98	27.48,28.98
	(b)	6.54	6.32	12.56	16.72	18.92	26.3
IRM_{-20mT}	(a)	0.108,0.276	0.219,0.317	0.268,0.362	0.25,0.261	0.28,0.296	0.32,0.325
$/IRM_{300mT}$	(b)	0.307	0.289	0.276	0.0.293	0.303	0.373
$-IRM_{-40mT}$	(a)	0.235,0.404	0.196,0.326	0.158,0.287	0.277,0.28	0.26,0.29	0.215,0.223
$/IRM_{300mT}$	(b)	0.188	0.214	0.27	0.183	0.163	0.181

Mean values in parentheses
χ values in cm^3 kg^{-1}
IRM_{300mT} values in 10^{-3} A m^2 kg^{-1})

two prime source types. Eq6.1, however, classifed 14 sample fractions of the gully pot with the roof grouping. Of the in-pipe deposition below the roof and road drainage confluence, Eq6.1 classified 5 sample fractions with the roof groupings, whereas Eq6.2 classified nine out of the twelve sample fractions with the roof grouping.

It would appear that despite the lower percentage of correct classification of surface sediments achieved by Eq6.1 this equation may be more useful as a tool to classify unknown sub-surface sediments. The results of the classification of the in-pipe deposits below the drainage confluence do suggest that there is some justification in the idea that classification of stormwater sediments by mineral magnetic characterisation is possible.

6.4 Mineral Magnetic Parameters in Relation to Heavy Metals.

Correlation studies reveal that relationships between mineral magnetic parameters and metals as determined on the basis of values for all size fractions are weaker than those found considering the values determined on bulk sediments alone. This is possibly due to a greater number of samples and also the greater possibilty of errors in analysis of very small samples in the less than 38 μm size fractions.

The major mineral magnetic concentration parameters did exhibit significant relationships with Cu and Pb which are both thought to be derived predominantly from motor vehicles. The coefficients are 0.59, 0.53, and 0.4 for χ and Cu, χ and Pb, and IRM_{300mT} and Cu, respectively. The correlation between IRM_{300mT} and Pb was found to be 0.31 which is a weaker relationship than would have been expected. Zinc did not exhibit good relationships with any mineral magnetic concentration parameters and this may reflect the isolated pollution event that affected the second sampling set.

The results of the correlation studies do suggest that there is a link between the metals, Cu and Pb, and mineral magnetic concentrations. The correlation is obviously weakened by metal concentrations increasing with decreasing particle size while the mineral magnetic parameters do not. It is therefore thought that the correlation still remains moderately strong as a result of the similarities in spatial variation of metals and mineral magnetic parameters. This would suggest that the essential aspect of the co-relationship of metals and mineral magnetic parameters is having the same significant source (i.e. vehicular traffic) in the road centre.

The general variation of mineral magnetic concentration related parameters with particle size when compared to the variation of heavy metal concentrations with particle size does give rise to some concern as to the effectiveness of the use of mineral magnetic parameters as tracer techniques for metals in stormwater. In stormwater the particulates will be of the finer size fractions. If the correlation observed is due to the spatial variation of metal concentrations and magnetic minerals and not to their particle size distribution, it is probable that no relationship will be found in the analysis of stormwater sediments. This conclusion is further supported by investigations of transformations in the associations and form of metals which occur within the below-ground system. In the case of Pb it has been shown that on average the dissolved metal increases by 49% and the suspended solid associated metal can increase by 200% (Morrison, 1985). Changes on this scale will weaken the relationship between mineral magnetic parameters and metals. Magnetic minerals will be conservative in character in the below-ground system, reflecting inherent properties of the sediment and not the chemistry of the sediment surface.

CHAPTER 7 SOURCE IDENTIFICATION AND TYPING.

In Chapters 5 and 6 the pollutant distributions within the Chilwell Gardens sub-catchment were discussed. It was found that with respect to the highway and associated surfaces, the motor vehicle was indicated as the dominant pollutant source. Significant pollutant concentrations and loadings, however were also found on the roof surfaces. In order that these prime sources could be confirmed, further investigations of source particulates entering the sub-catchment were undertaken.

The possible source or sources of pollutants and magnetic minerals within the catchment were indicated in Figure 1.1. These can be identified as;

atmospheric deposition
soil particulates
surface constructional materials
automobile derived particulates
litter and leaves.

The distribution of Cd has been found to be unclear and inconsistent, and in addition there has not been any indication of a co-relationship with mineral magnetic parameters. Consequently further investigation of Cd with a view to tracing it by mineral magnetic means was not carried out.

7.1 Atmospheric Deposition.

In order that background atmospheric deposition could be evaluated as a potential source of particulates within the Chilwell Gardens sub-catchment, samples of suspended particulates and total dry/wet deposition were collected. Sampling was over a 2 month period between September and November, 1984. The sampling site was located on the roof of the Community Centre which is to the immediate east of the Chilwell Gardens sub-catchment. The roof site was approximately 20 m from the roadside kerb and at an elevation of 4 m. Suspended particulates were collected on 0.8 μm pore cellulose filters and total particulate deposition collected in plastic bottles fitted with a receiving funnel. The funnel was screened with a 5 mm plastic mesh to prevent ingress of insects or erroneous gross particulates, such as leaf material. The contents of the bottles were filtered through a cellulose 0.45 µm filter upon return to the laboratory and the solid particulates dried prior to analysis. Attempts to sample dry deposition were unsuccessful as test runs of unexposed receiver surfaces yielded higher results than exposed surfaces.

7.1.1 Heavy Metals in Atmospheric Particulates.

The results of determinations of heavy metal concentrations associated with suspended atmospheric particulates are given in Table 7.1.

Table 7.1 Heavy Metal Concentrations (ng m^{-3}) in Suspended Atmospheric Particulates Adjacent to the Chilwell Gardens Sub-Catchment.

	Cu	Fe	Pb	Mn	Zn
Range (n=8)	52.8-72.9	548.1-997.4	82.5-369.0	25.7-42.2	61.0-180.3
Mean	62.9	706.3	221.1	32.4	124.8

The values compare favourably with background results previously obtained in UK studies (Peirson et al, 1973; Pattenden, 1974; McDonald and Duncan, 1979; Harrison and Williams, 1983; Duggan and Burton, 1983) and are also compatible with studies undertaken in Belgium (Kretzschmar et al, 1977). The results for Chilwell Gardens are typical of other non-industrialised suburban sites which reinforces the view that the site is not affected by any remote point sources.

Comparison of the data in Table 7.1 to concentrations determined for roadside sites adjacent to major roads (Table 2.10), show that the concentrations found 20 m from Chilwell Gardens are much less than those found within the same distance of major roads. The maximum levels found at the sampling site are less than any of those presented in Table 2.10. The influence of traffic in Chilwell Gardens on the metal concentrations in atmospheric particulates in the surrounding environment is therefore seen to be much more limited than that for major roads. It would be expected that the influence of traffic using Chilwell Gardens on metal deposition and enhanced concentrations in plants and vegetation would also be more limited.

As airborne particulates sampled at the site on the roof of the Community Centre appeared to be influenced to a minor extent, if at all, by vehicular pollution it was thought that deposition collected at this site would be representative of background levels affecting all areas of the sub-catchment. The heavy metal levels found in total particulate deposition are given in Table 7.2. As the main thrust of the research was to characterise and trace particulates within the sub-catchment, only the particulate element of bulk deposition was analysed.

Table 7.2 Total Particulate Deposition of Heavy Metals (μg m^{-2} day^{-1}) Adjacent to the Chilwell Gardens Sub-Catchment.

	Cu	Fe	Pb	Mn	Zn
Range (n=4)	3.9-56.3	40.9-606.0	16.6-90.0	14.3-72.3	11.1-96.3
Mean	24.8	281.9	45.3	41.0	47.6

Comparison of the data in Table 7.2 to other published data on total heavy metal deposition (Peirson et al, 1973; Cawse, 1974; Duggan and Burton, 1983; Harrison and Williams, 1983) clearly indicates lower levels at Chilwell Gardens. This is to be expected as the soluble metal content of the total deposition is not accounted for in this analysis.

As discussed in Chapters 5 and 6 airborne particulates cannot be solely responsible for the heavy metal concentrations observed within the sub-catchment as the levels vary with position on the paved surfaces as well as between roof and paved surfaces and therefore do not result from a uniform deposition of metals. It is important to assess atmospheric inputs, however, as they will contribute to the baseline metal concentrations in source sediments within the sub-catchment.

7.1.2 Mineral Magnetic Parameters of Atmospheric Particulates.

The mineral magnetic parameters for the airborne suspended solids and total deposition particulates are presented in Table 7.3.

Table 7.3 Mineral Magnetic Measurements in Atmospheric Particulates Adjacent to the Chilwell Gardens Sub-Catchment.

	IRM_{300mT} (10^{-3} A m^2 kg^{-1})	IRM_{-20mT} / IRM_{300mT}	$-IRM_{-40mT}$ / IRM_{300mT}	IRM_{-20mT} / $-IRM_{-40mT}$
Suspended Particulates				
Range (n=8)	2.89-14.74	0.404-0.561	0-0.075	7.0-1346
Mean	6.7	0.479	0.04	(345.9)
Total Particulate Deposition				
Range (n=4)	28.6-52.41	0.357-0.439	0.065-0.176	2.02-6.77
Mean	36.9	0.415	0.099	(5.0)

The concentration of magnetic minerals is indicated solely by measurements of isothermal remanent magnetisation at 300 mT, as the low weight of the samples prevented determination of susceptibility. The IRM_{300mT} values for suspended atmospheric particulates are comparable to those found for roof sediments and are generally less than those found for highway associated surface sediments (Table 5.6).

It can be seen that the characteristics of the suspended atmospheric particulates is generally less ferrimagnetic in character than that of the sampled assemblages representing highway associated surface sediments and roof sediments (Tables 5.6 and 7.3). As would be expected the suspended airborne particulates show greatest similarity to those assemblages sampled from the roof surfaces. This is particularly obvious when the values for the ratio $IRM_{-20mT}/-IRM_{-40mT}$ are considered. It can be seen from detailed comparison with the sediments collected from the two areas associated with the roof that the suspended airborne particulates exhibit greatest similarity to the tiled roof surface rather than to the roof gutter (Table 5.6 and 7.3).

Further indications of the similarity of suspended airborne particulates and roof sediments is given by equations Eq5.1 and Eq5.4, derived from the discriminant analysis of roof and highway associated surface particulate samples. These indicate that the airborne particulate samples would be classified with the roof grouping. Since airborne particulates are likely to be less than 63 µm in diameter equations Eq6.1 and Eq6.2 should also be applicable. When tested these equations also classified airborne suspended particulates with the roof sediment grouping. This does appear to confirm the idea that there is a distinct difference in the dominant sources of magnetic minerals as found in roof particulates and paved surface sediments, and additionally that those of the roof are predominantly influenced by airborne particulates.

The magnetic mineral concentrations as indicated by IRM_{300mT} for the total particulate deposition samples are similar to those found in road gutter sediments but cannot account for the range of IRM_{300mT} values found in the road centre. The mean IRM_{-20mT}/IRM_{300mT} and $-IRM_{-40mT}/IRM_{300mT}$ values are similar to the airborne particulate values; they indicate the possibility of the magnetic minerals being slightly more ferrimagnetic but this is not significant when compared to sediments from paved surfaces. The ratio of IRM_{-20mT}/IRM_{300mT} over $-IRM_{-40mT}/IRM_{300mT}$ gives a range of 2.02 to 6.77, with a mean of 5.0. These values fall between those of airborne particulates and those of the roof surface. Not unexpectedly the statistically derived equations Eq5.1, Eq5.4, Eq6.1 and Eq6.2 classify the total particulate deposition samples with the roof grouping. These results, together with those of airborne particulates suggest that airborne deposition, both wet and dry, is likely to be the dominant source of magnetic minerals in roof particulates. However it would appear that there is another source which moderates the characteristics of the particulates giving rise to a total assemblage with greater ferrimagnetic characteristics than those found in airborne particulates alone. This may be derived from the constructional materials of the tiles and gutters themselves.

It would appear therefore that while airborne and deposited particulates may contribute to the overall loadings of sediments within the catchment other sources must be present to give rise to the elevated concentrations of both magnetic minerals and heavy metal concentrations.

7.2 Soil Particulates.

Soil samples were taken from a garden adjacent to the sub-catchment (approximately 10 m from the nearest kerb), a sports field beyond the Community Centre (60 m from Chilwell Gardens which was the nearest road to the sampling location), and also from a shallow depression surrounding a tree set in the pavement. The latter sampling site will be referred to as the tree pit. Samples were taken from the top 4 cm of the soil profile at each site. In the case of the tree pit, a core was taken allowing analysis to be carried out down the soil profile.

7.2.1 Heavy Metals in Soil Particulates.

The results of the heavy metal analysis of the soil samples are presented in Table 7.4. The heavy metal concentrations found in the tree pit soil are greater than those of the garden, with the exception of Mn. The concentrations in the garden soil are in turn greater than those of the playing field soil. This gradation of metal levels with distance from the road would again suggest the highway as the principal source of heavy metals. This conclusion is further substantiated by the decreases in the metal concentrations that occur with depth. The concentrations found in the garden soil are generally less than those of the pavement samples (Table 5.1) which indicates that local garden soil cannot be the only source of heavy metals found in paved surface sediments. Additionally the tree pit soils cannot completely account for the high concentrations found in paved surface samples.

Table 7.4 Heavy Metal Concentrations in Soils Within and Adjacent to the Chilwell Gardens Sub-Catchment.

	Cu ($\mu g\ g^{-1}$)	Fe ($mg\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Mn ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)
Garden*	34.7	21.0	126.7	443.4	139.7
Playing Field*	10.3	25.8	48.3	189.3	46.1
Tree Pit					
a) 0-4cm (n=3)					
Range	75.2-102.4	19.3-25.1	140.4-190.9	293.2-423.4	256.4-557.9
Mean	86.2	22.9	170.4	388.8	391.8
b) 4-8cm*	45.3	19.4	153.0	406.1	221.6

* One sample only

There is a possibility that some input of soils does affect the levels found in pavement sediments. In Chapter 5 it was observed that Pb concentrations in road centre and road gutter sediments are generally greater than those of Zn but in pavement sediments the relative concentrations of Pb and Zn are reversed. The particulates responsible for this reversal appear to be those greater than 38 μm (Chapter 6). It can be seen from Table 7.4 that in the garden and tree pit soil samples, Zn concentrations were greater than those of Pb and therefore there may be a minor contribution of soil to the pavement sediments. This would have to result from windblown soil rather than washoff as the gardens are sunk below the level of the pavement.

7.2.2 Mineral Magnetic Parameters of Soil Particulates.

The results of mineral magnetic parameter measurements undertaken on the soil samples are presented in Table 7.5. The soil magnetic mineral concentration dependent parameters are generally less than those of paved surface sediments but are most similar to those of the pavement sediments. The soil concentrations are greater than those of the roof sediments and airborne particulates suggesting that sources other than

Table 7.5 Mineral Magnetic Measurements in Soils Within and Surrounding the Chilwell Gardens Sub-Catchment.

	χ (cm^3 kg^{-1})	IRM_{300mT} (10^{-3} A m^2 kg^{-1})	IRM_{-20mT} / IRM_{300mT}	$-IRM_{-40mT}$ / IRM_{300mT}	IRM_{-20mT} / $-IRM_{-40mT}$
Garden*	0.03	4.87	0.373	0.211	1.768
Playing Field*	0.167	1.23	0.289	0.181	1.597
Tree Pit					
a) 0-4cm (n=3)					
Range	0.079-0.108	9.54-20.91	0.246-0.313	0.157-0.259	0.95-1.994
Mean	0.094	16.01	0.289	0.195	1.585
b) 4-8cm*	0.079	8.5	0.294	0.126	2.333

* One sample only

airborne deposition may well contribute to the magnetic mineral concentrations. As in the case of heavy metals, the magnetic concentrations found in the tree pit soil are greater than those found in the garden soil and decrease with depth, indicating that the highway is a source of both heavy metals and magnetic minerals.

The values of the ratios between the two backfields, IRM_{-20mT} and $-IRM_{-40mT}$, with respect to IRM_{300mT} for the soil samples, fall within the range of values found for highway associated surfaces and roof surfaces (Tables 5.4 and 7.4). The garden soil and the sample taken at depth yield values outside of the range of the highway associated surface sediments. The soils therefore appear to be generally more haematitic, that is magnetically "harder", than highway associated surface sediments.

Application of equations Eq5.1 and Eq5.4 classifies all soil samples with the roof grouping. This confirms that they are not the primary source of particulates giving highway associated sediments their mineral magnetic characteristics.

7.3 Paved Surface Constructional Materials.

Samples of materials used in the construction of the road and pavement surfaces were collected to ascertain if abrasion of the dressed surface by vehiclar traffic was giving rise to the heavy metal and mineral magnetic concentrations observed. Samples of road chippings were taken from two local stockpiles, one which had been exposed to the urban environment for two weeks and the other for approximately one year. Both stockpiles consisted of Mount Sorrel granite chippings. Chippings of less than 1 mm were analysed. Samples of tarmacadam were obtained during pavement repair carried out in Chilwell Gardens but outside the sub-catchment being studied.

7.3.1 Heavy Metals in Paved Surface Constructional Materials.

The metal levels found in association with surface construction materials, particularly those in tarmacadam, (Table 7.6) are low compared to levels found in sediments collected from the paved surfaces. The combined range of levels for both tarmacadam and road chippings are of the same order to those given by Shaheen (1975) for asphalt. The relative enrichment of the metals Cu, Pb and Zn in highway associated surface sediments must, therefore, imply that the breakdown and wear of surface constructional material cannot itself explain the observed

Table 7.6 Heavy Metal Analyses of Surface Constructional Materials

	Cu ($\mu g\ g^{-1}$)	Fe ($mg\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Mn ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)
Road Chippings (n=4)					
Range	40.0-73.6	16.7-21.9	9.6-121.5	248.3-378.2	96.7-267.0
Mean	52.0	19.5	71.6	316.8	164.7
Tarmacadam (n=3)					
Range	1.4-2.7	0.6-2.2	7.2-16.0	80.3-165.6	43.5-110.7
Mean	2.1	1.3	13.4	109.6	67.8

sediment associated levels of these metals. With regard to Fe and Mn it would seem that the road chippings may contribute to the observed levels in highway associated sediments to some extent as the values found are similar to the lower end of the range of these metal values found in highway associated sediments (Table 5.1). However, it would appear that road chippings alone cannot account for the full range of Fe and Mn levels found in highway associated sediments. The relative concentrations of Zn and Pb suggest that, as in the case of soils, constructional materials may contribute to the observed concentrations found in the pavement sediments.

7.3.2 Mineral Magnetic Parameters of Paved Surface Constructional Materials.

The measurements of mineral magnetic parameters for the constructional materials is presented in Table 7.7. It can be seen that the magnetic mineral concentration dependent parameters for road chippings are similar to those of road gutter sediments (Table 5.1 and 7.7). The range of values determined for the tarmacadam sample is minimal and is much less than any values found in highway associated sediments. In contrast the road chipping values indicate that these materials may make some contribution to the mineral magnetic charateristics of the highway associated sediments.

Table 7.7 Mineral Magnetic Parameters of Surface Constructional Materials

	χ ($cm^3\ kg^{-1}$)	IRM_{300mT} (10^{-3} A $m^2\ kg^{-1}$)	IRM_{-20mT} $/IRM_{300mT}$	$-IRM_{-40mT}$ $/IRM_{300mT}$	IRM_{-20mT} $/-IRM_{-40mT}$
Road Chippings (n=4)					
Range	1.49-3.77	21.6-67.7	0.45-0.55	-0.03-0.16	-11.39-5.96
Mean	2.36	36.7	0.5	0.08	0.74
Tarmacadam (n=3)					
Range	0.02	0.1-0.2	0.55-0.68	0.26-0.46	1.48-2.12
Mean	0.02	0.1	0.6	0.33	1.86

The backfield ratio characteristics, however indicate that the road chippings exhibit very different characteristics to those of highway associated sediments. The values of the $\mathrm{IRM}_{-20mT}/-\mathrm{IRM}_{-40mT}$ ratio for road chippings are much greater than those of the paved sediments or the roof sediments. This would suggest that the road chippings have more haematitic character than the highway associated sediments collected in the sub-catchment. It would seem unlikely that materials with such differing characteristics from the highway associated source sediments are a primary source of particulates within the sub-catchment despite the observed similarity in the ranges of magnetic mineral concentration dependent parameters for road gutter and road chipping samples.

The difference between the mineral magnetic character of highway associated sediments and the highway construction materials is highlighted by the application of equations Eq5.1, Eq5.4, Eq6.1 and Eq6.2. These classify the road constructional materials with the roof grouping rather than that of the road. This suggests that while the constructional materials can be seen by visual inspection to constitute the majority of the sediment in roadside dusts the mineral magnetic signature of the sediment is dominated by less obvious constituents. These are not distributed with particle size (Chapter 6) which supports the idea of coagulation of minor constituents onto larger particles.

7.4 Automobile Derived Particulates.

Automobile derived particulates were obtained directly from a variety of small family "hatchback" vehicles, all petrol driven with front disc brakes and rear drum brakes. Samples originating from diesel buses were obtained from a discarded bus exhaust pipe and from the collection of atmospheric particulates in a bus depot in North London.

In Chapter 6 the size of emitted particulates was discussed in relation to the metal and magnetic mineral distributions in highway associated sediments. In order that it could be established if particulates of less than 63 µm nominal diameter were present in automobile derived particulates, samples of exhaust and brake particulates were sieved. The results are presented in Table 7.8 and confirm that vehicle derived particulates with a nominal diameter of 63 µm or less do occur, particularly in dusts from disc brakes and the internal areas of exhaust pipes.

Table 7.8 Percentage Size Distribution of Automobile Derived Particulates.

Particle Size (µm)	Exhaust Pipe Internal	Exhaust Pipe External	Drum Brake	Disc Brake
>500	0	46.4	0	0
250-500	0	29.8	6.3	9.8
125-250	16.5	11.3	16.3	9.8
63-125	10.8	7.8	50.8	12.1
38-63	13.3	3.5	14.7	10.5
<38	59.4	1.0	11.9	57.8

In the case of particulates from the external surface of the exhaust pipe, the size distribution depended on the force applied with the sampling brush. Larger particulates resulted from using increasing force. The results presented in Table 7.8 represent sampling of these particulates using the minimum of force practicable.

7.4.1 Heavy Metals in Automobile Derived Particulates.

The results of the heavy metal analyses of the various source particulates are given in Table 7.9. Bulk samples of the particulates were analysed; no analysis of size fractionated particulates was carried out.

The average concentration levels quoted in Table 7.9 indicate that automobile derived particulates could easily account for the elevated concentrations of heavy metals found in the sediments collected from the paved surfaces within the sub-catchment. The highest Pb concentrations are clearly associated with particulates sampled from the inside

Table 7.9 Heavy Metal Concentrations in Some Sampled Automobile Derived Particulates.

		Cu ($\mu g\ g^{-1}$)	Fe ($mg\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Mn ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)
Family Car Exhaust Particulates						
Inside	[n=3]	35.6-57.7 (47.7)	74.3-234.7 (129.9)	84187.7-119420.1 (103380)	103.0-881.2 (377.5)	1894.5-27436.0 (12478.6)
Outside	[n=3]	68.1-85.7 74.1	116.8-402.0 246.5	611.2-1991.8 (1118.5)	630.2-1284.2 (870.7)	63806.7-305501.9 (185306.9)
Exhausted Particles	[n=2]	36.3	142.0	210500	502.1	15488.2
Brake Particulates						
Disc	[n=1]	17680.5	348.8	1722.3	1577.8	7133.5
Drum	[n=2]	411.0, 740.9 (575.9)	197.6, 395.5 (296.6)	411.0, 549.2 (480.1)	1798.1, 1908.5 (1853.3)	1050.3, 2211.0 (1630.7)
Wheel Hub	[n=2]	14476.4, 15590.4 15033.4	286.7, 337.8 312.2	7426.3, 8422.7 (7924.5)	2253.4, 2441.9 (2347.6)	10720.1, 12656.4 (11688.3)
Paint Particulates						
New Paint	[n=1]	41.8	176.6	5061.9	249.6	8048.8
Corroded	[n=1]	55.1	236.0	32.286	636.2	6611.1
New Tyre Rubber	[n=2]	2.4, 3.9 (3.1)	0.2, 0.3 (0.3)	17.0, 60.8 (38.9)	2.2, 5.1 (3.6)	3455.8, 3622.9 (3539.4)
Bus/Diesel Inside Exhaust	[n=1]	52.5	21.9	272.4	udl	283.3
Air; Bus Station	[n=4]	163.9-297.8 (215.5)	4.0-12.5 (8.8)	428.6-1502.2 (958.6)	udl (udl)	419.0-1489.1 (715.8)

Mean values in parentheses

udl - under detection limits

surfaces of exhausts of petrol engined vehicles, as well as from those particulates collected on filters held at distances of within 4 cm from the exhaust tail pipe. Brake particulates, especially those associated with disc brakes, exhibit the highest Cu concentrations. Samples of particulates brushed from the external surfaces of exhaust pipes on petrol engined vehicles exhibit the greatest Zn concentrations. These concentrations were greater by a factor of ten than the Zn concentrations determined in internal samples. This suggests that the dominant source of Zn is the rusting and flaking of the external galvanised surfaces. Other Zn sources, including paint and disc brake associated particulates, also exhibit high concentrations which are greater than those found in tyre rubber. In terms of loadings, however tyre wear will produce a much greater contribution to highway associated surface particulates than the corrosion of vehicle bodywork or the wear of brakes. Brake and external exhaust particulates also exhibit high Fe and Mn concentrations. The concentrations found can clearly explain the elevated levels found in road centre sediments (Table 5.1) which have not been fully accounted for by soil or road construction materials. The results also suggest that the premise that Mn and Fe can be used as indications of background metal levels should not be applied in areas where vehicular traffic is present.

The results listed in Table 7.9 show that the bus exhaust particulates are not free of metals. The concentrations are less than those found in the exhaust particulates from petrol engines, with the sole exception of Cu. The exhaust particulates of both types of engines, however are not significant sources of Cu when compared to brake particulates. It is unlikely therefore that bus exhaust particulates make a significant contribution to the metal loadings found in street dusts.

Consideration of the data presented in Tables 7.8 and 7.9 shows that particulates with high concentrations of Cu and Pb occur in the less than 38 μm size fraction. In the case of Zn, external exhaust particulates are dominated by the larger size fractions. The majority of particulates from tyre wear are known be of less than 30 μm nominal diameter (Cadle and Williams, 1978). Therefore the patterns of Zn distribution with particle size may be influenced by particulates associated with high Zn concentrations occuring in more than one predominant size fraction as proposed in Chapter 6.

7.4.2 Mineral Magnetic Parameters of Automobile Derived Particulates.

The magnetic mineral parameters for vehicle derived particulates (Table 7.10) cover the ranges and characteristics of all sediment samples found in the sub-catchment. It might be expected that source materials should have higher concentrations of magnetic minerals than the sediment sub-set to which they are contributing. Consequently it might also be expected that the dominant source should have greater magnetic mineral concentration dependent parameter values than the maximum found in sampled sediments within the sub-catchment. The maximum χ and IRM_{300mT} values found in the samples collected at Chilwell Gardens were 7.26 cm^{3} kg^{-1} and 105.24 $*10^{-3}$ A m^{2} kg^{-1}, respectively; both in road centre sediments. Particulates from the external surfaces of petrol engine exhaust pipes, some samples of particulates from the internal surfaces of petrol engine exhaust pipes, brake particulates and corroded paint all exhibit greater values of these magnetic mineral concentration dependent parameters.

The highway associated surface sediments are generally more ferrimagnetic than those of the roof and soil. In addition it has been seen that the ferrimagnetic characteristics increase with the proximity of the sample area to the road centre. Therefore, the dominant source ought to be more ferrimagnetic than the road centre sediment samples. This would be indicated by an IRM_{-20mT}/IRM_{300mT} value of less than 0.191 and an IRM_{-40mT}/IRM_{300mT} value of less than -0.374. These characteristics are only found in the particulates collected from the internal surfaces of petrol engine exhaust pipes and in some samples taken from the external surfaces.

Applying the equations Eq5.1, Eq5.4, Eq6.1 and 6.2 all vehicular particulates would fall into the classification of the highway particulates with the exception of the new paint samples, the particulates from inside the bus exhaust and the atmospheric samples

Table 7.10 Mineral Magnetic Parameters as Found in Some Sampled Automobile Derived Particulates.

		χ (cm^3 kg^{-1})	IRM$_{300mT}$ (10^{-3} A m^2 kg^{-1})	IRM$_{-20mT}$ /IRM$_{300mT}$	IRM$_{-40mT}$ /IRM$_{300mT}$	IRM$_{-20mT}$ /-IRM$_{-40mT}$
Family Car Exhaust Particulates						
Inside	[n=3]	2.11-3.86 (3.32)	17.55-151.88 (64.137)	-0.126-0.024 (-0.036)	-0.394 - -0.65 (-0.55)	0.01-0.19 (0.09)
Outside	[n=3]	6.32-47.3 (23.81)	277.72-645.66 (378.34)	-0.079-0.46 (0.128)	-0.198 - -0.614 (-0.475)	0.011-2.3 (0.815)
Exhausted Particles	[n=2]	-	96.89, 98.65 (97.77)	0.119, 0.173 (0.146)	-0.46, -0.489 (-0.475)	0.242, 0.376 (0.309)
Brake Particulates						
Disc	[n=1]	123.06	393.67	0.507	-0.001	5074
Drum	[n=2]	117.64, 174.05 (145.85)	375.77, 1289.17 (832.47)	0.315, 0.862 (0.588)	-0.06, -0.418 (-0.239)	2.061, 5.278 (3.67)
Front Wheel Rim	[n=2]	273.32, 288.61 (280.96)	277.72, 286.61 (282.17)	0.454, 0.471 (0.463)	-0.042, -0.046 (-0.044)	10.239, 10.94 (10.589)
Paint Particulates						
New Paint	[n=1]	0.96	4.079	0.597	-0.192	3.109
Corroded	[n=1]	64.67	1225.451	0.249	-0.775	0.321
New Tyre Rubber	[n=2]	0.03, 0.05 (0.04)	0.2, 0.28 (0.24)	0.04, 0.057 (0.0483)	-0.022, -0.031 (-0.027)	1.795, 1.842 (1.819)
Bus/Diesel						
Inside Exhaust	[n=1]	94.62	38.512	0.421	-0.203	2.076
Air; Bus Station	[n=4]	- -	10.0-19.96 (15.14)	0.435-0.465 (0.446)	-0.104 - +0.089 (-0.002)	4.188-18.73 (9.389)

Mean values in parentheses

collected within the bus station. It would therefore appear that exhaust particulates from petrol engined vehicles are most likely to be the main source of the magnetic minerals contributing to the assemblages found in the sediment samples taken from the highway associated surfaces. It should be stressed, however that brake particulates, while not characterised as a source by direct comparison of their exhibited backfield ratios to those of road centre sediments, would normally fall into the overall classification of highway sediments as derived from the statistical analysis. These particulates may not be present in large enough quantities to dominate the mineral magnetic characteristics of the assemblage but they possess high magnetic mineral concentrations which may considerably augment the concentrations found. This could explain why the concentration parameters for internal exhaust particulates do not account for the concentrations in the assemblages, as indicated by χ and IRM_{300mT}, on their own.

The range of possible applications of mineral magnetic parameters is highlighted by these findings and it would appear that by their use diesel and petrol engine particulates can be differentiated. These parameters could therefore be applied to confirming the dominant source of particulates which contribute to building soiling in urban areas.

7.5 Litter.

For the purposes of this study, litter is taken to include leaves that drift into the sub-catchment from outside as well as discarded materials deposited by passers-by. The composition of typically sampled litter included;

leaves
paper litter
plastic litter
cigarette butts

The leaf samples were obtained from trees whose branches overhang the sub-catchment. The total bulk of the leaf was analysed as it was not intended to assess only the atmospheric particulates either adhering to or deposited on the leaf surface.

The paper and plastic litter fraction was an amalgamated sample of a variety of items that are commonly expected to be found as litter, including crisp packets, sweet packets and sheets of printed paper.

During the sampling of sediments it was found that a significant proportion of the extraneous litter removed by sieving the sediment through a 1000 μm sieve was made up of cigarette ends or "butts". The items analysed were therefore the remains of smoked cigarettes. In order that the cigarette "butts" were not contaminated by the act of extinguishing them, they were extinguished by immersion of the burning end in water. This avoided the cigarette reacting with, or collecting particulates from the the surface it was extinguished against.

All three samples represent potential litter rather than actual litter collected within the sub-catchment. The intention was to assess the heavy metal and magnetic mineral concentrations to be found in these materials prior to any contamination that may occur once they are deposited on an urban catchment surface.

7.5.1 Heavy Metals in Litter.

The results of the heavy metal analyses (Table 7.11) indicate that none

Table 7.11 Heavy Metal Concentrations in Potential Constituents of Litter.

	Cu ($\mu g\ g^{-1}$)	Fe ($mg\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Mn ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)
Leaves	23.7	1.87	205.6	342.4	184.7
Paper	4.3	0.87	udl	42	31
Cigarettes	32.9-83.0	1.0-1.07	0-0.3	85.9-107.8	43.0-73.8

udl = under detection limits

of the occasional sources analysed as "litter" can explain the concentrations of heavy metals found within the sub-catchment. All the concentrations found are well below the road centre concentrations and are most similar to those found in pavement sediments. This may be indicative of the assimilation of litter into pavement sediments.

7.5.2 Mineral Magnetic Parameters of Litter.

The determinations of mineral magnetic parameters for the litter samples were unreliable with the samples giving very low signals indicative of very weak magnetic mineral concentrations. This is hardly surprising as paper had originally been used as a packing material in test determinations of mineral magnetic parameters for sediment samples prior to the use of foam (Section 4.5.2.1).

Only the leaf samples gave reliable results with IRM_{300mT}, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT} values of 12.483 $*10^{-3}$A m^{2} kg^{-1}, 0.352 and -0.21, respectively. These values are similar to those of soil and roof samples. Use of the statistically derived equations Eq5.1, Eq5.4, Eq6.1 and Eq6.2 classify the leaf samples with the roof sediments. This almost certainly reflects the influence of the mineral magnetically "harder" atmospheric particulates which would have been present on the leaf surfaces.

The results of mineral magnetic parameter determinations made on the potential litter samples indicate that litter is significantly different in mineral magnetic character to the highway associated sediments. Additionally litter cannot account for the magnetic mineral concentrations in highway associated sediments as indicated by χ and IRM_{300mT} and clearly litter is not a predominant source of particulates contributing to highway associated sediments.

CHAPTER 8. HEAVY METAL LEVELS AND MINERAL MAGNETIC PARAMETERS IN STORMWATER PARTICULATES ORIGINATING FROM THE CHILWELL GARDENS SUB-CATCHMENT.

8.1 Introduction.

In Chapters 5 and 6 the source sediments within the Chilwell Gardens sub-catchment were investigated with regard to their characteristic heavy metal concentrations and mineral magnetic properties. As discussed in Chapter 1 there is a need to identify the accumulation and movement of heavy metals within the urban environment, and to define the resulting relative contributions of heavy metals associated with source sediments to the ultimate stormwater pollutant strength. The objective of investigating the suspended particulates in stormwater runoff from the Chilwell Gardens sub-catchment was to ascertain if the characteristics, and specifically the mineral magnetic properties of the source sediments as defined in Chapters 5 and 6, could be successfully utilised to quantify the contributions of source sediments. It has already been shown that primary magnetic characterisation is only successful in defining roof and highway associated sediments. The major concern of this subsequent investigation of stormwater particulates was, therefore, to define their characteristics in relation to these two source sediment types. It has been recently suggested that the major properties of the sediment load observed at a sewer outfall is derived from 'in-pipe' scouring and resuspension (Gujer and Krejci, 1987; Crabtree, 1988). An attempt has therefore been made to relate stormwater particulate characteristics to the sub-surface sediments found within the sub-catchment.

Samples of suspended sediments in stormwater runoff were collected at the sewer pipe exiting from the Chilwell Gardens sub-catchment (Figure 4.2; Section 4.7.2). Three storm events were captured at this site. In addition to these samples of the stormwater particulates, three samples of suspended particulates in roof runoff relating to each storm event were collected using the Warren Jones WJ40 effluent sampler. The roof runoff samples relate to initial bulk samples of runoff and are not regarded as being representative of the total loadings discharged from the roof during any specific storm event. These particulates do, however, allow a comparison of the characteristics of stormwater particulates present in roof runoff to be made with those of stormwater particulates found in combined roof and highway runoff.

8.2 Hydrological Characteristics of Storm Events.

Considerable instrumental difficulties meant that only three storm events were captured for the sub-catchment and in the case of one of these events full flow data is lacking. The three storm events were captured between 14th May 1985 and 5th July 1985. The hydrological characteristics of these events are given in Table 8.1 and variations in flow for the first two events are illustrated in Figures 8.1 and 8.2.

Table 8.1 Hydrological Characteristics of Recorded Storm Events at the Chilwell Gardens Sub-Catchment.

Date of Storm	Storm Code	Duration (min)	Maximum Flow ($l\ sec^{-1}$)	Rainfall Volume (l)	Runoff Volume Road (l)	Runoff Volume Roof (l)
14-5-85	C1	240	1.26	2290.75	813.44	998.81*
24-6-85	C2	70	0.95	1963.5	522.26	856.12*
5-7-85	C3	200	-	2945.25	1098.32*	1284.18*

* Estimated from rainfall data (see text below).

The first of the three storms (C1) could be considered as two separate storms of 20 minutes duration and 130 minutes duration respectively, with an interval of approximately 90 minutes between them. Owing to the interdependence of the characteristics of both events, however they have been considered as one storm event. All three events, C1, C2 and C3 are not contiguous in that there was another intervening storm event that occurred on the 21st June 1985 but was not captured.

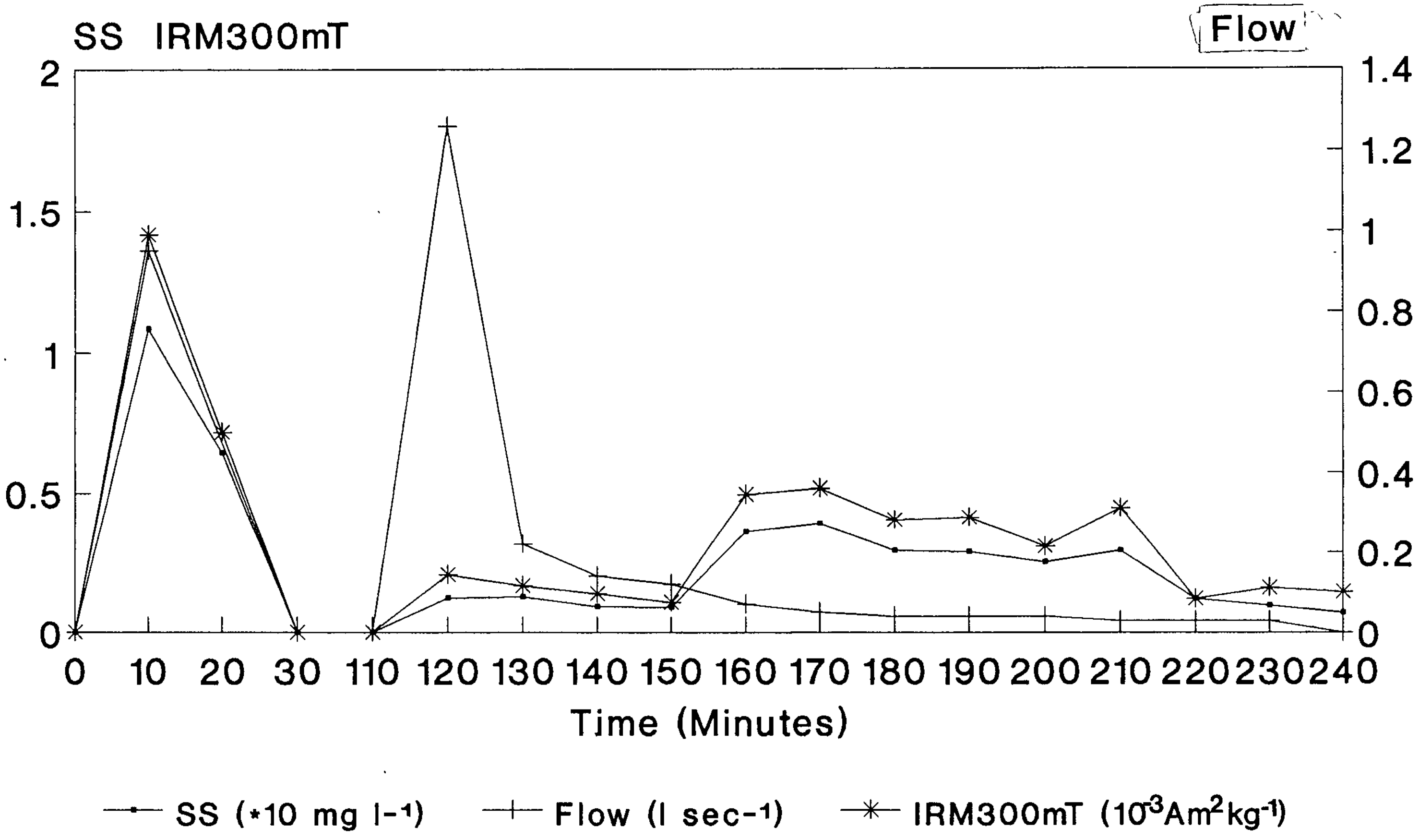


Figure 8.1 Variation of Flow, Suspended Solids and IRM300mT over Time for Event C1.

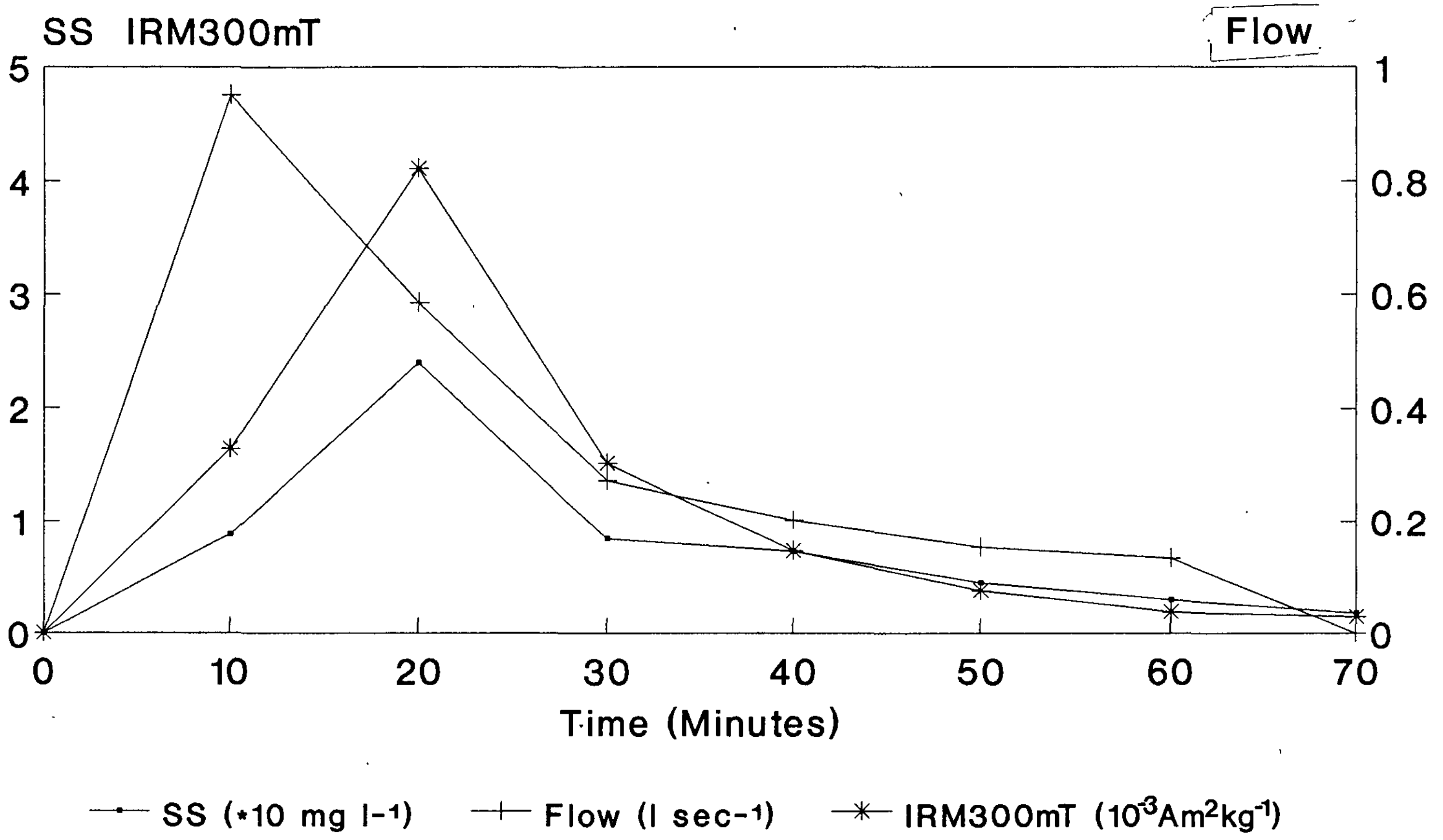


Figure 8.2 Variation of Flow, Suspended Solids and IRM300mT over Time for Event C2.

The runoff volume from the roof surfaces was calculated as being the product of rainfall depth and the net ground area covered by the roofs, assuming a negligible depression storage. In the case of event C3, the road runoff was calculated from the rainfall depth, the area of the highway associated surfaces and the depression storage for the highway surfaces of the sub-catchment as defined by Harrop (1984a).

The recorded storm events are similar in duration to those previously observed within the sub-catchment (Harrop, 1984a; Warren, 1987). The events are therefore thought to be fairly typical for the sub-catchment, although they necessarily only represent a limited range of the actual storm events that may be encountered on an annual serial basis.

8.3 Heavy Metals in Stormwater Particulates.

8.3.1 Heavy Metal Concentrations Associated with Stormwater Particulates.

Samples of stormwater were collected at five minute intervals during the storm events. In order that these could be directly related to flow measurements, which were taken at ten minute intervals, two consecutive samples were filtered through one cellulose 0.45 μm filter and the combined heavy metal levels determined. Where it was found that samples contained very small quantities of suspended particulates, such as occurred in the recessional phase of the storm, three combined samples were filtered (Chapter 4). The heavy metal and suspended sediment concentrations and loadings are summarised in Table 8.2. For events C1 and C2, two mean values for stormwater concentrations are given. The first value is calculated from the total loadings divided by the total volume of runoff. The second (shown in parentheses) is calculated as the mean of the individual concentrations found in each sample of stormwater particulates. For event C3 only the latter could be calculated. The mean concentrations as calculated from the total loadings and volume for events C1 and C2 are found to be broadly similar. The mean metal concentrations as calculated from concentrations determined in individual samples are also broadly similar for all three events. It can

Table 8.2 Heavy Metal Concentrations and Loadings Associated with Stormwater Particulates Captured During Storm Events at the Chilwell Gardens Sub-Catchment.

	Cu	Fe	Pb	Mn	Zn
13-5-85					
Concentration					
Mean ($\mu g\ l^{-1}$)	15.7(7.1)	2133.0(1171.9)	61.164(33.6)	78.487(44.8)	67.37(38.9)
Range ($\mu g\ l^{-1}$)	2.3-35	390.8-4361.2	6.7-129.9	4.1-153.1	13.3-135.5
Mean ($\mu g\ g^{-1}$)	237.3	41009	1029.8	1708.4	1634.6
Range ($\mu g\ g^{-1}$)	19.4-389.3	4491.7-61472.8	106.3-1653.2	140.3-3494.5	122.1-4005.1
Loadings					
Total (mg)	20.18	2739.22	78.55	100.70	86.51
24-6-85					
Concentration					
Mean ($\mu g\ l^{-1}$)	15.6(9.4)	1115.5(1084.0)	66.0(42.6)	79.8(61.5)	73.8(46.7)
Range ($\mu g\ l^{-1}$)	3.8-27.8	211.7-3183.7	5.7-89.6	39.4-108.8	10.5-103.9
Mean ($\mu g\ g^{-1}$)	124.8	13047.2	524.9	1103.7	581.6
Range ($\mu g\ g^{-1}$)	72.4-211.9	10848.5-16531.4	281.2-881.7	347.8-2470.5	420.6-960
Loadings					
Total (mg)	20.04	2328.74	84.73	101.77	94.75
5-7-85*					
Concentration					
Mean ($\mu g\ l^{-1}$)	(4.6)	(978.4)	(25.5)	(58.7)	(47.4)
Range ($\mu g\ l^{-1}$)	1.4-22.1	138.1-10687.1	1.2-322.3	32.1-115.2	10.7-327.1
Mean ($\mu g\ g^{-1}$)	97.8	12335.1	280.6	1376.9	914.9
Range ($\mu g\ g^{-1}$)	22.9-500.4	1631.8-46106.3	19.5-1208.9	369.1-5120.9	152.4-5895.9

* No loadings calculated owing to lack of flow data

Values in parentheses are the mean calculated as mean of all separate readings further be seen that the mean concentrations calculated from individual samples are generally lower than those calculated from the metal loading and runoff volume. This suggests, that if the flow had been recorded for event C3, the mean values for stormwater concentrations of heavy metals associated with suspended sediments would have been similar for all three storms. This similarity for all three events would appear to confirm that the storms are not atypical.

The metal concentrations (μg l^{-1}) associated with stormwater particulates are higher than the overall mean values found in a recent study of four monitored storm events for the same sub-catchment (Warren, 1987). This may simply represent a seasonal effect as the storm sampling in the previous study occurred between late July and mid September of the previous year. A further factor is undoubtedly the differing intensities of the sampled storms. The durations of storm events in both studies are similar, although the stormwater runoff volumes were generally greater in the storm events recorded in the previous study. The additional volume may have resulted in lower concentrations in terms of metal per unit volume.

This is, to some extent, substantiated by comparison of the mean concentrations in terms of metalper unit weight (μg g^{-1}). The mean metal concentrations associated with stormwater particulates in a number of previous studies are presented in Table 8.3.

Table 8.3 Average Metal Concentrations (μg g^{-1}) Associated with Stormwater Particulates as Recorded in Previous Studies.

	Cu	Pb	Zn	Reference
Chilwell Gardens, UK	83	1082	745	Warren, 1987*
South Oxhey, UK	126-482	514-2465	346-770	Morrison, 1985°
Bergsjön, Sweden	756-3364	411-1890	272-1312	Morrison, 1985°
Chalmers, Sweden	57-320	1062-3400	-	Svensson, 1987†

* Mean of four storm events
° Range of mean values for four storm events
† Range of mean values for road runoff for six storm events.

This data compares favourably with the concentrations found in this study (Table 8.2). Whilst the mean Cu concentration recorded by Warren (1987) at the same sub-catchment is slightly lower than the range of mean values recorded in this study, the mean concentration is within the full range of concentrations found. The mean values found in this study are also similar to those quoted by Morrison (1985) for stormwater samples collected at the outfall of the main catchment. Copper concentrations associated with stormwater particulates from a residential catchment at Bergsjön in Sweden are greatly elevated compared to the UK studies, although in general terms the levels conform to the Cu concentrations found in Swedish road runoff. This is undoubtedly due to the common usage of copper as a roofing material in Sweden, with abraded particulates being washed off by stormwater (Malmqvist, 1983; Morrison, 1985; Svensson, 1987). The mean Pb concentrations presented in Table 8.3 are slightly higher than the mean values in Table 8.2, whilst Zn is within the range of the mean values for the storms. Unlike the relative concentrations found in this study, the previous studies suggest that Pb concentrations are generally greater than those of Zn.

Literature values of total metal concentrations in stormwater (Table 2.16) can be seen to be generally greater than the concentrations determined for suspended stormwater particulates which were captured in this sub-catchment. This implies that dissolved metal concetrations may significantly contribute to the total concentrations observed in stormwater runoff. However, the Pb values are fairly typical of separate stormwater runoff quoted by Hall and Ellis (1985) in a review of urban pollutant discharges suggesting that the dissolved Pb concentrations influence the magnitude of the total concentration to a lesser extent. Ellis et al (1987) estimated that annual loadings of dissolved Cu and Zn in stormwater at the main South Oxhey catchment were two to three times greater than the annual loadings of solid associated metals, whilst for Pb the solid associated Pb loading was some five times greater than that of the dissolved Pb loading. It is apparent therefore that of the metals Cu, Zn and Pb, the latter would exhibit least difference between the concentration of total metal in stormwater and concentration of solid associated metal in stormwater.

An additional reason for disparity between Tables 2.16 and 8.2 is that the majority of data in Table 2.16 was recorded at catchments of much greater size which are both more heavily trafficked and nearer to large urban centres and therefore are likely to result in higher metal concentrations being recorded.

8.3.1.1 Investigation of Metal Concentrations Associated with Stormwater Particulates in Relation to Source Particulates.

The suspended sediment metal concentrations, expressed as $\mu g\ g^{-1}$, were compared to those found in the bulk and fractionated paved surface and roof gutter sediments. For Cu, Pb, Mn and Zn, the concentrations found were greater than those found in the bulk sediment samples, including the samples of in-pipe deposits. Elevated concentrations of metals associated with stormwater particulates compared to those found in roadside dustshave been noted in several studies. It has been suggested that fine particulates, with associated higher concentrations of heavy metals are preferentially removed by runoff and therefore will result in higher concentrations associated with runoff particulates (Harrison and Wilson, 1983; Revitt et al, 1981; Warren, 1987). The Cu, Fe, Pb, Mn and Zn concentrations of stormwater particulates are generally comparable with the finer fractions (less than 63 μm) of highway associated sediments and gully pot sediments (Table 6.1 and Table 8.2). The maximum concentrations of Mn and Zn associated with stormwater particulates (5121 and 5896 $\mu g\ g^{-1}$, respectively) are greater than the maximum concentrations observed in the source sediments (1494 and 2050 $\mu g\ g^{-1}$, respectively). For these metals it would appear that an additional explanation of the processes resulting in elevated metal concentrations associated with stormwater particulates is required (See Section 8.3.1.2). Iron concentrations associated with stormwater particulates, were seen to be lower than Fe concentraions in the finer fractions of highway associated surface sediments in the sub-catchment. It is also noteable that Zn concentrations and loadings in stormwater particulates tend to be greater than those of Pb whereas in highway surface sediments the inverse is true (Tables 5.1, 6.1 and 8.2).

The mean and maximum concentrations of the metals, Cu, Mn and Zn occurring in the finer fractions of roof sediments were found to be less than the mean and maximum concentrations in stormwater suspended sediments for events C1 and C2 (Tables 6.2 and 8.2). The mean Cu and Zn concentrations for stormwater sediments collected in event C3 were observed to be similar to those of the finer fractions of roof sediments but the maxima for Cu and Zn were much greater in stormwater particulates than in the fine roof particulates. The mean Fe and Pb concentrations in the finer fractions of roof sediment were also greater than those of stormwater sediments. The Pb concentrations in roof gutter sediments are generally greater than those of Zn, unlike the relative magnitudes of Pb and Zn concentrations and loadings in stormwater particulates. The mean Zn concentration of roof surface sediments is lsightly greater than that of Pb (Table 5.1). It would appear that roof particulates cannot fully provide the range of concentrations observed in stormwater particulates with respect to Cu, Mn and Zn, although the relative mean Pb and Zn concentrations in roof surface sediments imply that roof sediments may exert an influence on the concentrations associated with stormwater particulates.

Relating the concentrations associated with stormwater particulates to those of sediments deposited within the pipes of the drainage system does not allow this source to be cited as a more probable source of stormwater heavy metals than surface sediments. The concentrations of metals associated with in-pipe sediments reflect the immediate surface source sediments (Chapter 5). The Pb concentrations associated with in-pipe deposits were greater than those of Zn, as were roof gutter and highway associated sediments, and unlike the relative concentrations of Pb and Zn in atmospheric and roof surface particulates.

The only other probable source of stormwater particulates is bulk deposition. The metal concentrations ($\mu g\ g^{-1}$) associated with the particulate fraction of collected bulk deposition for each storm are given in Table 8.4. The concentrations of Cu associated with the solid fraction of bulk deposition were greater than the mean concentrations found in stormwater particulates. With respect to storm events C1 and C2, the Mn concentration associated with the solids in the bulk

Table 8.4 Heavy Metal Concentrations ($\mu g\ g^{-1}$) in the Particulate Fraction of Bulk Deposition.

	Cu	Fe	Pb	Mn	Zn
Storm C1	500.0	51847.6	1006.0	1743.9	1109.8
Storm C2	375.0	50078.9	855.3	1394.7	875.0
Storm C3	250.0	25135.2	635.2	827.9	717.2

deposition and the mean Mn concentration associated with stormwater solids were found to be similar. The mean Mn concentration for stormwater solids in event C3 was found to be greater than that of the Mn concentration in the solid phase of bulk deposition. Iron concentrations were greater than those of stormwater particulates for events C1 and C2. The concentrations of Pb and Zn in atmospheric particulates fell within the range of concentrations found in stormwater particulates. Unlike the Pb and Zn concentrations found in highway surface sediments, Zn concentrations in the solid fraction of bulk deposition were generally greater than those of Pb. It is not unusual for Zn concentrations in precipitation to be greater than Pb concentrations (Peirson et al, 1974; Andersen et al, 1978) nor for rates of Zn deposition to be greater than those of Pb (Duggan and Burton, 1983; Nürnberg et al, 1983). It has also been found that Zn concentrations in air are greater than those of Pb at sites some distance from a highway, while at a site proximal to the highway the relative magnitudes are reversed (McKee et al, 1980)(Table 2.10). The relative magnitudes of Pb and Zn concentrations and loadings found in stormwater particulates would therefore suggest that atmospheric inputs are exerting a significant influence on stormwater concentrations, and are probably an important source of stormwater particulates. The magnitude of Mn concentrations and loadings also supports this proposition.

Investigation of the concentration of metals associated with the particulates in roof runoff was also carried out and the results are presented in Table 8.5.

Table 8.5 Heavy Metal Concentrations ($\mu g\ g^{-1}$) Associated with Stormwater particulates in Roof Runoff.

	Cu	Fe	Pb	Mn	Zn
Storm C1	111.7	76727.3	3015.2	3356.1	3265.9
Storm C2	66.3	50596.3	1422.6	1245.1	1421.7
Storm C3	62.8	55304.2	1768.1	1518.1	2099.4

It can be seen that the Mn concentrations associated with particulates in roof runoff are in excess of the mean concentrations associated with stormwater runoff particulates. for storms C1 and C3, the Zn concentrations are greater than the Pb concentrations associated with particulates in roof runoff. The concentrations of Pb and Zn for storm C2 are similar in magnitude. Roof runoff particulates originate from bulk deposition at the time of the storm event, and *in situ* roof sediments derived from attrition of roof surfaces and dry deposition of atmospheric particulates. As the *in situ* roof gutter sediments do not exhibit greater Zn concentrations than Pb, it is felt that this data reinforces the suggestion that particulates in wet deposition are responsible for contributing to the Mn, as well as Fe, Pb and Zn concentrations in stormwater sediments. However, the sampler only allowed the trapping of an initial bulk sample of the roof runoff and is not fully representative of the storm as a whole. it is important therefore to investigate the variation of metal concentration over each storm event to assess whether the relationships highlighted by the mean concentrations are consistent throughout the storm.

8.3.1.2 Investigations of Variation of Metal Concentrations Associated with Stormwater Particulates over the Duration of Storm Events.

Variations in heavy metal and suspended sediment concentrations throughout the storm hydrographs of events C1, C2 and C3 are presented in Figures 8.1 to 8.5. it can be seen that there are distinct similarities in the variations of Cu, Fe, Pb, Mn, Zn and suspended particulates for all storms. The strong affinity of metals for stormwater suspended solids has been noted in other studies (Bourcier and Sharma, 1980; Wilber and Hunter, 1980). All storms exhibit an initial peak in metal concentrations and suspended sediments which reduces to a more constant level throughout the remainder of the event. In storm event C1 it can be seen that metal concentrations and suspended sediments exhibit a second smaller but less well defined peak. Similar secondary peaks have also been noted in previous studies and have been suggested to be due to input of fresh surface sediment from the impervious contributing areas (Ellis, 1976; Tucker and Mortimer, 1978; Morrison et al, 1984; Thornton and Saul, 1987).

If the metal concentrations (µg g^{-1}) associated with stormwater sediments were constant throughout the storm event the correlation between suspended solids and metal concentrations (µg l^{-1}) would be expected to have a coefficient of 1. The extent to which the variation of metal concentrations (µg g^{-1}) associated with stormwater particulates disrupts the expected correlation was investigated. It was found that for all storms the metals, Cu, Fe, Pb and Zn, all correlated well with suspended solids (Correlation coefficients >0.79). This suggests that the variation in metal concentrations (µg l^{-1}) is dominated by variation in the suspended sediment concentrations.

The variation of suspended solids did not consistently correlate with flow; good correlation was seen in storm C2, while it was very weak for storm C1. The correlation of metals with flow was also found to vary in a similar manner. Although two storms cannot be viewed as significant, this does suggest that variation in suspended solids concentrations is not simply a function of flow. The variation in stormwater concentrations and loadings of suspended solids is likely to be

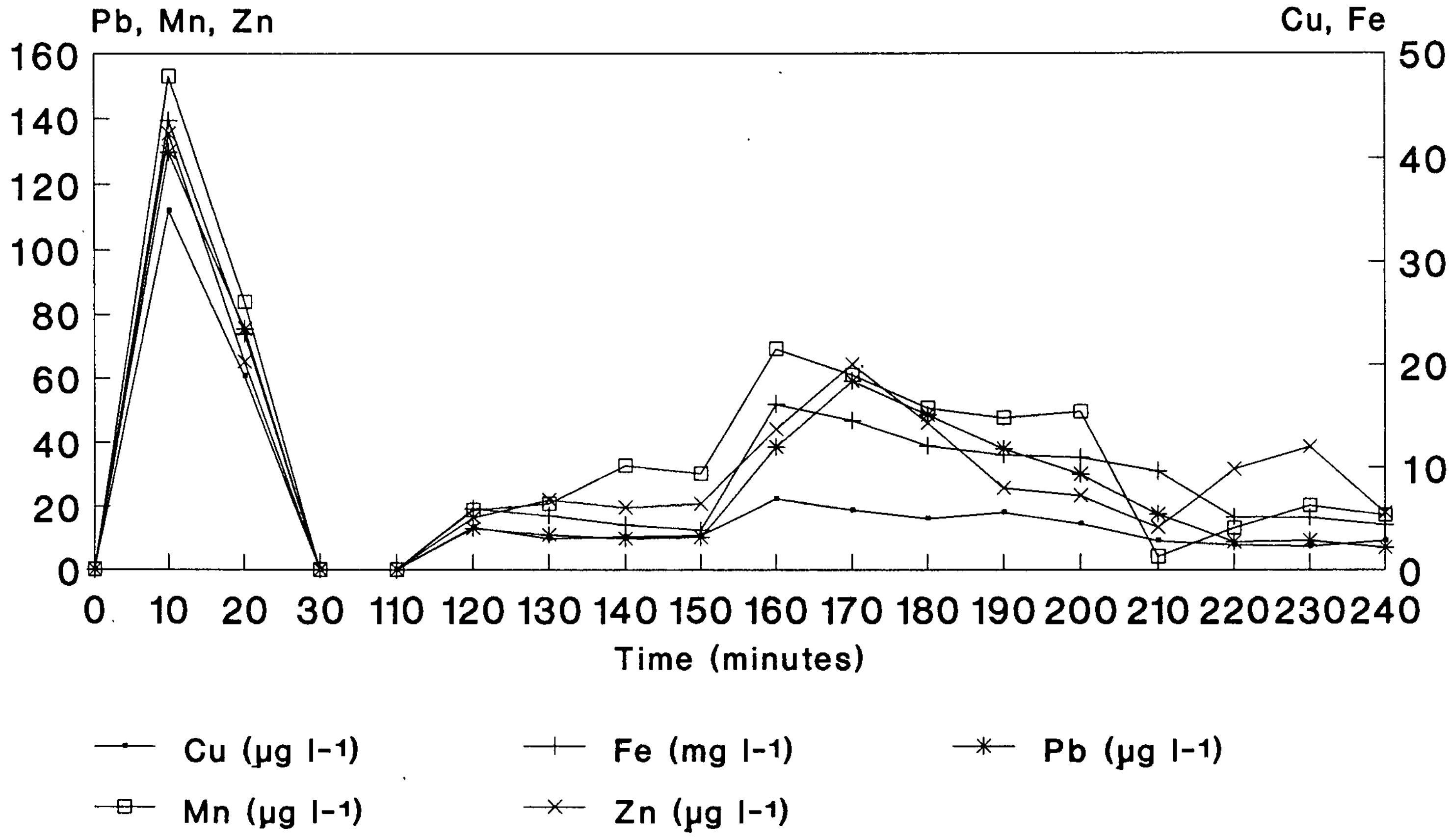


Figure 8.3 Variation of Particulate Associated Metals over Time for Event C1.

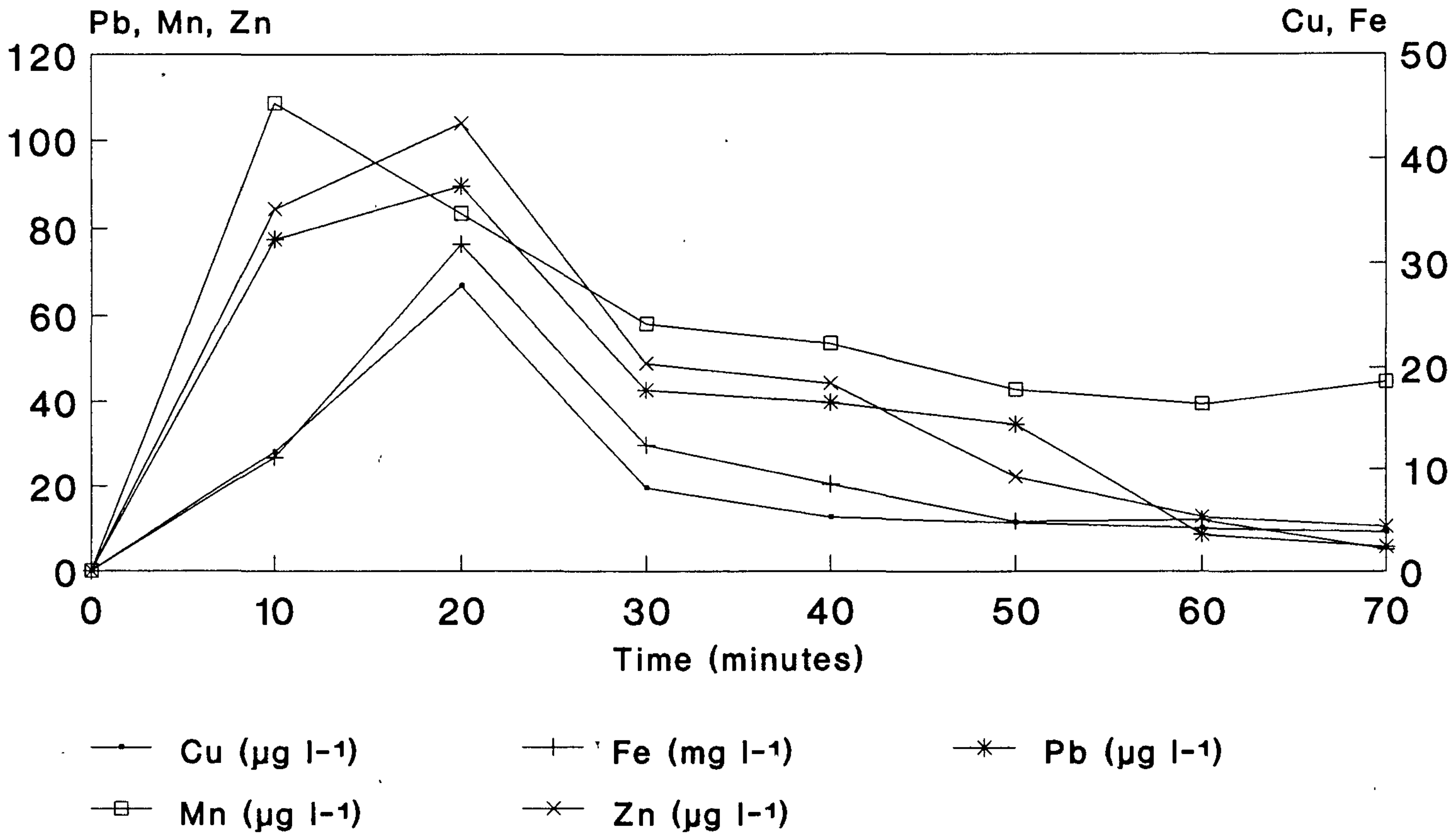


Figure 8.4 Variation of Particulate Associated Metals over Time for Event C2.

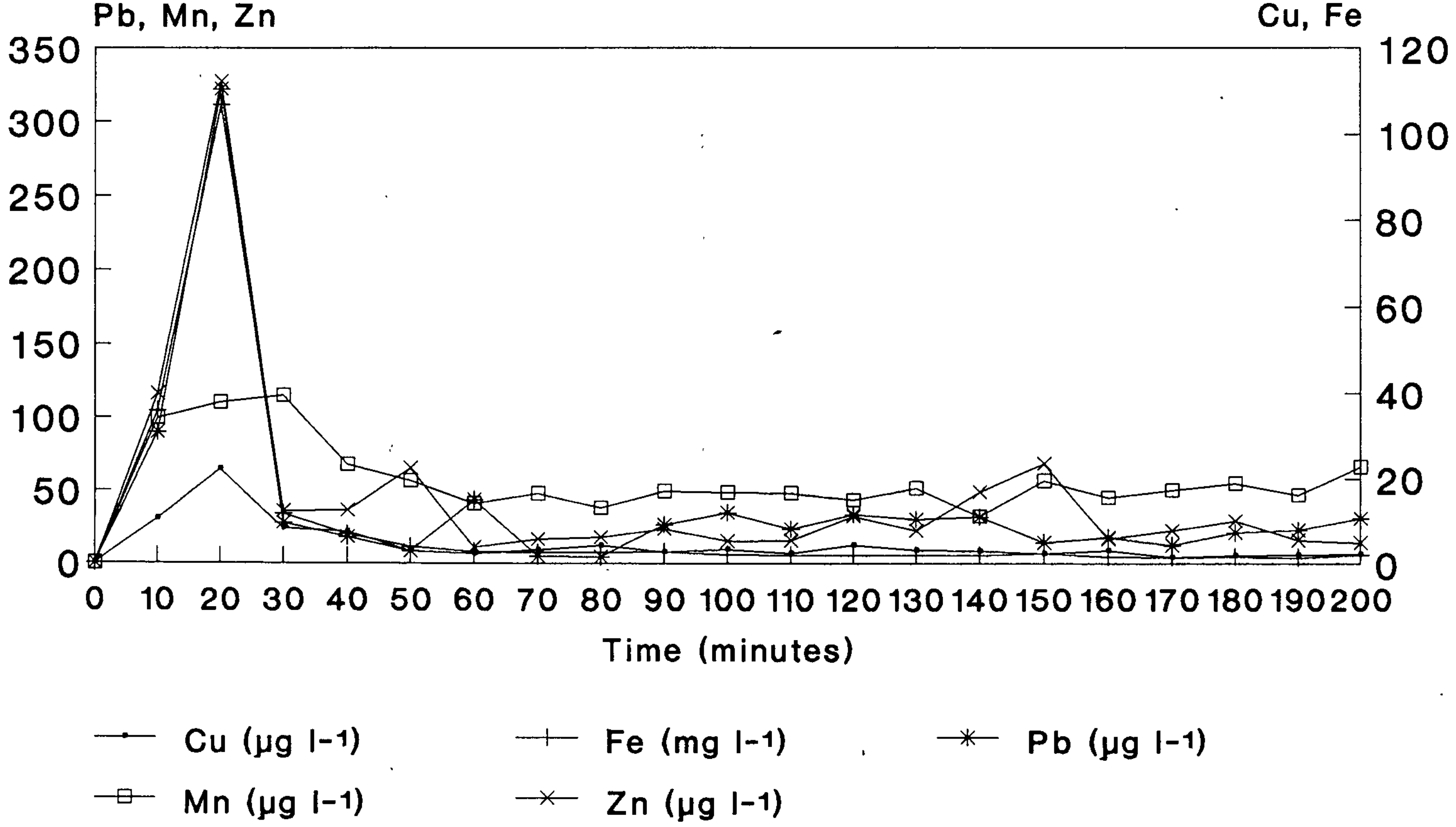


Figure 8.5 Variation of Particulate Associated Metals over Time for Event C3.

influenced by other factors, possibly including antecedent dry period, the characteristics of the rainfall event and conditions controlling in-pipe deposition during the previous storm event.

The variation in the metal concentration (μg g^{-1}) does exert a secondary influence, and in the case of Mn during events C2 and C3 possibly an equal influence, on the stormwater concentrations (μg l^{-1}). The metal concentrations (μg g^{-1}) may vary over the length of the storm as a result of a variety of factors. These include the sequencing of sediment supply, chemical changes at the solid surface of the particulates and hydraulic sorting of particle size during stormwater transport.

The ranges of metal concentrations and loadings for the potential sources were used in the previous section to assess the dominant source of stormwater particulates. It appeared likely that elevated Cu, Mn and Zn (the latter relative to the Pb concentration of the same sample) concentrations resulted from atmospheric particulates. Neither the samples of the particulate fraction of the bulk deposition nor those of the initial bulk sample of roof runoff, however, can fully explain the peak concentrations of Cu, Mn and Zn observed in stormwater over the duration of the storm. Use of the characteristic metal concentrations derived from comparing concentrations ranges of possible sources does not show good agreement. For C3, use of Mn concentrations in excess of 1500 μg g^{-1} as indicators of the dominance of atmospheric inputs suggests this occurs between 30 and 50 minutes, and additionally at 70 minutes after sampling was initiated. The use of a Zn concentration which is elevated in relation to Pb concentrations indicates the dominance of atmospheric particulates between 90 and 110 minutes after initiation of sampling. This lack of agreement highlights the care needed to be taken in using metal concentrations as indicators of sources.

The concentrations of metals associated with stormwater particulates may not reflect the source sediments but result from the changes in concentration due to chemical reactions during transport. The chemical reactivity of a particulate will increase as its physical size decreases due to an increase in the ratio of surface area to volume. Morrison et al (1988) have suggested the existence of several surface reactions affecting road dust particulate metal concentrations including solubilisation of adsorbed metals by acidic rainfall, adsorption of metal onto the surface of particulates within the gully pot and bio-degradation.

The relationship between the surface area and the volume of a sphere is;

$$\frac{(4\pi r^2)}{(4\pi r^3/3)} = 3\ r^{-1} \qquad \text{(Eq 8.1)}$$

The model equation being; $y = ax^b$ (Eq8.2)

where y = a function of the ratio of surface area to volume
x = a function of the radius
a & b = constants

The metals associated with particulates are variable in their solubility and Ellis and Revitt (1982) found that extraction efficiencies for metals by rainwater in road dusts were independent of road type and in the order Cd > Zn, Cu > Mn > Pb. Harrison and Wilson (1983) found that the order of soluble to particulate associated metal concentrations in stormwater was Mn > Cd, Cu > Fe, Pb. It would appear that Fe and Pb are least soluble and therefore most likely to covary with suspended solids if solubility and chemical processes are the major controlling factors with regard to metal concentrations associated with stormwater particulates. This is found to be the case for events C1 and C3. For event C2, Fe exhibits the strongest correlation with suspended solids while Pb is weaker than Cu or Zn. This may result from the short duration of the storm event and the antecedent dry period of three days which could limit the time over which metals would enter solution and the amount of metals available to enter into solution.

The elevated concentrations of metals in stormwater compared to those of bulk road dusts has been postulated to be due to the coarser fractions of road dust being associated with the bedload while the finer fractions remain as suspended sediment (Harrison and Wilson, 1983). If this were simply the case, during low intensity flows only the finest sediment could be mobilised and remain suspended and therefore high metal enrichments would be expected to be associated with low suspended solid concentrations. Plots of Cu, Fe, Pb, Mn, and Zn concentrations against suspended solid concentrations (Figures 8.6-8.10) indicate that there is some tendency for this trend to occur.

The metal concentrations in source sediments have been found to generally increase with decreasing particle size, and this is most accentuated for the metals Cu, Pb and Zn (Chapter 6). Taking the road and roof gutter sediments as most representative of those sediments to be immediately removed to stormwater without further physical sorting the distribution of these sediments was investigated. the distributions for metals were exemplified by the model;

$$y = e^{a+bx} \qquad \text{(Eq8.3)}$$

The results of the regression equations for the curves in Figures 8.6 to 8.10 are given in Table 8.6 and indicate that the best fit occurs with the model approximating to the surface area to volume model (Eq8.2). Surface area dependent processes would therefore appear to be an important influence on concentrations of solid associated metals in stormwater.

Morrison et al (1988) suggest that where the road dust sorting curve (Model $y = e^{a+bx}$) and the surface area dependent uptake curve (Model $y = ax^b$) intercept, the dominant control on particulate metal levels changes. The 'metal process intercept' (M_I expressed in mg l^{-1} suspended solids) gives an indication of the relative importance of surface area uptake processes per metal and can be related to the extent of enrichment of metals in suspended solids over source sediments. The order of increasing M_I values is Pb < Cu < Mn < Zn < Fe. this corresponds generally with the order of enhancement of stormwater sediments as indicated by maximum observed concentrations (Tables 6.1, 6.2, 6.3 and 8.2). The greatest enhancement was for Zn (maximum stormwater concentration 5896 μg g^{-1}; maximum sediment concentration 2050 μg g^{-1} in <38 μm road centre fraction) followed by Mn (maximum

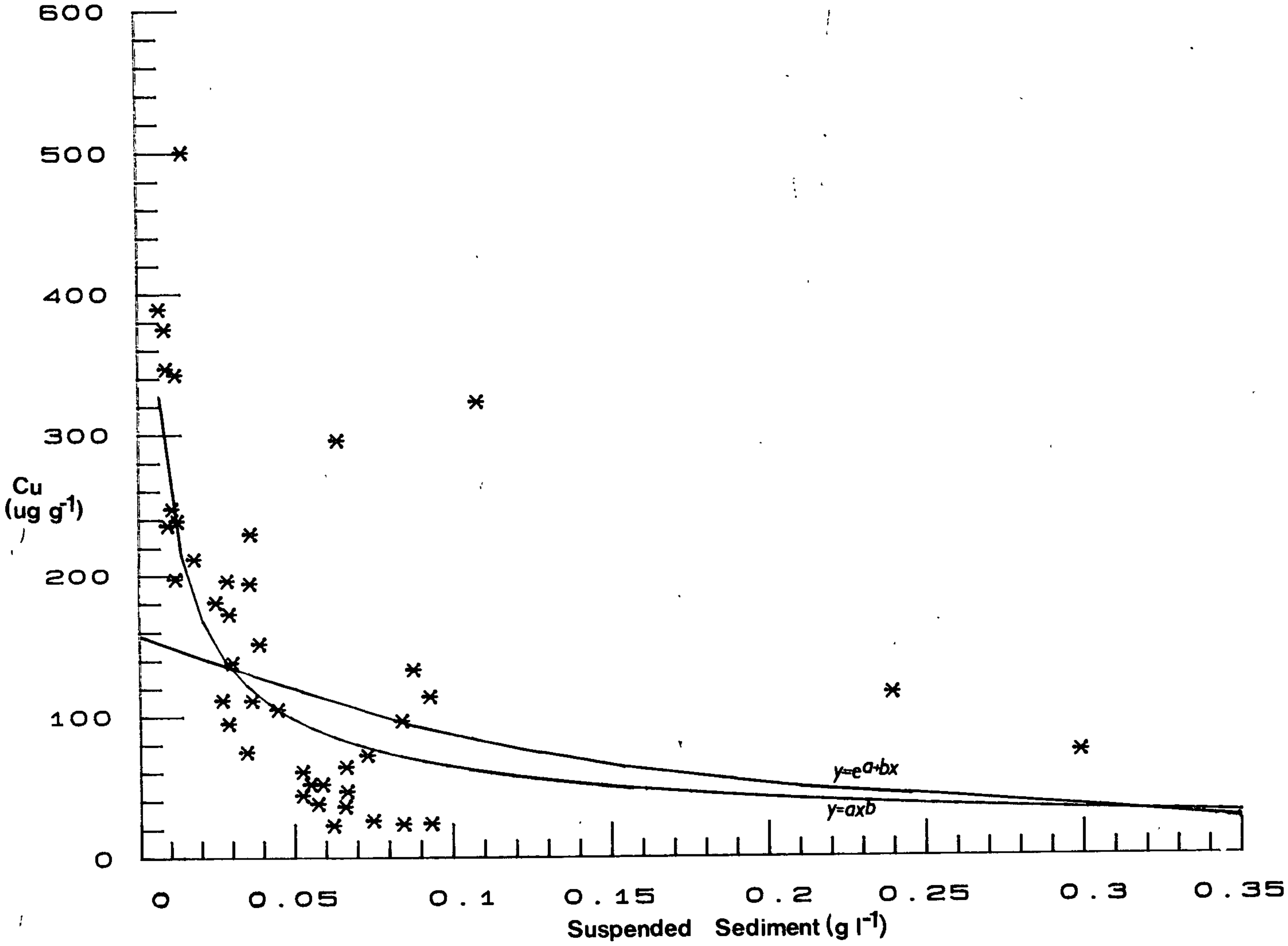


Figure 8.6 Stormwater Particulate Associated Cu Variation with Suspended Solid Concentration.

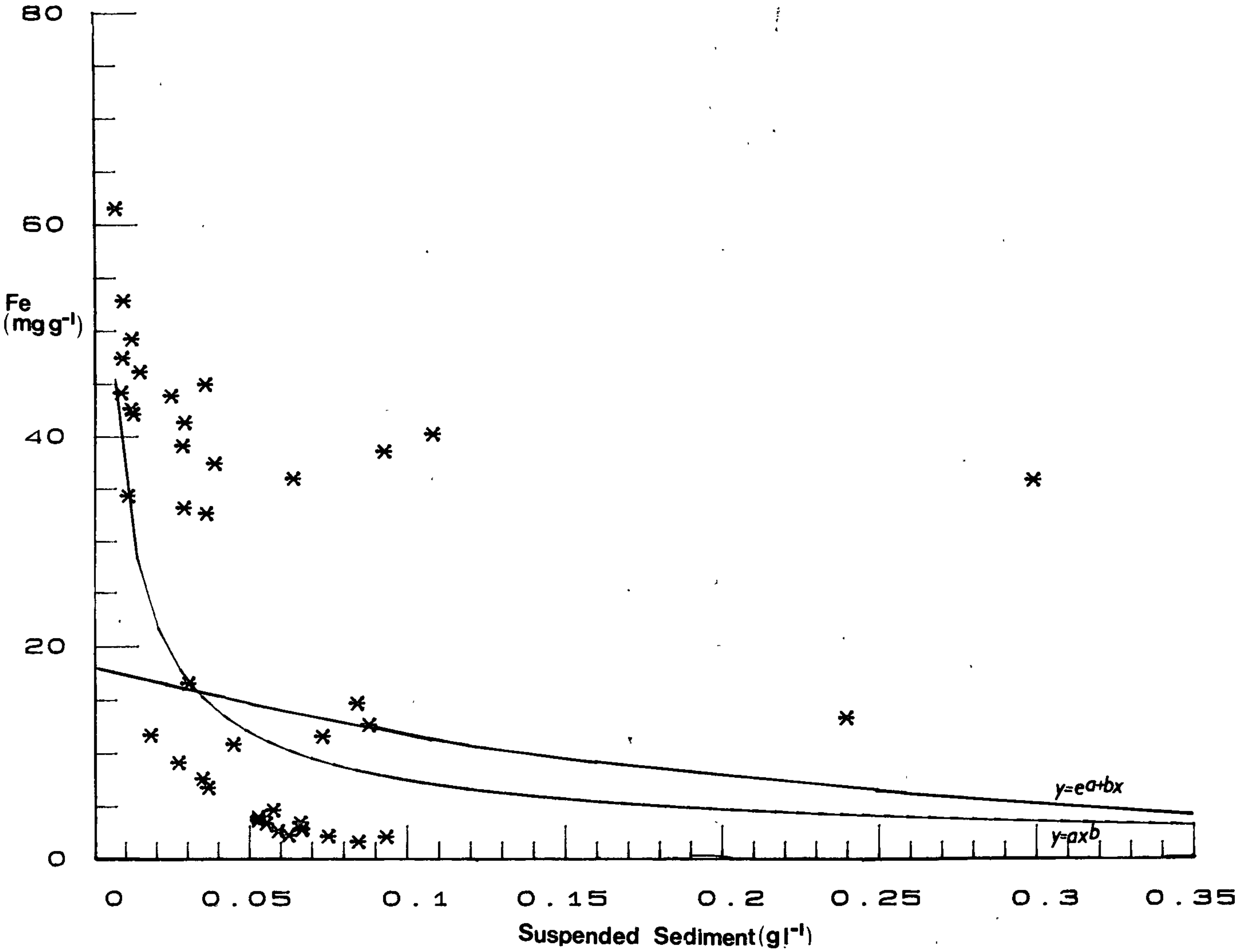


Figure 8.7 Stormwater Particulate Associated Fe Variation with Suspended Solid Concentration.

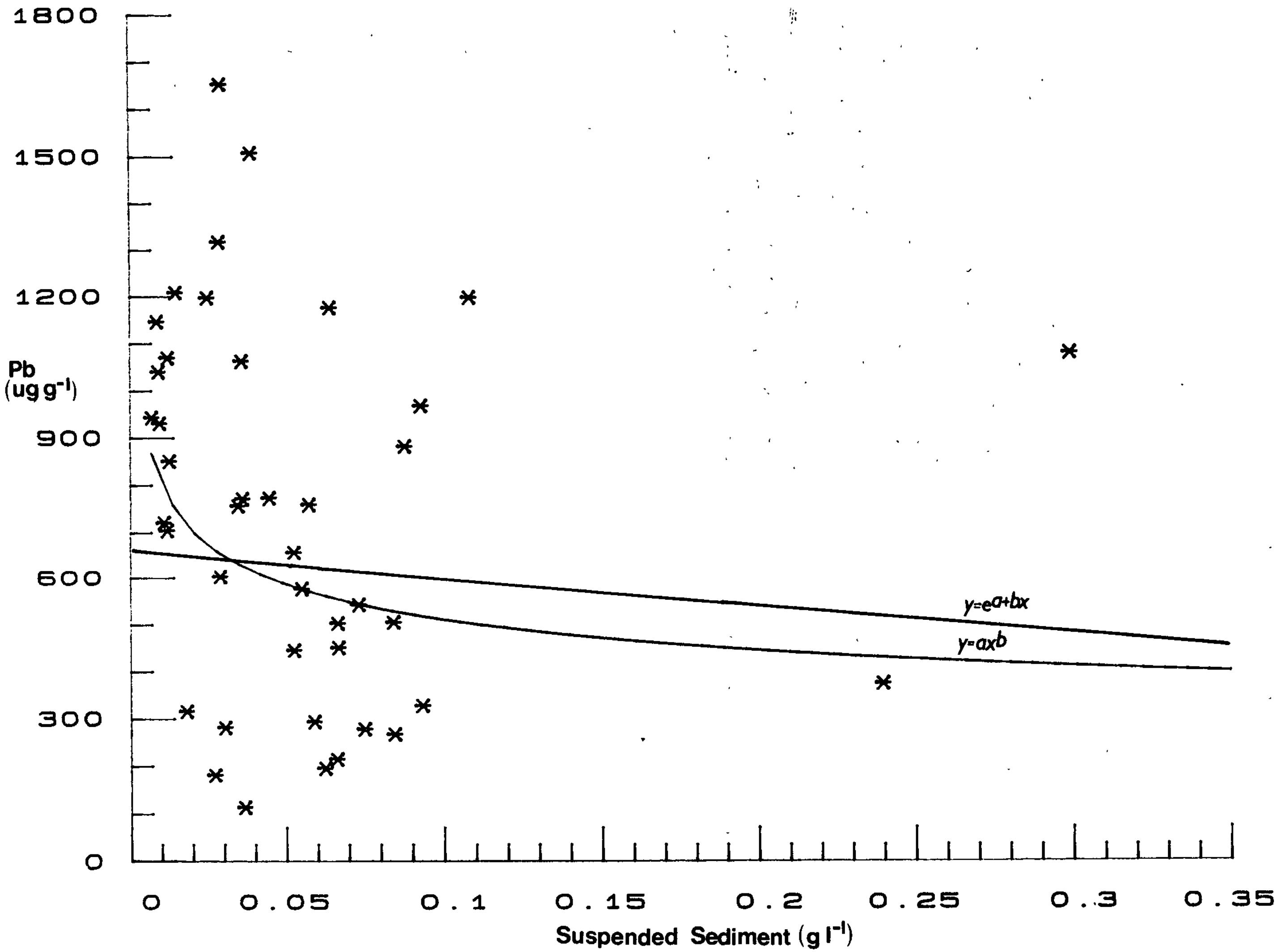


Figure 8.8 Stormwater Particulate Associated Pb Variation with Suspended Solid Concentration.

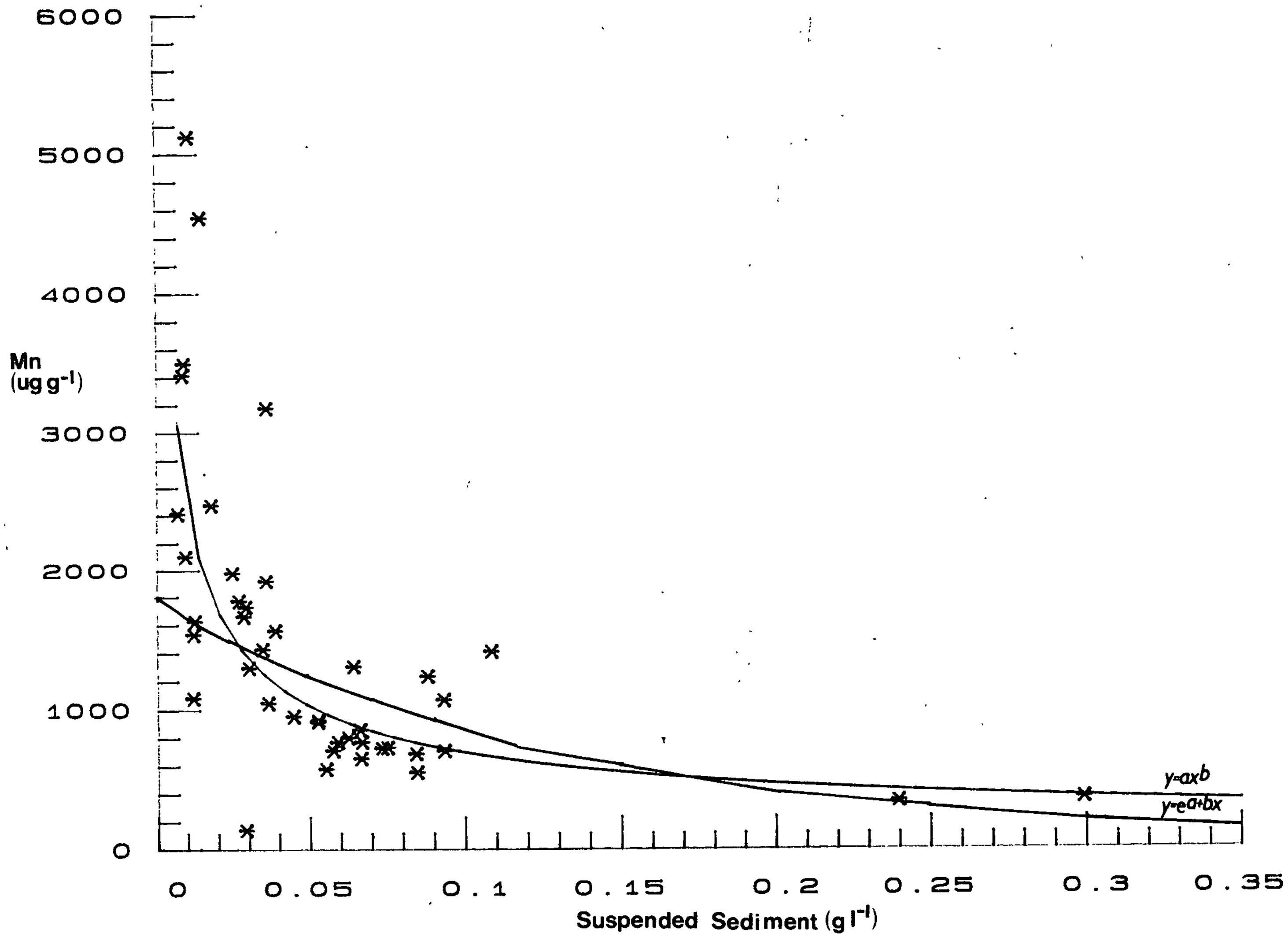


Figure 8.9 Stormwater Particulate Associated Mn Variaition with Suspended Solid Concentration.

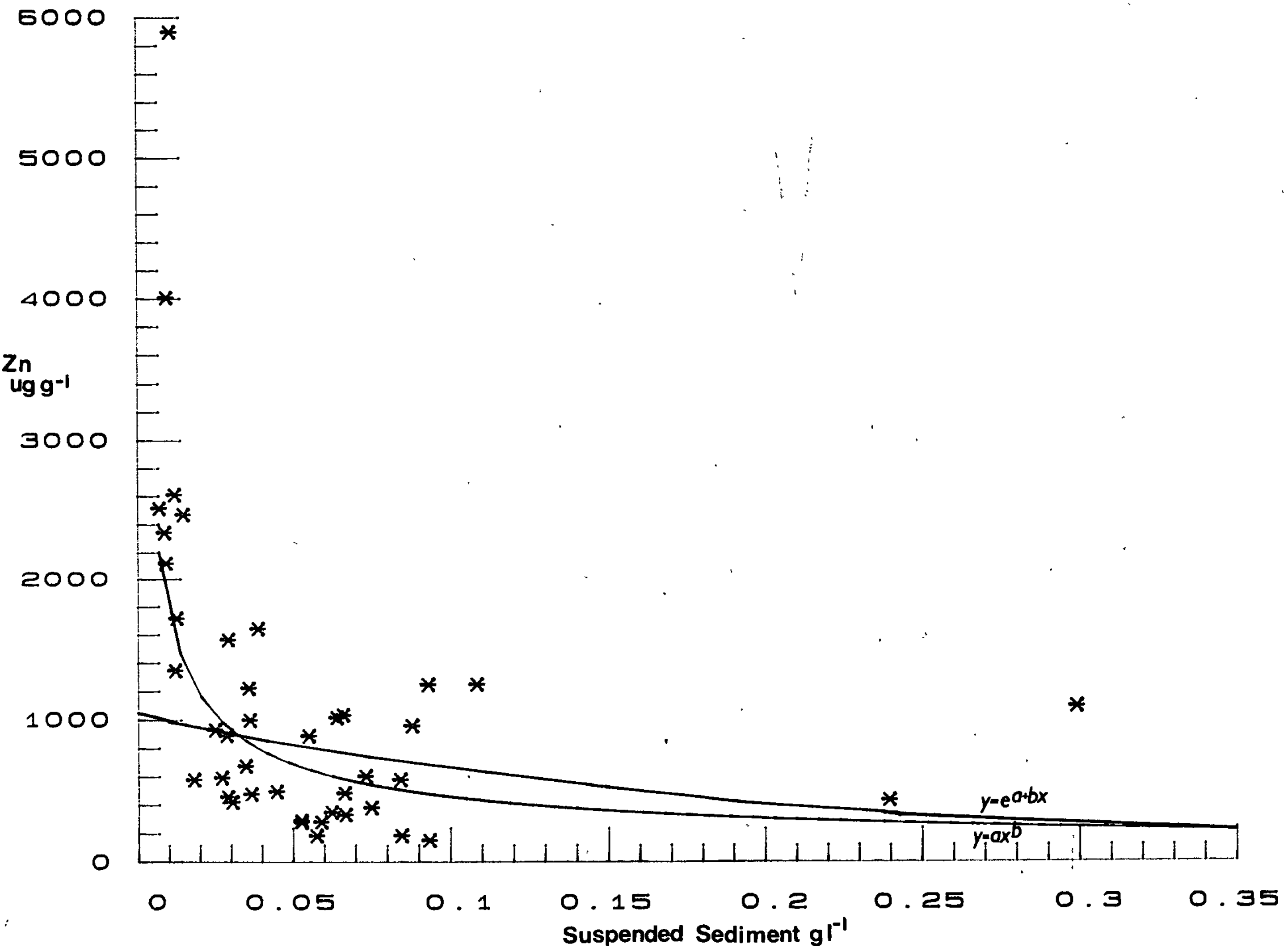


Figure 8.10 Stormwater Particulate Associated Zn Variation with Suspended Solid Concentration.

Table 8.6 Regression Equations of Solid Associated Metals and Suspended Solids.

Metal	Figure	Model	r^2	M_r (mg l^{-1} SS*)
Cu	8.6	$y = e^{a+bx}$	0.13	
Cu	8.6	$y = ax^b$	0.4	31.4
Fe	8.7	$y = e^{a+bx}$	0.01	
Fe	8.7	$y = ax^b$	0.07	34.5
Pb	8.8	$y = e^{a+bx}$	0.34	
Pb	8.8	$y = ax^b$	0.48	26.4
Mn	8.9	$y = e^{a+bx}$	0.09	
Mn	8.9	$y = ax^b$	0.37	32.6
Zn	8.10	$y = e^{a+bx}$	0.04	
Zn	8.10	$y = ax^b$	0.26	34.2

(n = 42) (SS* Suspended Solids)

stormwater concentration 5121 μg g^{-1}; maximum sediment concentration 1494 μg g^{-1}in 38-63 μm road gutter fraction). The enhancement of Mn and Zn concentrations associated with stormwater particulates compared to source sediments was noted in Section 8.3.1.1 and it would seem probable that surface adsorption of Mn and Zn onto fine particulates is the explanatory process for this enhancement. The maximum Cu concentrations in stormwater and sediments were similar while for Fe and Pb maximum sediment concentrations were approximately three times the maximum observed in stormwater. The order would appear to be correct with the exception of Fe. This may have resulted from poor distribution of Fe with particle size in highway associated sediments.

If Fe is taken to behave in a similar manner to Pb, the order is seen to conform to the derived order of solubility (Mn > Zn > Cu > Fe > Pb) suggested by the work of Ellis and Revitt (1982) and Harrison and Wilson (1983). The tendency for metal concentrations to increase with decreasing suspended sediment concentration seems to be linked to the solubility of the metal as found in road dusts and stormwater. This is probable as the fine particulates will preferentially adsorb metals present in high concentrations in solution and the lightly bound surface adsorbed metals on particulates will be the first phase of solid associated metal to be leached from particulates. This supports the suggestion by Morrison et al (1988) that the variation of metal concentration with suspended sediments results from a combination of chemical reactions at the particle surface and of physical sorting.

8.3.2 Metal Loadings Associated with Stormwater Particulates.

Flow measurements were made for storms C1 and C2 so that the loadings of metals associated with stormwater particulates could be calculated. It has already been noted that both storms exhibit peak metal and suspended sediment concentrations in the first phase of the storm events. It was expected that a 'first flush' phenomenon would be observed with respect to stormwater loadings. The probability of a 'first-flush' being observed is almost certainly catchment specific and also likely to be related to the complexity of the catchment drainage as well as the characteristics of the storm event. A combination of long tortuous drainage runs and short direct drainage runs would be likely to result in a less pronounced 'first-flush' phenomenon. Additionally the shape of the sewered catchment can influence the character of the 'first-flush' (Thornton and Saul, 1987). It is likely therefore in a highly impermable compact sub-catchment such as Chilwell Gardens which has a time of concentration of 3-6 minutes and a simple shape with few irregularities, that the phenomenon may well be more pronounced than is generally observed.

In the case of storm C1, the majority of the pollutant loadings were discharged in the first 30 minute phase of the event although it should be noted that this phase accounted for only 31% of the total volume (Figure 8.11). The percentage loading for the heavy metals Cu, Fe, Pb, Mn and Zn discharged in this first phase was 76%, 70%, 75%, 67% and 66% respectively. It can be seen that the metal loadings of the first phase make up a much larger proportion of the total metal loading for the storm than does the mass volume of runoff during this phase. The metal

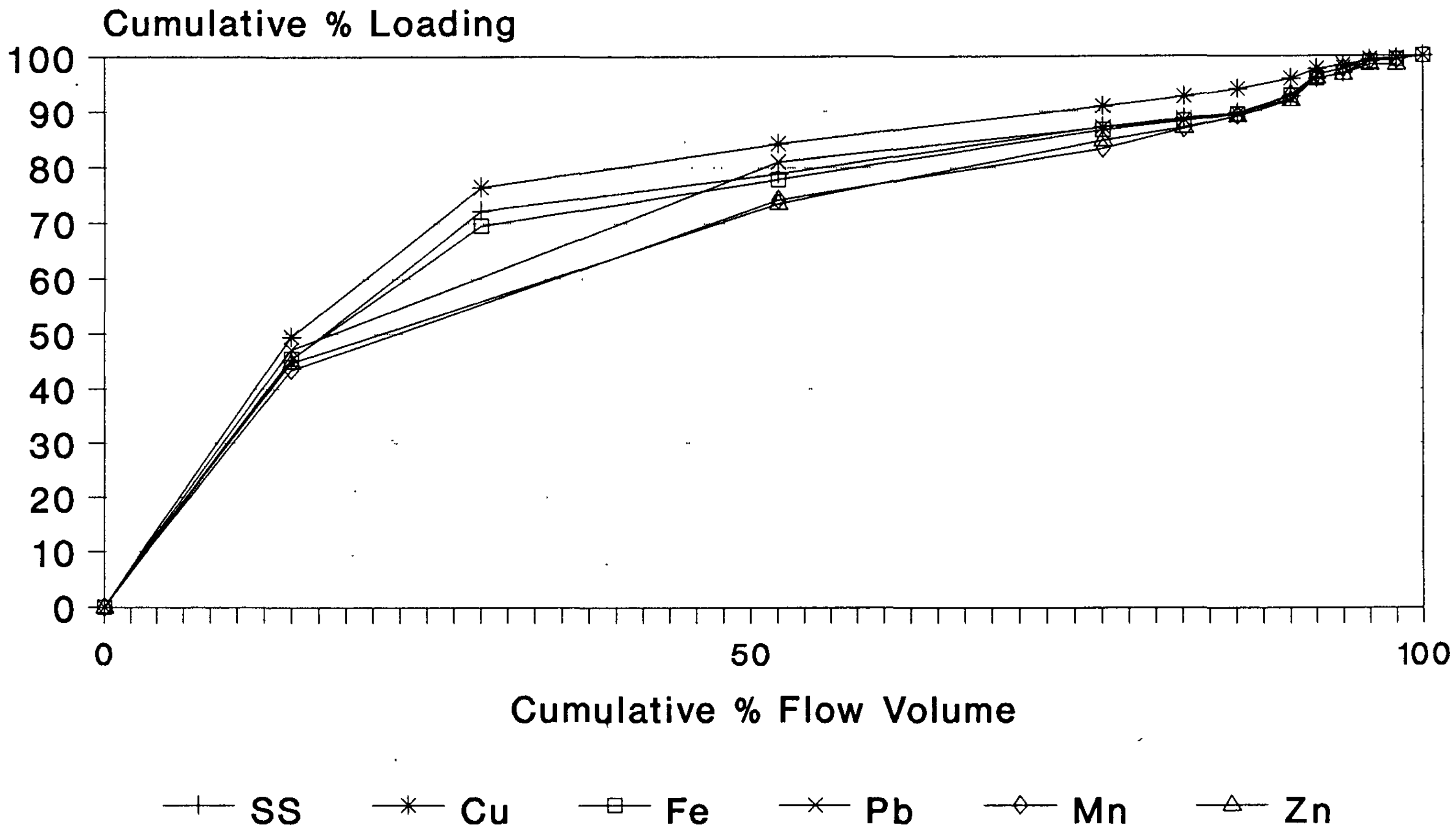


Figure 8.11 Cumulative Percentage Loadings of Flow Volume and Particulate Associated Metals for Event C1.

loadings can be viewed not merely as resulting from variations of flow but also as a function of elevated concentrations of metals associated with stormwater particulates occuring in the early phase of the storm. Suspended solids also exhibited a first flush with 72% of the total suspended solids loading being discharged in the initial flow phase. The percentage mass loadings and the percentage of the total runoff volume discharged became less disparate as the second phase of the storm progressed (Figure 8.11).

For storm C2, the peak pollutant discharges occur after the peak flow was recorded (Figures 8.2 and 8.12). The percentage of the total runoff volume discharged exceeded the cumulative percentage of the total Cu, Fe and suspended solids loadings discharged during the first ten minutes of the storm. After twenty minutes the situation had reversed. Similar and more pronounced lags between peak flow and the peak pollutant loadings have been observed in other studies (Ellis, 1976; Tucker and Mortimer, 1978). Twenty minutes after the start of the storm the percentage of total runoff volume discharged was 54%, while for Cu, Fe, Pb, Zn and suspended solids the percentage of the total metal loading was 81%, 77%, 75%, 76% and 77% respectively (Figure 8.12). The percentage of the total loading of Mn associated with stormwater particulates discharged at this point in the storm was 68% being intermediate between percentage of the runoff volume discharged and the percentage of suspended solids and other metal loadings discharged.

A more detailed breakdown of this phenomenon would have been possible if flow had been recorded for the third storm event, and additionally if flow had been recorded at intervals of less than 10 minutes. This would have enabled the time and magnitude of the peak flow to be determined more accurately. It seems likely that the peak flow for storm C1 may be misleading; the loadings appear to be anomalously low compared to those of event C2. It is thought that the flow may have been greater during the first ten minutes of both phases of the storm than that actually recorded. Therefore the intial loadings for both phases of the storm should be greater than those presented here. The data nevertheless does reveal that the most polluting discharge occurs over the first half of both storm events.

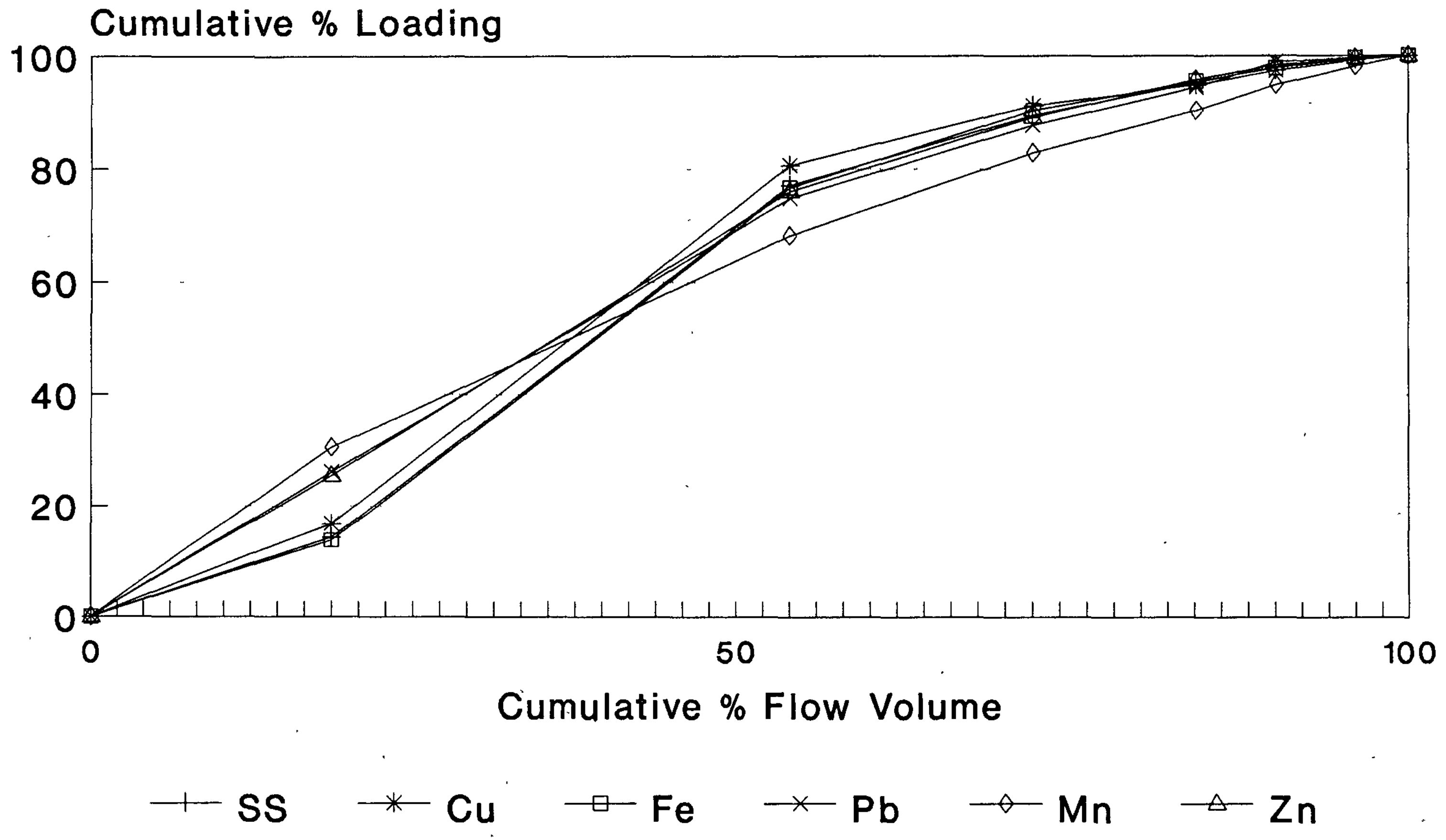


Figure 8.12 Cumulative Percentage Loadings of Flow Volume and Pariculate Associated Metals for Event C2.

8.4 Mineral Magnetic Parameters in Stormwater Particulates.

All collected samples of stormwater particulates were subjected to mineral magnetic analysis but owing to their low weight, χ could not be determined. IRM_{300mT} and the ratios of the magnetisation of the samples in certain applied reverse magnetic fields to that of IRM_{300mT} were determined on all samples.

8.4.1 Variations in IRM_{300mT} in Stormwater.

IRM_{300mT} exhibited similar trends to those of Cu, Fe, Pb and Zn, and suspended solids concentrations ($\mu g\ l^{-1}$) i.e. there was a tendency for peak values to occur in the first phase of the storms (Figures 8.1 and 8.2). The variation of IRM_{300mT}, which is related to the concentration of magnetic minerals in the samples, over the storm events was investigated and related to the variations in suspended solids and flow. For storm C1, IRM_{300mT} correlated well with suspended solids ($r > 0.99$) but not with flow. For storm C2, IRM_{300mT} correlated well with suspended solids and flow ($r > 0.89$), and for storm C3 IRM_{300mT} exhibited good linear correlation with suspended solids ($r > 0.9$).

Although the values of IRM_{300mT} represent the concentration of magnetic minerals, the values also vary with changes in the mineralogy of samples and in the magnetic domain size of the particulates within the sample. Assuming all samples to have similar mineralogies and domain sizes, values of IRM_{300mT} loadings can be calculated. This assumption has severe limitations as the main thrust of the research relies on the samples having different mineralogies. It has been shown in Chapters 5 and 6 however, that the mineral magnetic parameters for source sediments indicate that the overall mineralogy is magnetitic rather than haematitic in character. With this knowledge, it is thought that the calculated IRM_{300mT} loadings can be considered to be indicative of the relative scales of loadings throughout the storm. The figures, however, cannot be taken as exact expressions of the weight of magnetic minerals present.

In agreement with the good correlations found between IRM_{300mT} and suspended solids, a 'first-flush' of IRM_{300mT} loadings was observed for event C1. In the first twenty minute phase 54% of the total IRM_{300mT} loading was discharged. For storm C2, 81% of the total IRM_{300mT} loading was discharged in the first twenty minutes of the storm. From this it can be seen that the majority of magnetic minerals associated with stormwater particulates, like the majority of metals and suspended solids, are discharged in the early phases of the storm event. The exact percentage is likely to be inaccurate owing to the inherent assumptions involved in calculating loadings. However, the results can be taken to represent overall trends as regards the loadings of magnetic minerals in stormwater particulates.

8.4.2 Mineral Magnetic Characterisation of Stormwater Particulates and their Implications as Regards Stormwater Sequencing.

An important aspect of this research was to assess the application of mineral magnetic methods to the evaluation of storm sequencing by comparing the mineral magnetic characteristics of individual stormwater sediment samples with those of source samples. A summary of the mineral magnetic characteristics of stormwater particulates is given in Table 8.7.

Table 8.7 Mineral Magnetic Characteristics of Stormwater Particulates Captured at the Chilwell Gardens Sub-Catchment.

		IRM_{300mT} (10^{-3} A m^2 kg^{-1})	IRM_{-20mT} / IRM_{300mT}	$-IRM_{-40mT}$ / IRM_{300mT}	IRM_{-20mT} / $-IRM_{-40mT}$
Storm C1	Range	9.96-20.08	0.243-0.487	0.022-0.4	2.55-21.6
	Mean	14.01	0.431	0.112	7.85
Storm C2	Range	6.31-18.65	0.172-0.423	0.26-0.322	0.64-16.21
	Mean	12.41	0.291	0.191	3.9
Storm C3	Range	2.18-19.45	0.073-0.463	0.029-0.553	0.13-15.62
	Mean	9.69	0.283	0.245	3.1

By comparing the mineral magnetic characteristics of stormwater particulates to the characteristics of the particulates captured in the initial bulk sample of roof runoff (Table 8.8), it can be seen that generally the roof runoff particulates exhibit greater IRM_{300mT} values than those exhibited by stormwater particulates. For event C1 the backfield ratios of roof runoff particulates are similar to the mean values of the stormwater particulates but this is less evident for C2 and C3. It would appear that while roof runoff is making a contribution to the mean mineral magnetic characteristics of stormwater particulates other sources are also contributing.

Table 8.8 Mineral Magnetic Characteristics of Stormwater Particulates in Roof Runoff.

	IRM_{300mT} (10^{-3} Am^2 kg^{-1})	IRM_{-20mT} / IRM_{300mT}	IRM_{-40mT} / IRM_{300mT}	IRM_{-20mT} / IRM_{-40mT}
Storm C1	30.820	0.426	-0.087	-4.91
Storm C2	22.84	0.423	-0.1	-4.21
Storm C3	15.775	0.427	-0.035	-12.23

Comparison of the mean values of mineral magnetic characteristics of stormwater particulates (Table 8.7) with the mineral magnetic characteristics of source sediments (Tables 5.6 and 6.5-6.7), indicates that for the majority of stormwater particulate samples the IRM_{300mT} values are similar, albeit slightly lower than those found in the pavement sediments. They are also generally much lower than the values found in road gutter and road centre sediments. The backfield ratios for stormwater particulates are the inverse of those for paved surface sediments, i.e. absolute IRM_{-20mT}/IRM_{300mT} values are greater than absolute values of IRM_{-40mT}/IRM_{300mT}. It would therefore appear unlikely that the dominant source of particulates in the stormwater sediments is from paved surface sediments.

The samples of in-pipe deposits have similar characteristics to the samples of stormwater particulates although the sediment deposited within the roof drain exhibits lower values of IRM_{300mT} (Table 5.6) than the peak values found in stormwater particulates. The predominant characteristics of urban sewer sediments have been previously suggested to be derived from the scouring of 'in-pipe' sediments and subsequent resuspension. The initial assessment of the mineral magnetic data presented here would appear to lend support to this theory.

Other possible sources of magnetic minerals in stormwater have also been assessed. Ellis et al (1981) suggest that the character and properties of the mineralogy of stormwater particulates can be dominated by the materials of the road surface itself. The mineral magnetic characteristics of highway constructional materials (Table 7.4) and those of stormwater particulates were therefore compared. There is little or no similarity between local tarmac samples and stormwater particulates. There is some similarity however, between the granite chippings and stormwater samples. It has been shown in Chapter 7 that the backfield ratios exhibited by particulates derived from road constructional materials are very different to those of source sediments as found on highway associated surfaces, even when fractionated. It would appear illogical, therefore, to suggest that the materials of the road itself could give rise to the magnetic mineral characteristics of stormwater particulates without being masked by the influence of the other contributions of highway associated sediments.

The magnetic characteristics of stormwater particulate samples have also been compared to those of roof particulates and soil samples (Table 5.6 and 7.4). It can be seen that there are distinct similarities between the characteristics of stormwater particulates and roof sediments and soils. The upper range of IRM_{300mT} values for stormwater particulates is greater than that of roof and soil sediments. The backfield ratios of stormwater particulates are slightly higher for IRM_{-20mT}/IRM_{300mT} and slightly less for IRM_{-40mT}/IRM_{300mT}. This would be indicative of a slightly mineral magnetically "harder" assemblage. There is no direct supply of soil to the sub-catchment as the gardens are sunk below the pavement surface, so any soil entering the sub-catchment would have to be windblown. It therefore appears that a likely source of particulates giving rise to the observed mineral magnetic characteristics of stormwater sediments might be roof sediments. The major contribution to roof sediments is from atmospheric particulates. Comparing the data in Tables 7.3 and 8.9 with that of Table 8.7 shows that there are distinct similarities between the characteristics of atmospheric particulates and stormwater particulates. The total deposited particulate samples, which include particulates in rainfall, exhibit greater IRM_{300mT} values than stormwater particulate samples. It might be expected that the source particulates would have higher values of parameters related to the concentration of magnetic minerals compared to stormwater particulates as the concentration is likely to be diluted by inputs of particulates having lower concentrations of magnetic minerals, such as organic material.

Table 8.9 Mineral Magnetic Characteristics of Total Particulate Deposition for Each Storm Event.

	IRM_{300mT} (10^{-3} Am^2 kg^{-1})	IRM_{-20mT} / IRM_{300mT}	IRM_{-40mT} / IRM_{300mT}	IRM_{-20mT} / IRM_{-40mT}
Storm C1	28.598	0.433	-0.085	-5.11
Storm C2	33.298	0.433	-0.071	-6.09
Storm C3	62.903	0.425	-0.054	-7.86

Goettle (1978) as well as Mance and Harman (1978) and Malmqvist and Svensson (1988) have suggested that the input of atmospheric particulates greatly affects stormwater pollutant levels. From the data collected here it is not possible to clearly identify if the stormwater particulates are reflecting the input from granite chippings, atmospheric particulates or in-pipe deposited sediments. The circumstantial evidence however, would indicate the latter two source sediments to be the most probable dominant sources of stormwater particulates.

8.4.2.1 Graphical Assessment of Stormwater Characteristics.

The variations in sample magnetic mineralogy throughout individual storms were assessed by inspection of three-dimensional plots of the three mineral magnetic parameters, IRM_{300mT}, IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT} (Figures 8.13-8.15).

The majority of the suspended sediment samples collected during storm event C1 exhibit similar characteristics (Figure 8.13). One outlier from the main grouping can be easily identified. This sample was collected 30 minutes after the initial sampling and at the start of the second phase of the storm. The graphical presentation of the data for the suspended particulates collected during storm C2 shows that the samples fall into three groups (Figure 8.14). The first group consists of three samples, collected during the first thirty minutes of the storm event, having relatively high IRM_{300mT} values and relatively low IRM_{-20mT}/IRM_{300mT} values. The samples of the other two groupings, collected later in the event, exhibit similar but lower IRM_{300mT} values; these two groups being formed of two pairs of increasing mineral magnetic "hardness" (Figure 8.14). The storm event C3 is much more complex with much greater variation being exhibited in the sample characteristics (Figure 8.15). This results in a three-dimensional plot which does not immediately suggest distinct sample groupings.

The three-dimensional plot of bulk sediments (Figure 5.13) shows that the roof grouping falls to the right of the plots. The main grouping of samples in Figure 8.13 corresponds to the mineral magnetic character of the roof grouping, with slightly elevated IRM_{300mT} values indicating increased concentration of magnetic minerals in the stormwater samples. In Figure 8.14 the group consisting of three samples would appear to be in the region of the three-dimensional plot comparable to that occupied by highway associated sediments in Figure 5.13. The other samples are split into paired groups of two, the "hardest" pair in the region of the three-dimensional plot occupied by the roof grouping in Figure 5.13, and the final pair being borderline between these groupings.

The comparison allows a limited interpretation of Figure 8.15 in that it

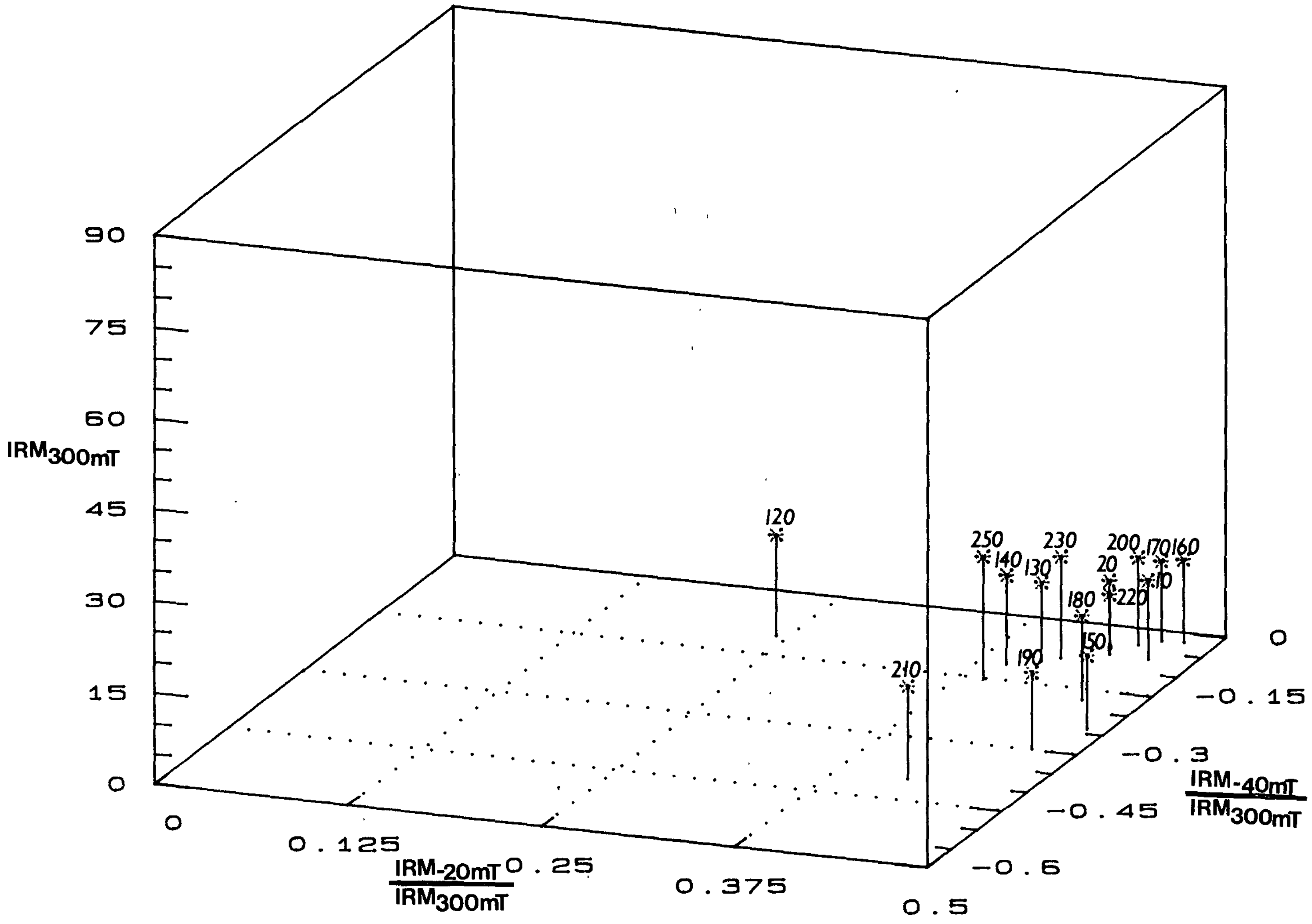


Figure 8.13 Tri-axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event C1.

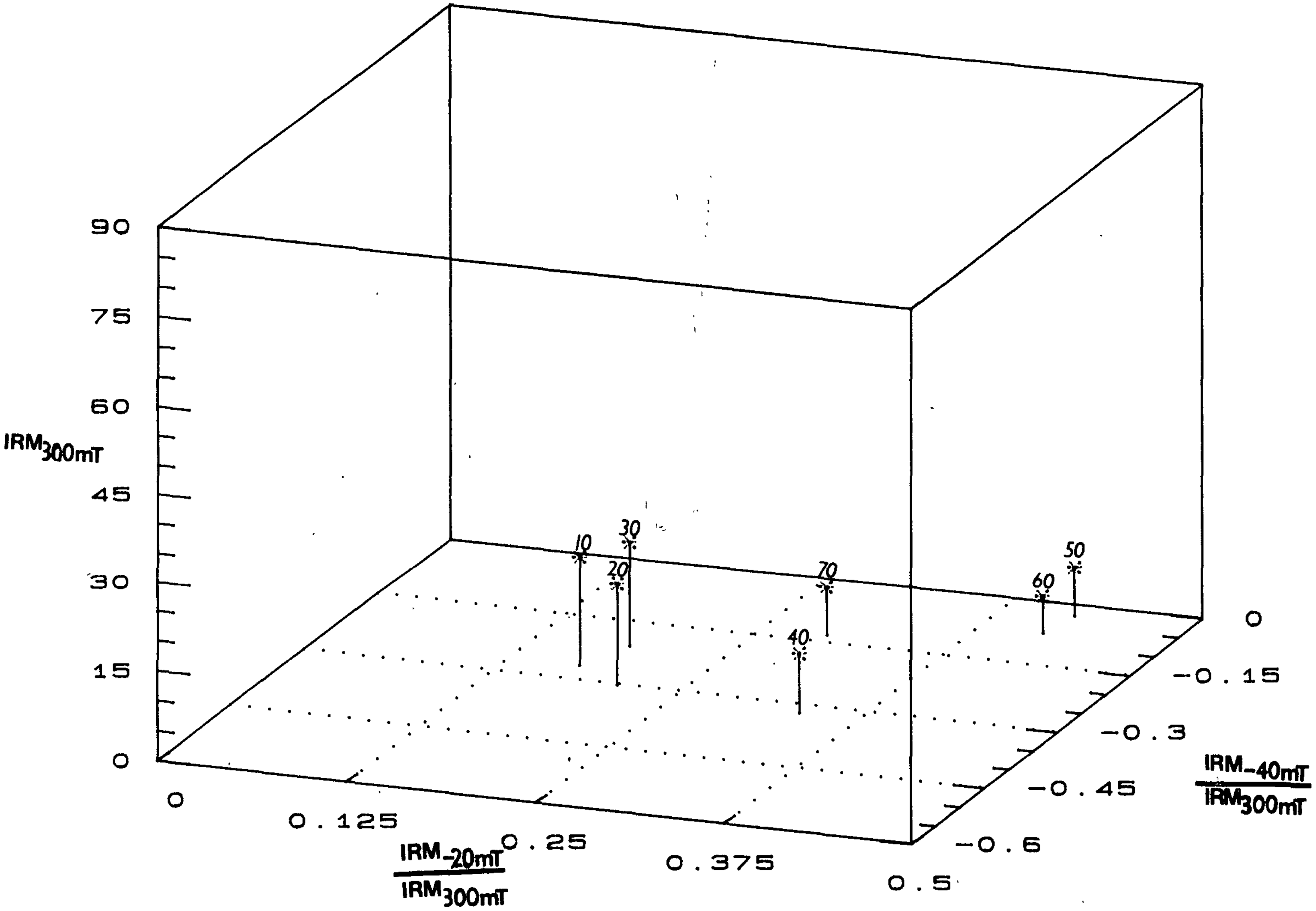


Figure 8.14 Tri-axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event C2.

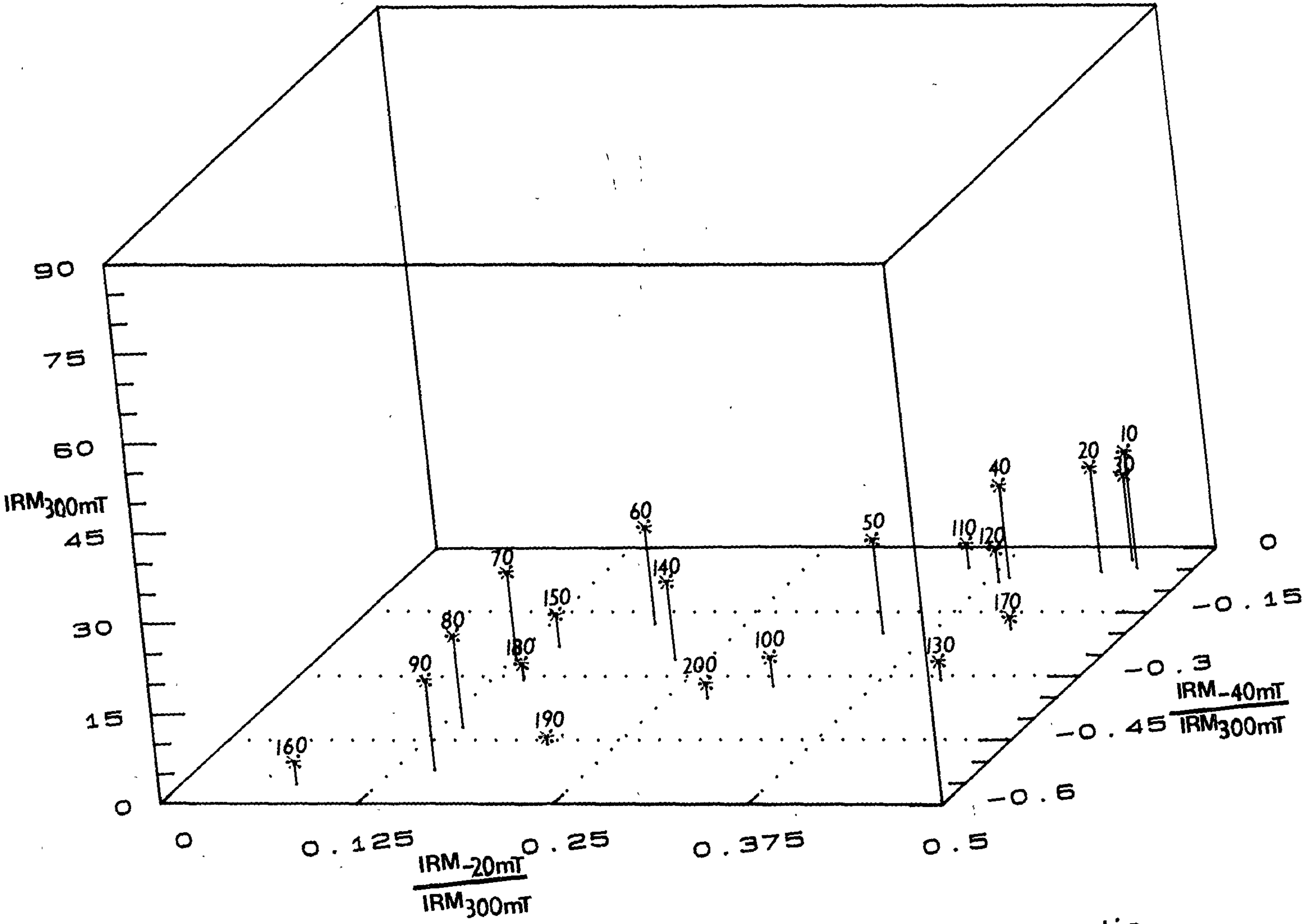


Figure 8.15 Tri-axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event C3.

can be seen that the samples with values of IRM_{-20mT}/IRM_{300mT} which are greater than 0.3 should be grouped with the roof samples. Samples with values of IRM_{-40mT}/IRM_{300mT} less than -0.23 would appear to be similar to the highway sediments grouping with two intermediate samples of low IRM_{300mT} values occurring in between these two major groupings.

The time (in minutes) of sample collection for the stormwater particulates after the initiation of sampling is indicated in Figure 8.15. It can be seen that the first four samples are similar, falling within the roof grouping, the sample collected at 50 minutes after the start of sampling being at the edge of this characterisation. The samples collected between 60 and 90 minutes show a distinct similarity to paved surface characterisation, followed by the sample at 100 minute having intermediate characteristics, similar to that collected at 50 minutes. The dominant source of particulates appears to change again for samples collected at 110, 120 and 130 minutes, the samples falling within the atmospheric particulate category. The samples at the end of the storm from 150 minutes onwards would appear to fall within the paved surface category, with the exception of the sample collected at 170 minutes. From this it might appear that, unlike the other two storms, the dominant source of sediments sampled during the event of 5 July changed several times during the storm event.

8.4.2.2 Statistical Assessment of Characteristics of Stormwater Particulates.

The characteristics of stormwater particulates were also assessed using the equations derived in Chapters 5 and 6. The equations Eq5.1, Eq5.3 and Eq5.4 were first applied. These equations were chosen as Eq5.1 was derived from all surface source sediments. Eq5.4 was used as this was derived from the sample characteristics of the two initial source areas (roof and road centre sediments), and therefore was felt to most closely resemble the source particulates before transport and modification of the particulates within the sub-catchment. The equation E5.4 was also used as this represents the closest surface source sediments (road gutter) to the sampling point of the stormwater particulates. The discriminant equations based on size fractions (Eq6.1 and Eq6.2; Chapter 6) were also applied. It can be seen from Table 8.10 that for storm C1 the application of the equations derived from statistical analysis clearly indicate that the sample of stormwater particulates collected at the onset of the second phase of the storm would be classified with bulk highway associated sediments. The equations derived from the fractionated samples do not identify any sample with highway associated sediments except that collected at 210 minutes. Looking at the two samples identified with the road grouping in detail, it is found that the sample collected at 120 minutes had an IRM_{300mT} above the average

Table 8.10 Classification of Stormwater Particulate Samples Using Equations Derived from Statistical Analysis.

	CLASSIFICATION	
	Road Grouping	Roof Grouping
	(Time of sample after initiation of sampling)	
Storm C1*		
E5.1	120	10,20,130-240
E5.3	120	10,20,130-240
E5.4	120	10,20,130-240
E6.1	-	All samples
E6.2	210	10,20,120-200,220-240
Storm C2		
E5.1	10-30	40-70
E5.3	10-30	40-70
E5.4	-	10-70
E6.1	10,30	20,40-70
E6.2	10,30,40	20,50-70
Storm C3		
E5.1	60-90,140-160,180	10-50,100-130,170,190,200
E5.3	60-90,140-160,180,190	10-50,100-130,170,200
E5.4	90,160	10-80,100-150,170-200
E6.1	60-100,130,140-160,180,190	10-50,110,120,170,200
E6.2	60,70,150,	10-50,80-140,160-200

* No samples at intervals 30-110 minutes due to 90 minute interval between the two phases of the storm.

for the storm with a lower IRM_{-20mT}/IRM_{300mT} than the average for the storm. The sample at 210 minutes had a higher than average IRM_{300mT} with a very low IRM_{-40mT}/IRM_{300mT} of -0.4.

The use of the equations derived from the discriminant analysis (with the exception of Eq5.4) indicates that for storm C2 the initial samples are associated with the road grouping. Equation Eq6.2 is derived from the fractionated road centre sediments and this classifies the samples collected at 10, 30 and 40 minutes with the road centre grouping. This would suggest that the sample collected at 20 minutes is derived from highway sediments or in-pipe residues but does not have such defined characteristics to be grouped in all cases with the road centre sediments. The sample collected at 40 minutes is only categorised with the highway associated sediments by Eq6.2. It would appear therefore that for the initial phase of the storm the highway associated sediments dominate the stormwater particulates and after 30 minutes there is a change in dominance to the roof associated sediments which occurred around 40 minutes after sampling. This is a distinctly different distribution to that of storm C1 and may result from the short intense nature of storm C2 or alternatively the short antecedent dry period, there having been a rainfall event three days previously, on the 21st June 1985.

The stormwater samples collected during storm C3 give indications of changing dominance of source sediments at several points throughout the storm. There appears to be dominance of highway associated sediment during the periods 60-90 minutes, 140-160 minutes and at 180 minutes from the onset of sampling. As would be expected the classification places more samples with the road grouping for equations Eq5.1 and Eq6.1, which represent all highway associated sediments. Fewer samples are classified with the more extreme road centre sediments. There is no agreement between the equations of Eq5.4 and Eq6.2 which reflects their derivation from differing data bases. However, all samples highlighted as classified with the road centre groupings by either Eq5.4 or Eq 6.1 fall into the group of samples identified by the three other equations as belonging to the highway associated sediment grouping.

The use of discriminant analysis to derive equations to classify stormwater sediments with regard to dominant source sediments would therefore appear to have been successful. It should be noted that discriminant analysis is based on the statistical probabilities of a sample belonging to a group and in Chapter 5 and 6 it was shown that there was a high probability that the equations classified samples correctly. However, in Chapter 5 it was shown that there was a tendency for all roof sediments to be classified correctly while some road sediments would have been misclassified with the roof sediments. As a result of this there is a strong probability that the equations have correctly highlighted samples where highway associated sediments dominate but there is a minor probability that a few samples may have been misclassified with the roof grouping.

8.4.2.3 Assessment and Comparison of the Classification of Stormwater Particulates.

The classification of stormwater particulate samples by subjective assessments from graphical presentations and from statistical analysis compare extremely favourably. Both methods highlight the sample collected at the start of the second phase of storm C1 as exhibiting predominant highway sediment characteristics. The statistical analysis also suggests that the sample collected at 210 minutes may also be classified as being derived from predominantly highway associated sediments although the graphical assessment does not concur with this conclusion.

For the storm event C2, both graphical and statistical methods indicate a predominance of sediments with similar characteristics to highway associated sediments dominating the opening phase of the storm with later samples exhibiting similar characteristics to the roof/atmospheric samples.

The storm event C3 is the most complex of the three but despite this the two methods show good agreement. Both indicate that the samples collected between 60 and 90 minutes, 140 and 160 minutes and at 180 minutes were predominantly characteristic of highway associated sediments. The assessment from the graphical presentation also suggests that the samples collected at 130, 190 and 200 minutes should be classed with this grouping.

The sequencing of sediment supply as indicated by the mineral magnetic results suggest that in event C1 the first phase of the storm is dominated by roof runoff. The start of the second phase is dominated by runoff from the paved surfaces but this is then overwhelmed by the roof runoff. This would be expected as the pitched roof surfaces are less able to attenuate rainfall, while road surfaces are known to have a degree of depression storage before runoff occurs (Harrop, 1984; Pratt and Harrison, 1986). This property of road surfaces occurs as a result of hollows, cracks and a large amount of absorbent material occurring in the gutters. The initial sewered runoff would therefore result from roof surface discharges. Pratt and Harrison (1986) have observed that the time from the start of a storm event to initiation of roof runoff could be as little as one minute. The highway derived sediment will contribute once sufficient rainfall has fallen to wet the surface and the drag and lift forces exerted by flow overcome the gravitational and mass forces acting on a particulate and mobilises them. The re-occurrence of the roof runoff as a dominant source may have occurred for a variety of reasons including that of a limitation of the supply of particulates from the road surfaces. It has been suggested that the supply of particulates is one of the major limitations on pollutant discharges from highways. This limitation is essentially one of transport as the supply is potentially unlimited. The hydraulic force required to move the remaining sediment, however, does become a limiting factor (Ellis and Harrop, 1984; Pratt and Adams, 1984).

Alternatively, the sequencing of source sediments in storm C1 may be explained by the sediment from the paved surfaces having just entered the sub-surface system at the end of the first phase of the storm and then being deposited there as the first phase finished. On the occurrence of the next phase of the storm, the deposited sediment is immediately scoured and mobilised, consequently dominating the first sample collected in the second phase. The scouring of in-pipe deposits has been cited as a major factor in the 'first-flush' phenomenon (Pratt and Adams, 1984) and is believed to dominate sediment yields discharged by stormwater systems (Crabtree, 1988). This phenomenon would explain the results obtained for event C1.

Event C2 occurred three days after a previous runoff event and it is likely that the road surfaces had not dried out thoroughly and therefore had a reduced depression storage capacity. The rainfall intensity for event C2 was 1.78 mm hour^{-1} compared to 0.61 and 0.93 mm hour^{-1} respectively for events C1 and C3. These two factors most probably account for the dominance of highway associated sediment in the first phase of the storm. The roof runoff becomes dominant in the later stages as a result of the rapid exhaustion of the readily mobilised particulates present on the road surface. A similar explanation to that given for the predominance of highway associated sediments at the beginning of the second phase of C1 may also be applicable where sub-surface deposits of sediment, with predominant paved surface characteristics, dominate the opening phase of the storm.

The mineral magnetic data indicates that storm event C3 begins with a predominating supply of sediment from the roof and ends with major contributions from the paved surfaces. In the case of event C2, the samples collected at the end of the storm exhibited predominantly roof grouping characteristics. The sediment deposited in-pipe at the end of the storm is also likely to have similar characteristics and any in-pipe sediment flushed out at the start of the following storm would be expected to have similar characteristics, as indeed appears to be the case. The changes in the dominant source during the storm may be due to changes in flow which was not measured due to mechanical difficulties. The rainfall record however, does suggest that approximately 56% of the rainfall volume occurred in the first 30 minutes of the storm whilst 33% occurred between 125 minutes and 150 minutes. This suggests that the second dominant period of highway associated sediments may be due to an intensification of the rainfall in the second half of the storm event.

The characterisation of stormwater sediment by use of mineral magnetic methods has been carried out on a limited number of storms but it does suggest that in a simple sub-catchment, initial flushing is of in-pipe deposits which are dependent upon the dominant source of stormwater sediment at the end of the preceding storm. Highway and roof associated sediments are the main contributors depending on the storm characteristics.

In an attempt to identify sequencing by other methods, an amount ofsediment was removed from the roof gutter and replaced by a similar amount of sand marked with fluorescent dye. The marked sand was made up in the same proportions with respect to size range as previously analysed roof gutter samples. Unfortunately no trace of the fluorescent-marked sand was found in the samples of stormwater particulates captured in the subsequent storm although none of the coloured sand remained in the roof gutter. The only trace of the sand was found in the sediment trapped behind the weir plate at the in-pipe sampling point and consisted of three grains, greater than 125 μm. From this it must be assumed that the marked sediment was extremely efficiently routed through the drainage system, although no indication can be made of the timing of the flushing event. The application of marked sand was not followed up and this tracer work is obviously an area where further research could be profitably extended.

8.5 Mineral Magnetic Parameters and Heavy Metal Relationships.

The relationship between IRM_{300mT}, expressed in units of 10^{-6} A m^{-2} l^{-1}, and concentrations of heavy metals and was investigated. Heavy metals (μg l^{-1}) exhibit good correlations with suspended solids for all three storms (Section 8.3.1.2). IRM_{300mT} also exhibited good correlations with suspended solids for all three storms (Section 8.4.1). There were therefore, good correlations between IRM_{300mT} and Cu, Fe, Pb and Zn for all three storms ($r > 0.88$). The variation in Mn against IRM_{300mT} did not exhibit good correlations for events C2 and C3, although for event C1 a good correlation was seen. These correlations are dominated by suspended sediment variations. When metal concentrations (μg g^{-1}) and IRM_{300mT} (10^{-3} A m^{-2} kg^{-1}) were compared significant correlations were only found for event C3, and for Fe and IRM_{300mT} for event C1.

It would appear therefore that changes might occur to sediments in the sub-surface drainage system which affect the strong linear co-relationships observed between magnetic minerals and heavy metals in surface sediments. This is not entirely surprising as the variation in metal concentrations ($\mu g\ g^{-1}$) associated with stormwater sediments has been suggested to result from the combined effects of size sorting and the removal of fine particles, as well as to surface reactions on the particulates. IRM_{300mT} does not show a similar distribution to that of metals with particle size (Chapter 6) and it is not thought that the chemical reactions and solubilisation that occur will effect the mineral magnetic characteristics of the particulates. The relationship, however, does not always break down and can exist as found for event C3.

The evidence of the good correlations of IRM_{300mT} and Cu, Fe and Pb concentrations for event C3 allows further inferences to be made as to the predominant source sediment of stormwater particulates. The co-variation of metals and magnetic minerals suggests that the source of magnetic minerals and pollutants could be related. If the source is the same for both magnetic minerals and metals it is probable that the values reflect atmospheric inputs rather than road constructional materials as the latter have been found to contribute negligible amounts of metal to the environment.

8.6. Mass Flow Studies of Sediment and Associated Metals through the Sub-Catchment During Storm Events C1, C2 and C3.

The characterisation of stormwater sediments by mineral magnetic parameters (Section 8.4.2) allows the total weight of sediment and metals discharged during the storm event to be sub-divided and attributed to a dominant source. The mass of sediment and metal discharged in runoff during the time interval represented by the sample was attributed to the grouping the sample was categorised with by mineral magnetic characterisation (Table 8.11). There is a tendency for the statistical classification to class all roof sediments correctly but also to classify highway associated sediments with the roof sediment grouping (Sections 5.3.1 and 6.4.3). As a result, for any sample

Table 8.11 Estimated Loadings (mg) from Source Sediments During Storm Events C1, C2 and C3 Based on the Mineral Magnetic Characterisation of Sediments.

	Cu	Fe	Pb	Mn	Zn	Suspended Sediment
Event C1						
Road	1.6	227.9	5	7.1	6.2	4630
Intermediate	0.1	30.4	0.6	0.1	0.4	917
Roof	18.5	2480.9	73.0	93.6	79.9	62778
Event C2						
Road	18.3	2104.2	74.4	84.4	84.6	157275
Intermediate	0.8	121.1	5.7	7.6	6.3	10437
Roof	1.1	103.4	4.6	9.7	3.9	8107
Event C3*						
Road	3.0	230.3	25.8	53.2	27.3	64982
Roof	9.5	2737.4	86.0	95.1	104.5	102176

* Loadings based on average concentration for classified samples and estimated total runoff from source area. Method of calculation does not allow an 'Intermediate' category.

classified by more than one equation as being part of the highway associated grouping, the sediment and metal loadings discharged at the time the sample was collected were attributed to that source. If a sample was only classified with highway associated sediments by only one equation, the discharged loadings were ascribed to the Intermediate category. The figures given as 'Intermediate' are in all probability derived from highway associated sediments but it was felt that the approach taken prevents too rigid an interpretation being placed on the values given. It should be noted that this study is not truly quantitative and it is not the intention to suggest that the loadings attributed to each source in Table 8.11 should be viewed as more than being indicative of scale.

Although flow was not recorded for event C3 an attempt to assess the relative contributions was made by calculating the mean of those samples classified as road derived sediment and the mean of those classified as derived from the roof and multiplying both mean concentrations by the estimated runoff from the appropriate surface. As the loading per sample cannot be calculated, no samples could be categorised as 'Intermediate'. Any sample categorised with highway associated sediment by any equation was therefore attributed to that source. This method is liable to underestimate the loadings involved. The results should be taken as qualitative rather than quantitative and their inclusion here is purely as an indicator of the dominant source and to illustrate how mineral magnetic parameters may be used to evaluate contributing sources.

The study of sequencing patterns in Chilwell Gardens by use of mineral magnetic parameters identifies an overall dominance by sediments classified with the roof grouping. In event C2 the sediment derived from highway associated surfaces, which may include in-pipe sediments, is the dominant source. In Section 8.3.2 the importance of the 'first-flush' contribution to stormwater loadings was identified. It appears that the dominant sediment source indicated by mineral magnetic characteristics during the initial phase of the storm is the dominant source for all of the storm.

The balance of the total mass of metal and particulates deposited within the sub-catchment prior to each storm event and the total mass discharged for each event was estimated (Table 8.12). The mass of metals and particulates deposited within the sub-catchment was estimated from the total surface area of the highway and pavements and the ground area covered by the roofing of the three housing blocks. Deposition of metals and particulates from vehicular sources was also estimated and included in Table 8.12. These figures were based on traffic counts carried out at Chilwell Gardens which estimated the daily weekday traffic as approximately 100 cars and 20 commercial vehicles. The range of probable

Table 8.12 Estimated Inputs of Particulates and Particulate Associated Metals from Atmospheric and Vehicular Sources for the Periods Prior to the Storm Events C1, C2 and C3.

	Cu (mg)	Fe (mg)	Pb (mg)	Mn (mg)	Zn (mg)	Particulate Matter(g)
EVENT C1						
Input						
Atmospheric Deposition	122,3	12684,6	246,1	182	271,5	244,7
Vehicular	3,6-10,3	64,4-90,3	66,3-275,0	<0,1-1	8,1-71,3	2,7-10,0
Output						
Runoff	20,2	2739,2	78,6	100,7	86,5	68,3
EVENT C2						
Input						
Atmospheric Deposition	85	11355,4	193,9	316,2	198,4	226,8
Vehicular	2,2-6,2	38,6-54,2	39,8-165,0	<0,1	4,9-42,8	1,5-6,0
Output						
Runoff	20	2328,7	84,7	101,8	94,8	175,8
EVENT C3						
Input						
Atmospheric Deposition	91	9149,1	231,2	301,4	261,1	364
Vehicular	7,2-20,6	128,8-180,7	132,6-550,0	1,0-1,4	16,3-142,5	5,1-20,0
Output						
Runoff	11	2331	97,4	139,9	112,9	160,4

input from Pb in petrol was calculated as in Section 2.1.3. The input of brake particulates was based on the figures for emission of particles from brakes given by Jacko and DuCharme (1973) and Malmqvist (1983) of 11 and 8 mg vehicle km^{-1}, respectively. The concentration in brakes was taken from findings in this study on dust from disc brakes and in addition from figures given by Shaheen (1975). The input from braking operations was estimated as the product of these figures. Finally the input from tyres was estimated as in Section 2.1.3 and using the concentrations given by Hedley and Lockley (1975), Shaheen (1975), Christensen and Guinn (1979), and as determined in this study. This resulted in a possible range of the mass of metals and particulates resulting from tyre wear.

The inputs to the highway surfaces do not include wear of constructional surfaces. It was felt that while this source is certainly likely to contribute, the only estimations of such wear available are for roadways with traffic densities of greater than 4500 vehicles per day. The estimated total input from brakes, exhausts and tyres to the environment from vehicles using Chilwell Gardens has been assumed to be deposited on the highway associated surfaces. It is known that the majority of exhaust particulates and tyre particulates are deposited within 100 m and 5 m of the roadside respectively. In assuming that they are deposited within 3 m distance of the kerb, it is thought that the resulting over-estimate will be offset by not including wear of highway associated surfaces.

The input of all metals and particulates far outweighs the discharged output as determined in runoff. Malmqvist (1983) and Warren (1987) have also found in their studies of urban catchments, that inputs were greater than the output as measured in runoff. It would appear from the estimates given in Table 8.12 that Fe, Mn and sediment loadings removed in runoff are greater than the input from vehicular sources but for Cu, Pb andZn the loadings are of of a similar magnitude. The atmospheric input is generally greater than the mass of metal or particulate removed by runoff or contributed by vehicular sources. The exception to this is Pb where the upper extreme of estimated vehicular input is of a similar order to the input by atmospheric deposition. For event C3 the upper extreme of vehicular input is greater than the measured atmospheric input. The important contribution made by vehicle derived Pb in stormwater quality is illustrated by this data.

For the event C2 the estimation of sediment derived from highway associated surfaces in runoff is 157.3 g (Table 8.11). It can be calculated that the mass of sediment deposited on highway associated surfaces (56.4% of the total catchment area) from both atmospheric and vehicular sources is approximately 129-134 mg. It would appear therefore that there is a shortfall of sediment supply. This may be accounted for by the omission of road wear in the calculations but as discussed this is liable to be taken into account by the inclusion of airborne and sedimentary emissions from vehicular sources in the balance for the sub-catchment. It would appear likely, despite these reservations, that the sediment supply from highway associated surfaces is critical for event C2, with a possibility of depletion of all sediment on these surfaces. There are several explanations that could account for this;

a) The sediment on highway associated surfaces is not reduced to zero after the previous storm. A proportion of this is removed in runoff in event C2 as well as the total removal of all particulates deposited between the prior storm event and C2. This would result in a net loss of sediment from the highway associated surfaces.
b) Sediment deposited in the sub-surface drainage system and which is of similar character to highway associated sediments, is removed by the scouring action of an intense storm.
c) The samples include a proportion of sediment other than that derived from highway associated surfaces but masked by the dominant sediment.

Of these explanations it is felt that (b) is the most probable. The sediment loading, especially that of the road gutters where the majority of sediment collects, increases from winter to summer (Section 5.2.4). It would be expected therefore, that there should be a net increase of sediment on the highway associated surfaces not a net loss. The loadings ascribed to highway associated surfaces due to the mineral magnetic characterisation of the sampled suspended sediments may contain a minor proportion of particulates from roof surfaces as well as the dominant sediment type. It can be argued that the inverse is true with later loadings attributed to roof sediments containing a proportion of sediment derived from highway associated surfaces. Additionally the proportion of atmospheric to vehicular particulates deposited on highway surfaces prior to the storm C2 is in excess of twenty two to one. With such an inherent quanitity of highway associated surface sediments potentially being made up by atmospheric particulates it would be expected that if there was a substantial input of sediment other than that derived from highway associated surfaces the samples would be classified as being derived from highway associated surfaces.

CHAPTER 9 HEAVY METALS AND MINERAL MAGNETIC PARAMETERS IN SOURCE SEDIMENTS AND STORMWATER PARTICULATES IN THE SOUTH OXHEY CATCHMENT.

9.1 Introduction.

It has been shown in Chapter 8 that the use of mineral magnetic parameters allows some indication of the sequencing of suspended sediments during a storm event. The restriction of the initial research to a small well-defined sub-catchment allowed source sediments to be readily and easily identified. In order that the technique could be assessed when applied to the larger parent South Oxhey catchment, the potential source sediments within the main catchment had to be firstly evaluated in terms of their mineral magnetic parameters. The potential of these source sediments as pollution storage reservoirs was also assessed through a determination of their associated heavy metal concentrations.

9.2 Investigation of Source Sediments in the South Oxhey Catchment.

The Chilwell Gardens sub-catchment was originally chosen as it was thought to be typical of arterial residential roads found within a post-war, overspill suburban catchment. To widen the sample framework to include other areas within the parent catchment samples were collected from areas and road types of rather different characteristics to those represented by Chilwell Gardens (Figures 9.1 and 9.2).

Roadside dust samples were collected from two of the major roads within the catchment as well as from a residential cul-de-sac. The roadside dusts were collected from points on a transect across these roads. Samples of road gutter dusts and dusts from the road centre were collected at Prestwick Road (Site B, Figure 9.1) with a continuation of the transect beyond the road to include surface soil samples from open mown grass (Figure 9.2a). At the Oxhey Drive site (Site C, Figure 9.1) samples were taken along a transect from the road centre extending into

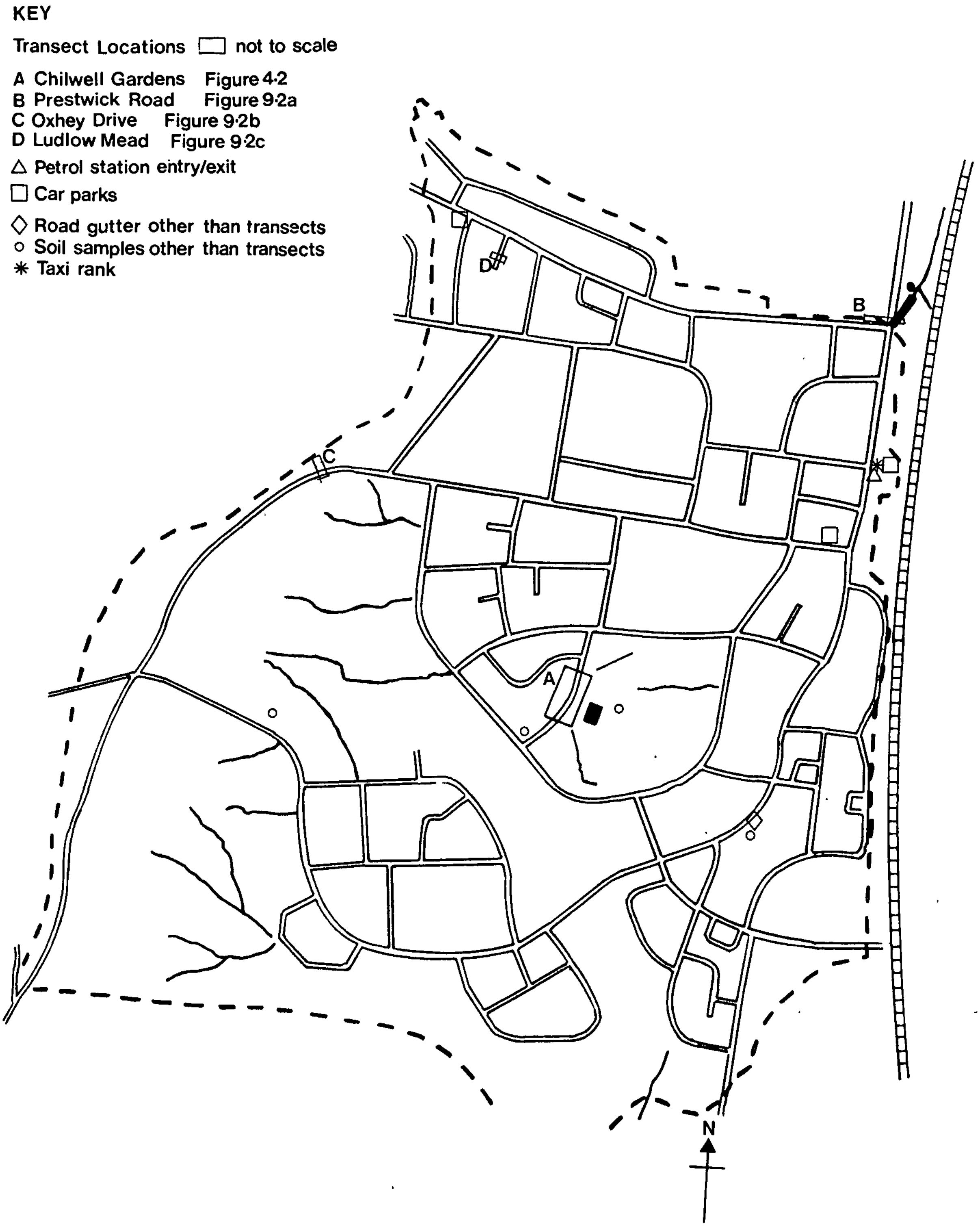


Figure 9.1 Sampling Locations within the South Oxhey Catchment.

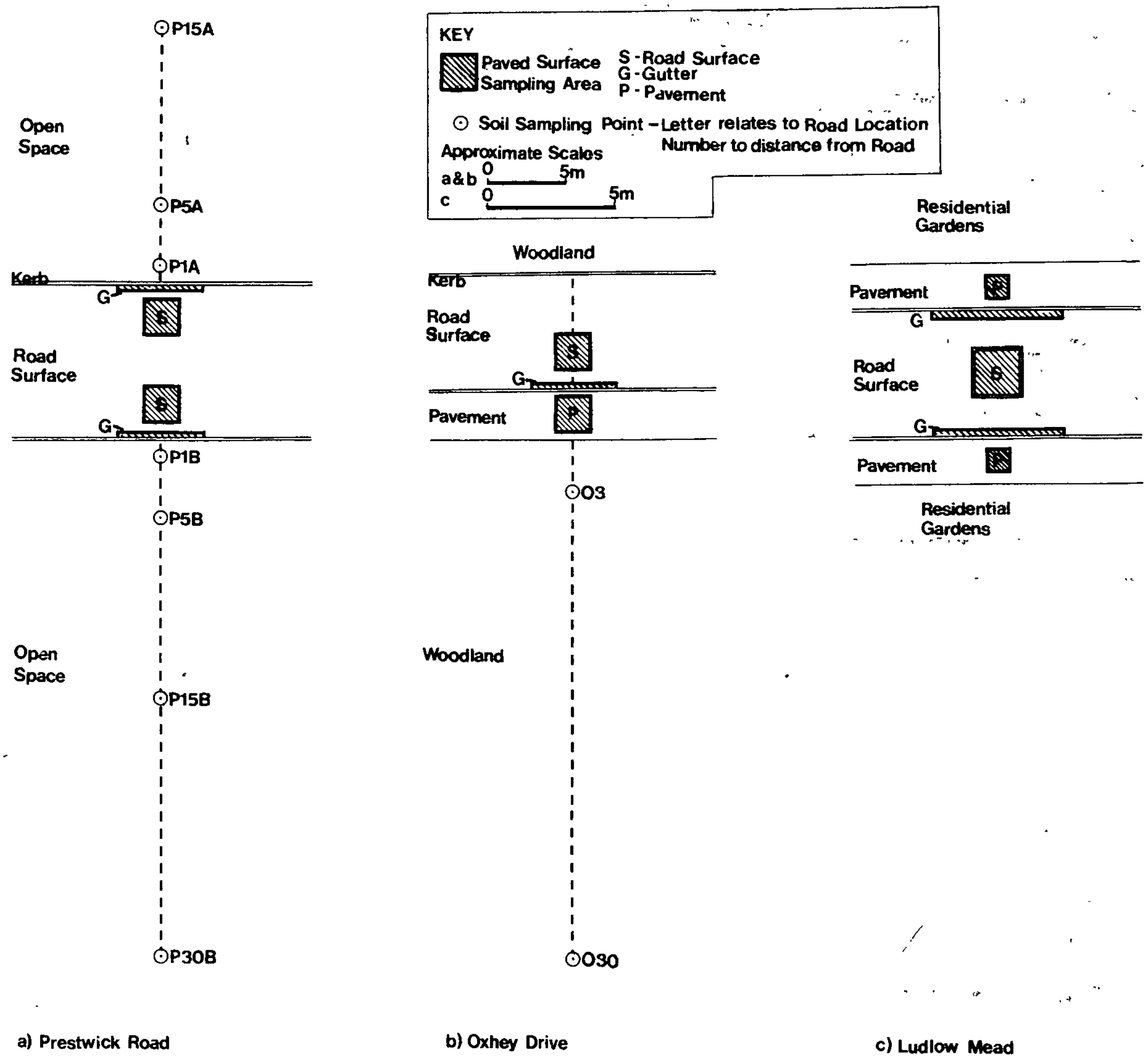


Figure 9.2 Detailed Sampling Locations on the Transects Across Three Differing Road Types.

the adjacent woodland. Samples included road centre, road gutter and pavement dusts and two samples of surface woodland soils (Figure 9.2b). The samples from Ludlow Mead cul-de-sac (Site D, Figure 9.1), were taken from a transect across the width of the road including pavement, road gutter and road centre dusts (Figures 9.2c). Prestwick Road is a major access route entering the parent catchment and is surrounded by open space whilst Oxhey Drive is another access route and is surrounded by woodland and is situated on a substantial incline. Ludlow Mead was chosen to be representative of the large number of residential cul-de-sacs present within the parent catchment. Additionally, road gutter samples of dusts were collected from roadside areas subject to uses other than residential parking, such as car parks, a taxi rank and the access road to a petrol station.

9.2.1 Heavy Metals in Source Sediments in the South Oxhey Catchment.

The heavy metal concentrations determined in the samples of potential source sediments in the main catchment are presented in Table 9.1 and show that there is a wide range of levels present in different source types. The woodland and open spaces, where anthropogenic activity is not intense, exhibit very low concentrations of heavy metals compared to the paved surface samples. As would be expected, the petrol garage slip road gave rise to a sample with high metal concentrations, although it was not untypical of road gutters generally. The taxi rank sample had a lower Pb level than other gutters. This area is reserved for the use of the black Hackney style London taxis which operate on diesel fuel which is Pb free. The levels therefore reflect Pb from petrol engined vehicles passing the taxi rank and deposition of dispersed Pb emitted from exhausts or due to dispersal from the road centre. The most surprising result was that the car park samples had similar or lower metal concentrations than pavement samples. Harrison (1979) found greatly elevated levels of metals in open air car parks and the results found in this study suggest that some general factor, such as cleaning practices or deflation, may be exerting a major influence on the levels found in car parks in the South Oxhey catchment.

Table 9.1 Heavy Metal Concentrations in Soils and Paved Sediments in the South Oxhey Catchment (excluding Chilwell Gardens).

	Cu ($\mu g\ g^{-1}$)	Fe ($mg\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Mn ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)
<u>Soil</u>					
a) Woodland (n=3)	18.6-29.7 (24.6)	7.7-14.9 (11.2)	104.6-255.1 (184.4)	241.2-451.0 (371.2)	44.2-224.2 (110.9)
b) Open Space (n=10)	10.1-48.0 (20.1)	4.5-25.8 (12.8)	48.3-231.8 (111.4)	65.3-636.9 (321.1)	23.7-142.5 (81.2)
<u>Paved Surfaces</u>					
a) Car Parks (n=3)	38.4-104.0 (77.9)	10.3-31.3 (21.7)	339.4-1114.5 (600.5)	207.6-827.8 (559.4)	69.3-188.2 (111.1)
b) Taxi Rank (n=1)	72.6	30.5	297.7	1475.7	167.5
c) Petrol Garage Entry/Exit (n=1)	456.5	30.8	1468.7	752.1	218.7
d) Pavements (n=3)	62.6-70.7 (70.3)	14.0-38.9 (23.6)	191.7-1777.2 (915.3)	390.0-1994.8 (1255.9)	281.6-364.1 (310.6)
e) Road Gutter (n=6)	85.5-218.7 (133.6)	21.0-30.4 (24.4)	640.3-2528.6 (1310.4)	417.0-3361.6 (1459.5)	291.6-506.3 (357.1)
f) Road Surface (n=4)	91.4-869.1 (343.2)	38.9-47.1 (43.1)	998.7-8112.3 (3463.5)	397.2-4052.0 (1335.9)	439.3-592.3 (508.8)

Mean values in parentheses

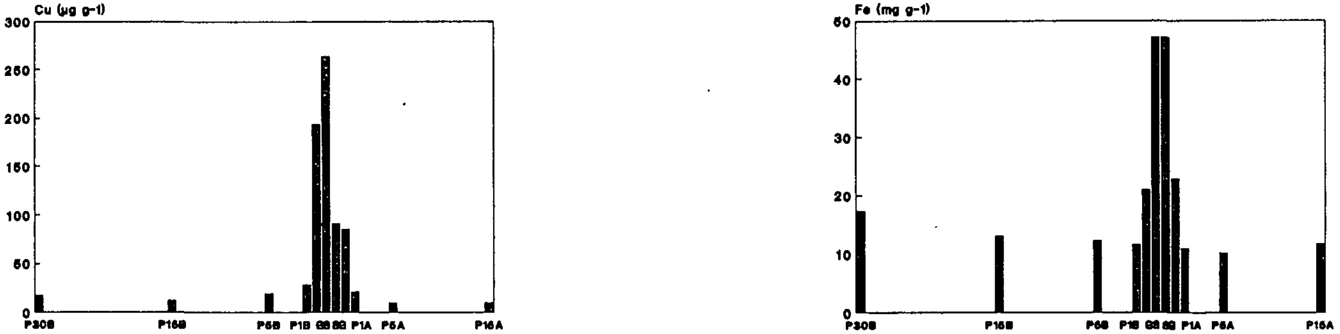
The results from pavements, road gutters and road surfaces in the main catchment indicate that Chilwell Gardens experiences lower pollution levels from heavy metals than the majority of other locations where paved surface dust samples were collected. This may simply reflect the fact that Chilwell Gardens is much less densely trafficked than the majority of alternative roads where samples were taken. The effect of cold starts and stationary engine acceleration on exhaust emissions of Pb, and the production of Cu in brake particulates during braking, as discussed in Section 2.1.3, would also suggest that elevated levels may result from the intensity of parking, starting and accelerating activity at or adjacent to the kerbside sampling sites in the parent catchment.

9.2.2 Variations in Heavy Metals with Distance from Road Centres.

The variation in heavy metal concentrations with distance from the road centre can be seen in Figures 9.3, 9.4 and 9.5. In all cases the peak Cu, Pb and Zn concentrations occur in the road centre sediments and decrease with distance from the road. This decrease appears to be generally exponential, a phenomenon which has been noted by other authors in connection with major highways (Ward et al, 1977; Albasel and Cottenie, 1985; Warren and Birch, 1987). It is interesting, however, to note that this distribution pattern can be identified on low trafficked roads serving residential areas. This serves to emphasise the importance of minor roadways as pollution sources within residential areas. Iron concentrations exhibit a similar but less consistent tendency to decrease from a peak concentration in the road centre.

The importance of minor roads is further emphasised by the results from the cul-de-sac where the greatest Pb concentrations were recorded (Figure 9.5). Similar observations have been made by Day et al (1975) and it is thought that the elevated concentrations may result from a greater incidence of cold starts, car maintenance activities on street parked cars and less frequent street cleaning.

Investigation of the co-variation of metals shows a strong correlation between Cu and Pb, Fe and Zn, Cu and Mn and Pb and Mn (Table 9.2). The



For sample type and locations refer to Figure 9.2.

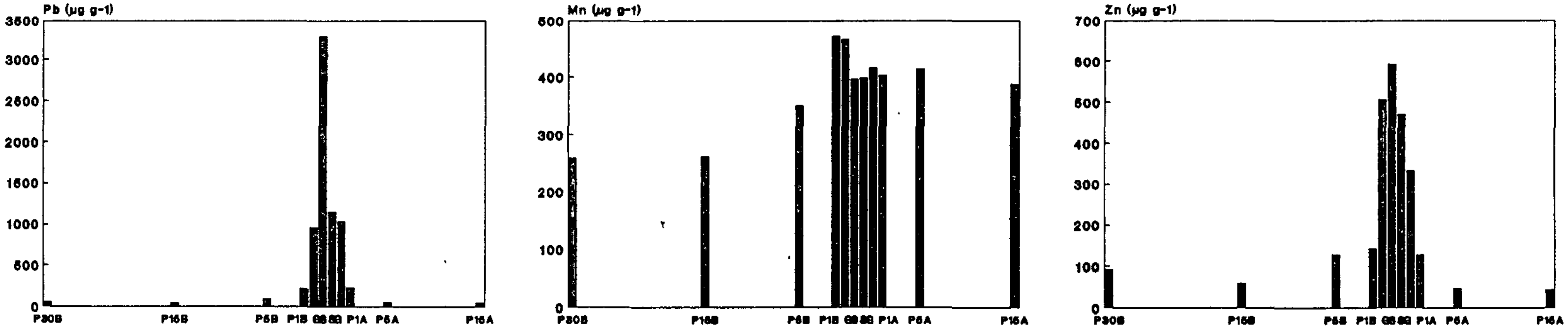
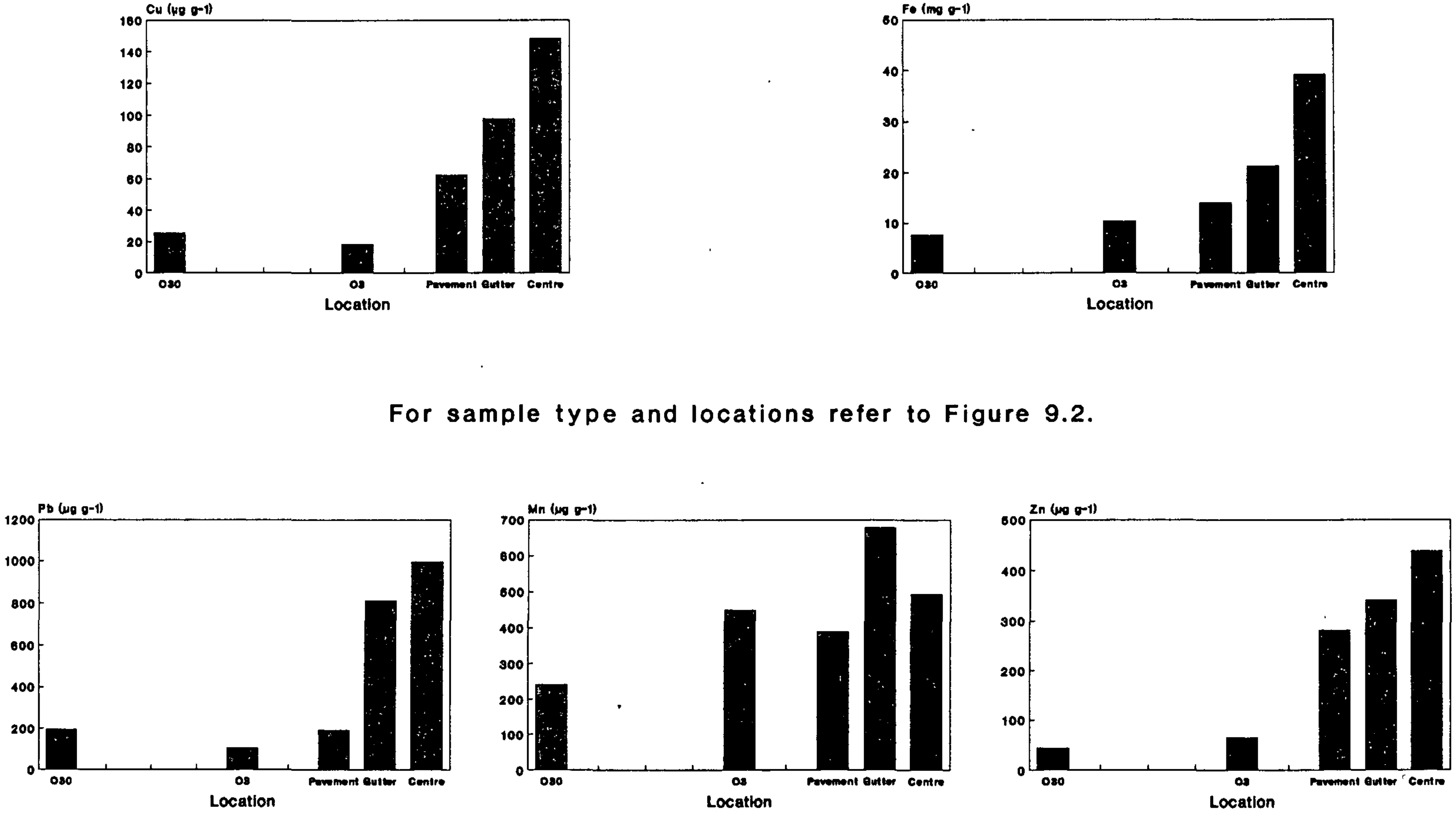
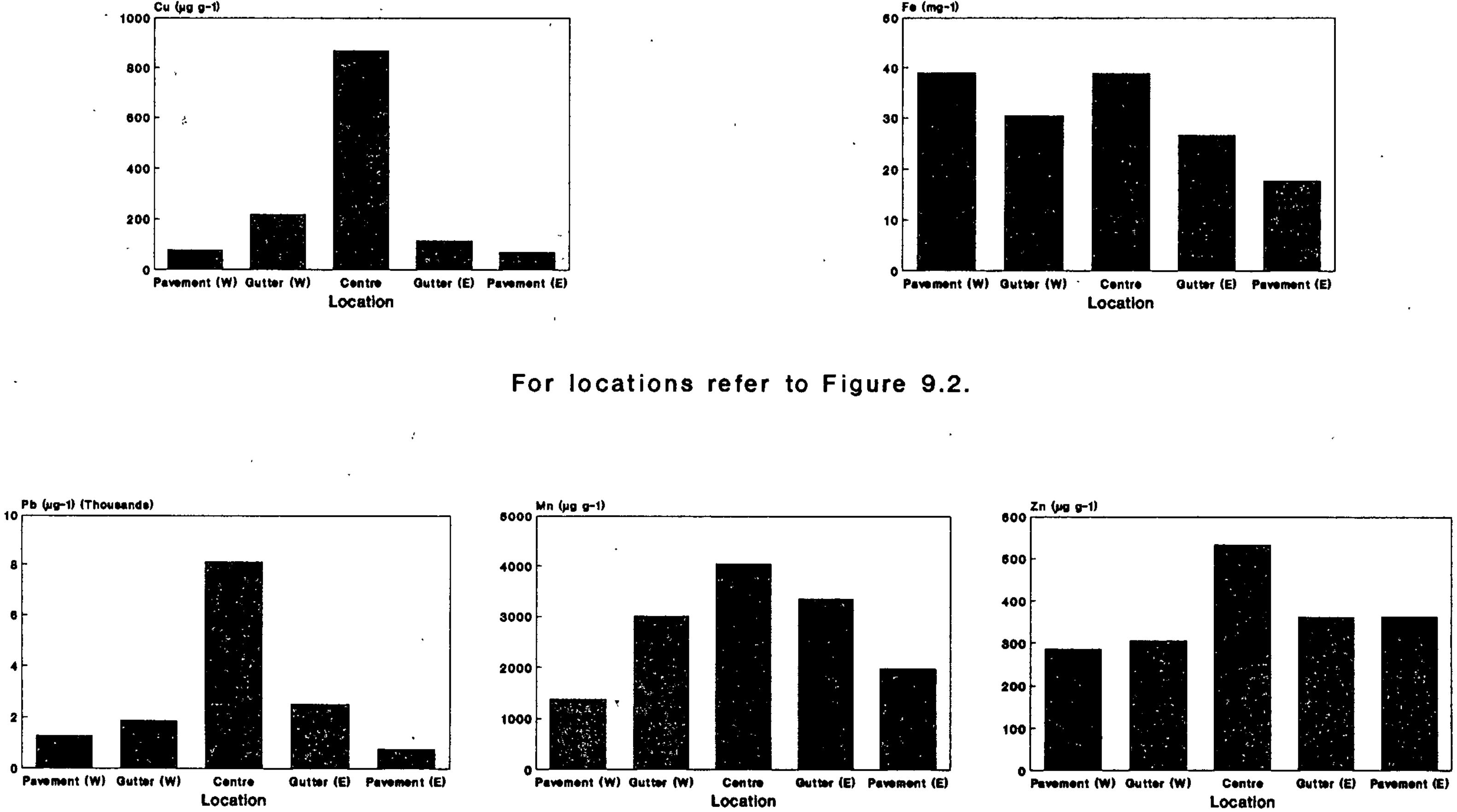


Figure 9.3 Variation of Metal Concentrations with Distance from the Centre of Prestwick Road.



For sample type and locations refer to Figure 9.2.

Figure 9.4 Variation of Metal Concentrations with Distance from the Road Centre of Oxhey Drive.



For locations refer to Figure 9.2.

Figure 9.5 Variations of Metal Concentrations with Distance from the Road centre of Ludlow Mead.

relationship between Cu and Zn and Pb and Zn, while significant, was not as strong as might be expected. Comparison with the results of investigations into the co-variation of metals in the Chilwell Gardens sub-catchment reveals that the correlations found here are much stronger. This most probably reflects the inclusion of roads with greater traffic density and therefore a more obvious distribution of metals about a line source.

Table 9.2 Correlation Matrix for Metal Concentrations in Transect Samples.

	Cu	Fe	Pb	Mn	Zn
Cu	1	0.54	0.96	0.69	0.61
Fe		1	0.63	0.35	0.82
Pb			1	0.76	0.63
Mn				1	0.38
Zn					1

(n = 26)

The strong correlation between Cu and Pb again emphasises the dominance of vehicular sources as the major pollutant source for these metals. The correlations of both Cu and Pb with Mn is unexpected and not readily explained. They are possibly indicative of a minor contribution of Mn to the urban environment from vehicular sources that only becomes apparent in proximity to roads with higher traffic densities than those within the sub-catchment initially studied. The observed correlation between Fe and Zn, combined with a less strong correlation of Fe with Cu or Pb, suggest that whilst there is an indication of vehicular sources dominating the distribution of metals about highways, other sources are also influencing the distribution of these metals. Both Fe and Zn exhibit an increase in concentration between the soil sample taken at 15 m from the road kerb and the sample at 30 m from the road kerb which may be due to the influence of another source of metals such as fertilizer or grass treatment of the open space.

9.2.3 Metal Loadings in Highway Associated Sediments.

The loadings of metals as calculated from the samples collected throughout the parent catchment are presented in Table 9.3. The sediment mass was found to be a major influence on metal loadings. Where sediment loadings were similar to those of Chilwell Gardens, such as in the pavement locations, metal loadings were comparable (Tables 5.4 and 9.3). Despite the presence of elevated metal concentrations in road surface sediments compared to Chilwell Gardens (Tables 5.1 and 9.1), metal loadings in road surface sediments were much lower reflecting the low sediment loadings of road surfaces in the main catchment (0.3-3.8 g m^{-2}) compared to Chilwell Gardens (1.2-27.9 g m^{-2}). The road gutter sediments exhibited a much greater range of loadings of both sediment and metals than that observed in Chilwell Gardens. This variation may not be purely as a result of location but may also reflect the cleaning of the sampling areas at Chilwell Gardens every other month by the vacuum sediment sampling techniques. The build up of sediment in the sub-catchment only occurred during the intervals between sample collections. However, the samples collected in the parent catchment were from areas which had not been sampled previously and therefore could represent the build up of sediment over a considerable period of time.

The car park areas exhibited loadings intermediate between the road gutters of Chilwell Gardens and the road gutters of the parent catchment. This suggests that a considerable accumulation of metals is occurring in these areas compared to other road surfaces, despite the relatively low concentrations compared to other studies (Section 9.2.1). The controlling factor on the concentrations observed may well be dilution by other detritus such as litter which is contributing to the car park dusts.

The loadings at the entry/exit road to the petrol station reflected the high Pb concentrations observed, having a disproportionately high Pb

Table 9.3 Heavy Metal Loadings of Highway Associated Sediments in the South Oxhey Catchment (excluding Chilwell Gardens).

		Sediment (g m^{-2})	Cu (μg m^{-2})	Fe (mg m^{-2})	Pb (μg m^{-2})	Mn (μg m^{-2})	Zn (μg m^{-2})
Car Parks	(n=3)	19.2-307.4 (119.1)	740-28086 (10673)	198-7226 (2795)	6685-104326 (48411)	3993-254480 (92736)	1456-21291 (9509)
Taxi Rank	(n=1)	41.7	3026	1271	12415	61547	6984
Petrol Garage Entry/Exit	(n=1)	73.9	333742	2276	108569	53601	16169
Pavements	(n=3)	2.8-58.3 (23.5)	198-3654 (1523)	50-819 (410)	2176-11840 (8399)	5585-22744 (13716)	1020-16392 (6689.5)
Road Gutters	(n=6)	14.5-475.3 (202.4)	2369-85665 (26200)	442-10861 (4467)	20905-491737 (169278)	443746-254481 (116597)	4456-223886 (80382)
Road Surface	(n=4)	0.3-3.8 (1.8)	68-2151 (715)	14-148 (73)	982-20078 (6478)	118-10029 (3079)	177-1661 (753)

Mean values in parentheses

loading compared to the sediment loading for a road gutter sample. The sample from the taxi rank area also reflects the concentrations found with metal loadings being similar to pavement samples rather than road gutters depite the sediment loading being greater than the mean pavement sediment loadings.

9.2.4 Mineral Magnetic Parameters in Source Sediments in the South Oxhey Catchment.

The source sediment samples from the South Oxhey catchment were analysed to determine their mineral magnetic characteristics. The results of this analysis are presented in Table 9.4. Comparison of the data in Tables 5.6 and 9.4 shows that roof and soil sediments are very similar magnetically. The backfield ratios for both types of source sediment samples indicate that the samples are not as magnetically "hard" as atmospheric particulates i.e. in an applied magnetic field the magnetic minerals align with the field more readily than the assemblages present in atmospheric particulates. The roof and soil samples are seen to be magnetically "harder" than sediments from paved sources. It is likely that this reflects the deposition of atmospheric particulates as a major source of particulates to both areas. Additionally windblown soil has also been found to make up a considerable proportion of airborne particulates (Hunt, 1983) so there may be considerable continuity between the two groupings. Owing to these similarities it is unlikely that any distinction between the two sources will be possible for an unknown sample.

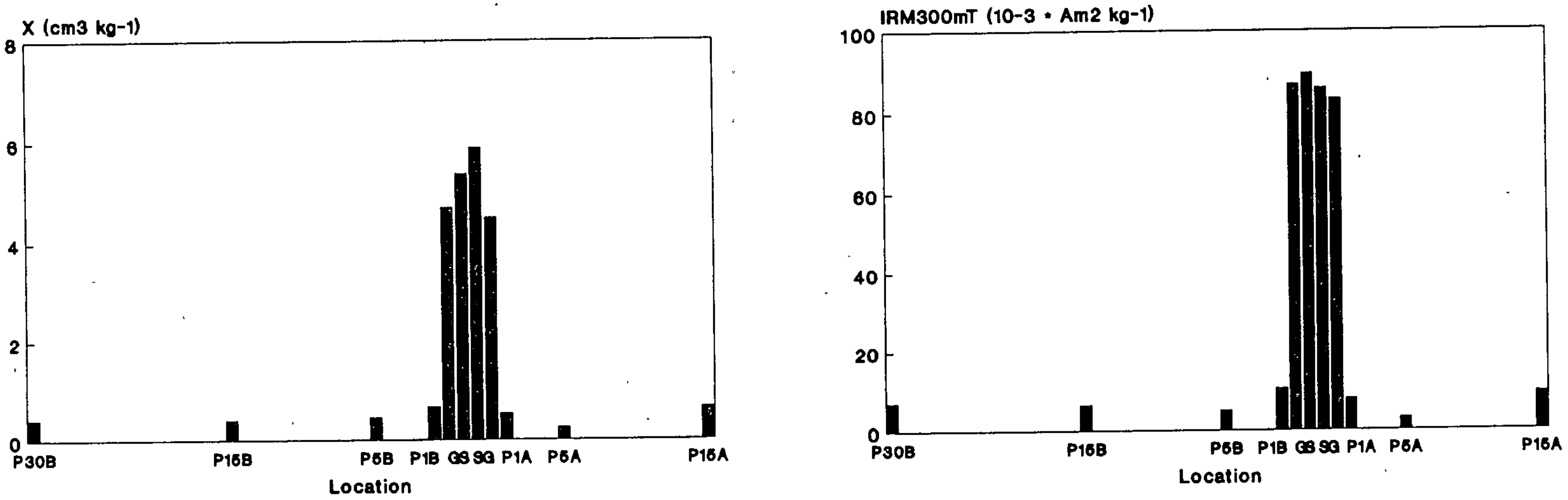
9.2.5 Variations in Mineral Magnetic Parameters with Distance from Road Centres.

The variation in mineral magnetic characteristics with distance from the highway was investigated by analysing the samples collected along the transects perpendicular to the three roads. The mineral magnetic concentration related parameters, χ and IRM_{300mT}, exhibit a decrease in magnitude with distance from the road centre (Figures 9.6 to 9.8). The

Table 9.4 Mineral Magnetic Parameters for Soils and Paved Surface Sediments in the South Oxhey Catchment (excluding Chilwell Gardens).

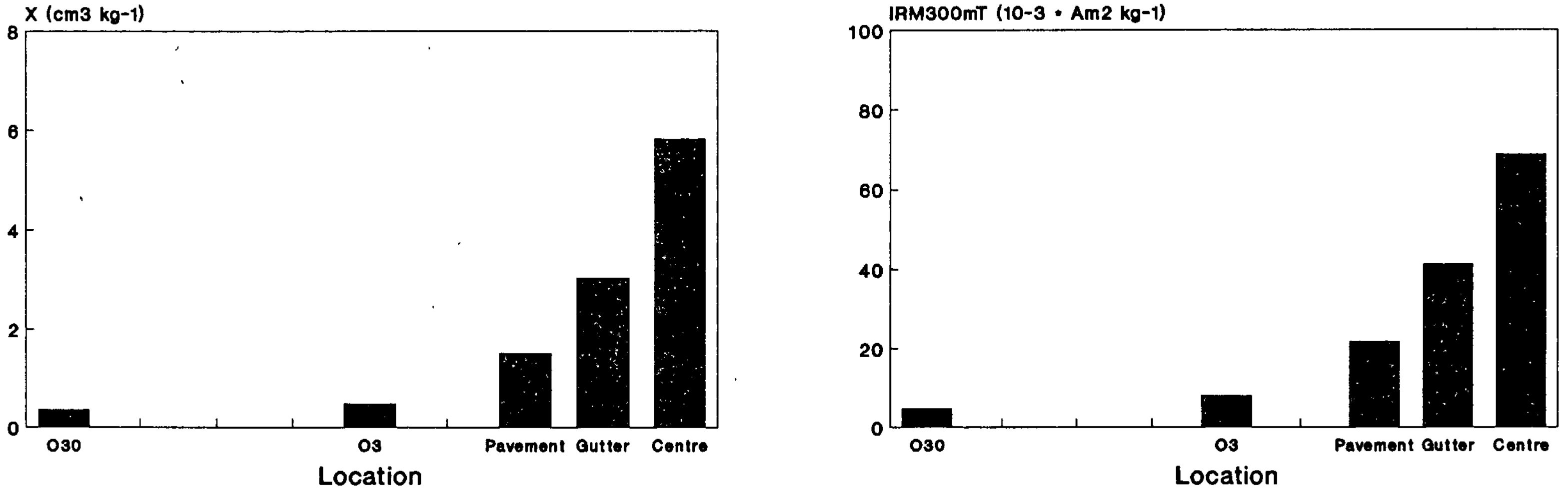
	χ (10^{-6} m^3 kg^{-1})	IRM$_{300mT}$ (10^{-3} Am^2 kg^{-1})	IRM$_{-20mT}$ /IRM$_{300mT}$	-IRM$_{-40mT}$ /IRM$_{300mT}$	IRM$_{20mT}$ /-IRM$_{40mT}$
<u>Soil</u>					
Woodland (n=3)	0.35-0.99 (0.6)	4.6-12.9 (8.5)	0.235-0.348 (0.277)	0.162-0.26 (0.214)	1.12-2.39 (1.63)
Open Space (n=10)	0.17-0.79 (0.43)	1.2-10.3 (6.2)	0.262-0.431 (0.321)	0.096-0.276 (0.179)	0.84-4.47 (2.1)
<u>Paved Surfaces</u>					
Car Parks (n=3)	2.26-5.84 (3.43)	26.8-79.1 (45.6)	0.19-0.249 (0.229)	0.271-0.345 (0.317)	0.55-0.91 (0.74)
Taxi Rank (n=1)	5.05	55.1	0.204	0.308	0.66
Petrol Garage Entry/Exit (n=1)	5.25	77.6	0.232	0.351	0.66
Pavements (n=3)	1.51-2.73 (2.29)	11.2-54.7 (31.7)	0.073-0.232 (0.154)	0.276-0.401 (0.327)	0.52-0.84 (0.7)
Road Gutters (n=6)	2.75-4.7 (3.87)	36.6-86.9 (69.0)	0.027-0.242 (0.136)	0.026-0.342 (0.227)	0.41-2.23 (0.87)
Road Surface (n=4)	5.37-7.12 (6.05)	66.6-146.7 (88.2)	0.032-0.412 (0.218)	0.032-0.453 (0.29)	0.24-1.43 (0.82)

Mean values in parentheses



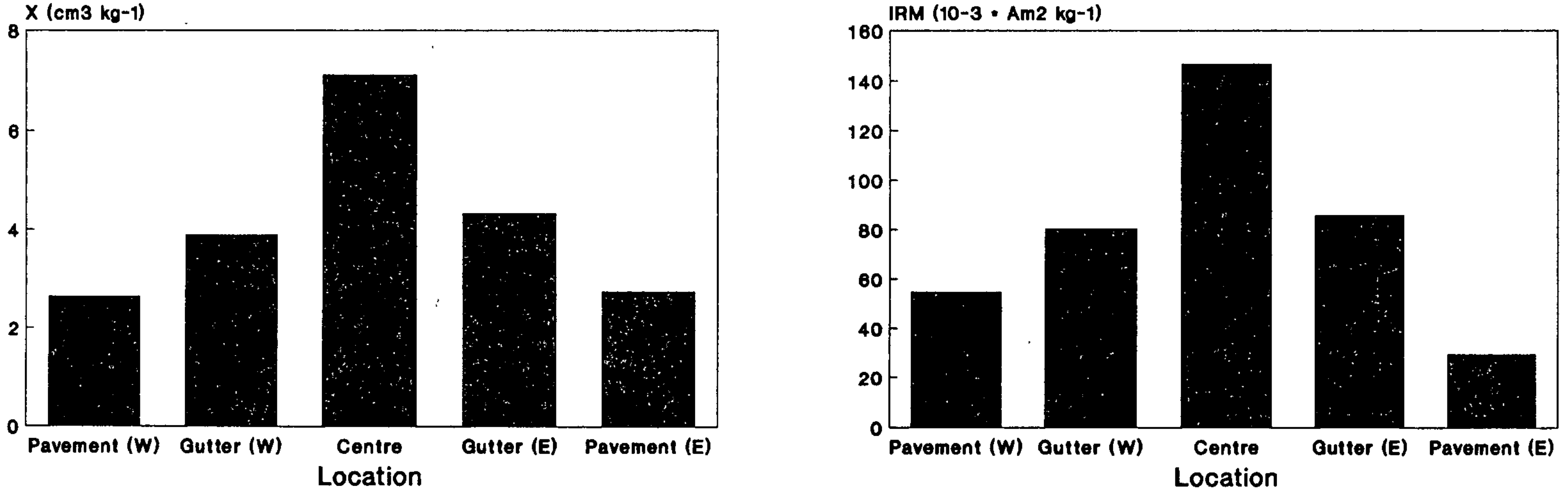
For type and location of samples refer to Figure 9.2.

Figure 9.6 Variation of X and IRM300mT with Distance from the Centre of Prestwick Road.



For type and location of samples refer to Figure 9.2.

Figure 9.7 Variation of X and IRM300mT with Distance from the Road Centre of Oxhey Drive.



For location of samples refer to Figure 9.2.

Figure 9.8 Variation of X and IRM300mT with Distance from the Road Centre of Ludlow Mead.

mineral magnetic characteristics, as identified by the backfield ratios IRM_{-20mT}/IRM_{-40mT} vary with type of sampling area. Those samples from highway associated surfaces have characteristics typical for paved surfaces (0.243-0.841) with the exception of Prestwick Road (0.741-2.23) which is believed to occur as a result of the values of IRM_{-20mT}/IRM_{300mT} and IRM_{-40mT}/IRM_{300mT} being close to zero (-0.037 to 0.057). Additionally there is no pavement at this site so it is probable that greater input of soil particulates to roadside dust could influence the magnetic character. The soil samples have magnetically "harder", i.e. haematitic, characteristics resulting in IRM_{-20mT}/IRM_{-40mT} values greater than 1.1 for woodland soils and 1.6 for open space soils. The mineral magnetic characteristics of the soil samples appear to become progressively "harder" with distance from the highway (Figures 9.9-9.10). The soil samples collected at 15 m and 30 m from the centre of Prestwick Road were found to have characteristics very similar to those of atmospheric particulates. This is not surprising as it would be expected that as the influence of vehicular sources declines with distance from the road the dominant source of magnetic minerals will increasingly become atmospheric deposition. The influence of the particulates resulting from vehicular sources can be seen therefore to extend within relatively narrow zones either side of the highway elevating the concentrations of magnetic minerals and modifying the magnetic characteristics of the sediment samples. Despite this influence, however, the main characteristic of the sediment type is retained. It may be that if surface deposited particulates were collected rather than taking a surface soil scrape, the characteristics of the sample would be found to be significantly influenced by particulates from vehicular sources.

9.2.6 Statistical Analysis of Source Sediments in the South Oxhey Catchment.

The results obtained from the mineral magnetic analyses (Table 9.4) were used to form the data base for a discriminant analysis together with the mean values for the highway associated sediments collected at the sub-catchment and the individual values for the roof sediments collected

For type and location of samples refer to Figure 9.2.

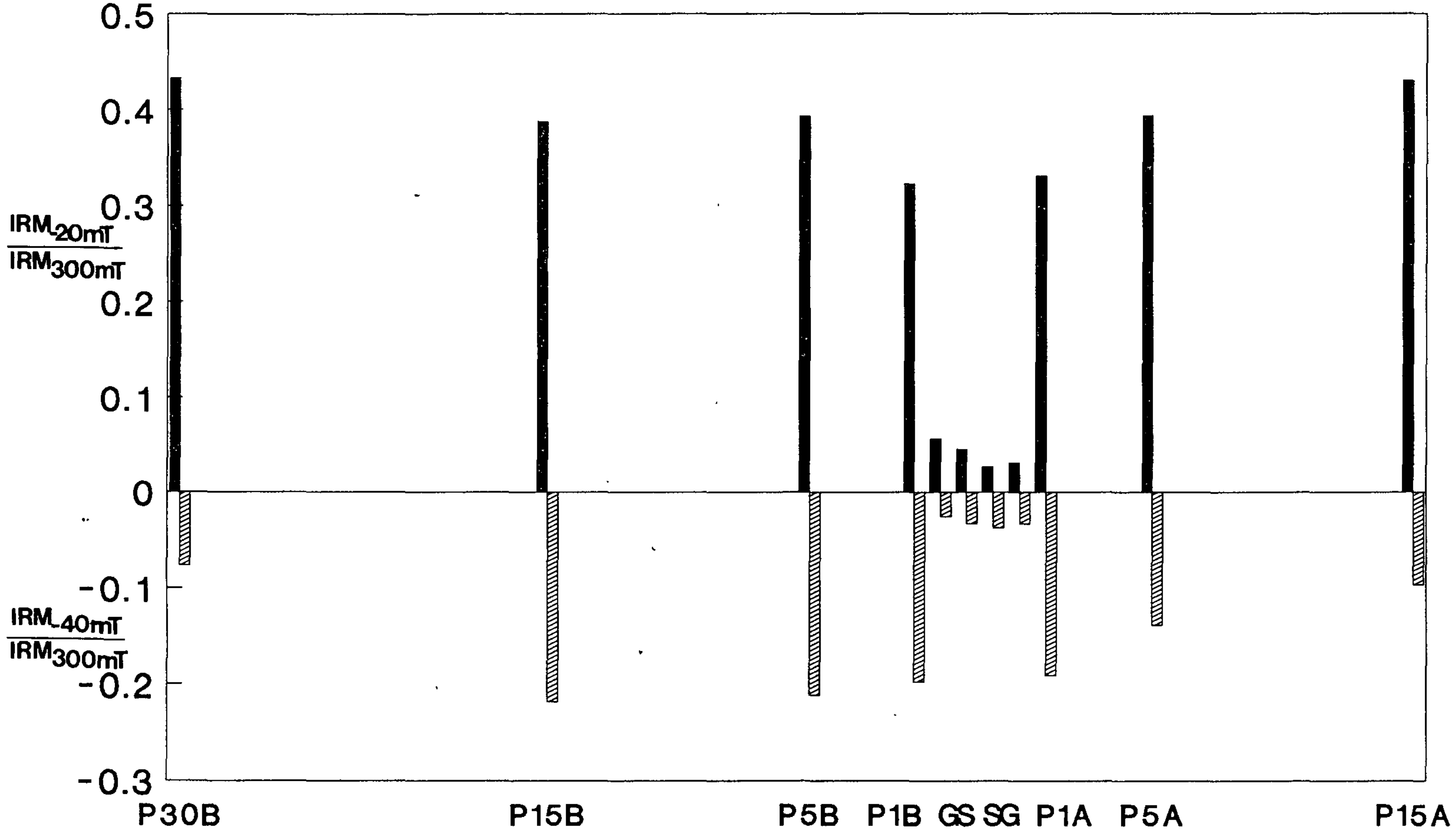


Figure 9.9 Variation in Backfield Ratios with Distance from the Centre of Prestwick Road.

For sample type and location refer to Figure 9.2.

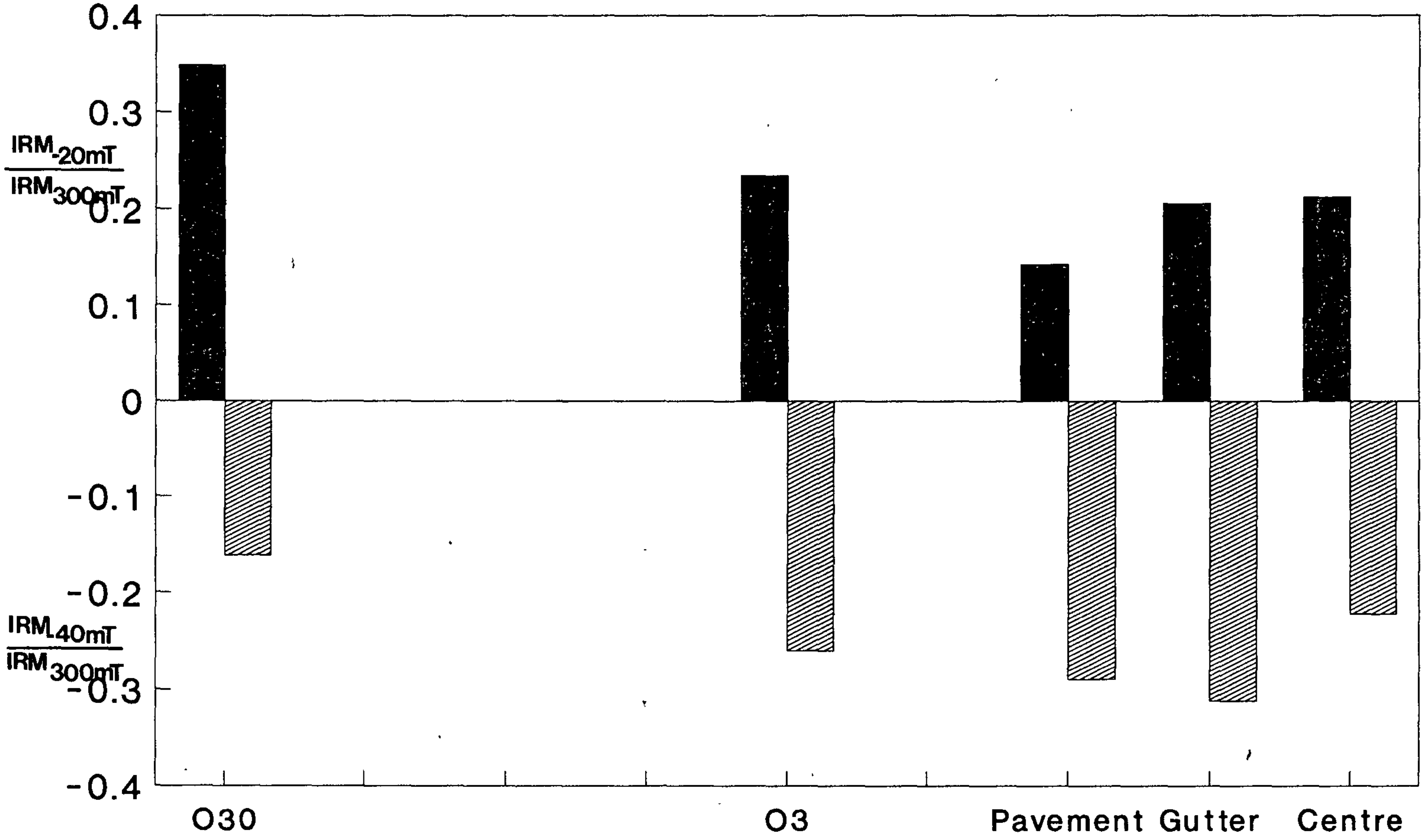


Figure 9.10 Variation of Backfield Ratios with Distance from the Road Centre of Oxhey Drive.

at the sub-catchment. The mean values for the highway associated sediments of the sub-catchment have been used as the inclusion of all the determinations would have given a biased weighting of the statistical analysis towards the previous sub-catchment findings. All the roof sediment values were included as these were the only roof sediments analysed and a distribution of mineral magnetic parameter values was needed for the statistical analysis rather than two individual mean measurements for roof gutter and roof surface sediments. A graphical presentation of the mineral magnetic characteristics of the samples included in the statistical analysis is given in Figure 9.11. In a comparable pattern to that demonstrated for Chilwell Gardens, the highway associated surface sediments fall to the left of the graph with roof, and in this case soil, samples falling to the right (Figures 5.13 and 9.11). The roof and soil samples also have much smaller values of IRM_{300mT} values than the sediments from highway associated surfaces.

With three groupings present in the statistical analysis, the resulting equations are more complex and describe three planes that intersect.

Road/Roof Interface:

$$(0.0939*IRM)-(34.143*TR)-(22.34*FR)+0.0909 \qquad [\text{Eq } 9.1]$$

Road/Soil Interface:

$$(0.089*IRM)-(38.8026*TR)-(23.4934*FR)+1.4326 \qquad [\text{Eq } 9.2]$$

Roof/Soil Interface:

$$(-0.0049*IRM)-(4.6592*TR)-(1.1529*FR)+1.3417 \qquad [\text{Eq } 9.3]$$

where $IRM = IRM_{300mT}$ $(10^{-3}\ A\ m^{2}\ kg^{-1})$
$TR = IRM_{-20mT}/IRM_{300mT}$
$FR = IRM_{-40mT}/IRM_{300mT}$

The overall classification of the results of the discriminant analysis of the source sediment samples is summarised in Table 9.5. The discriminant analysis reveals that the highway associated sediments can be successfully distinguished from the soil and roof sediments.

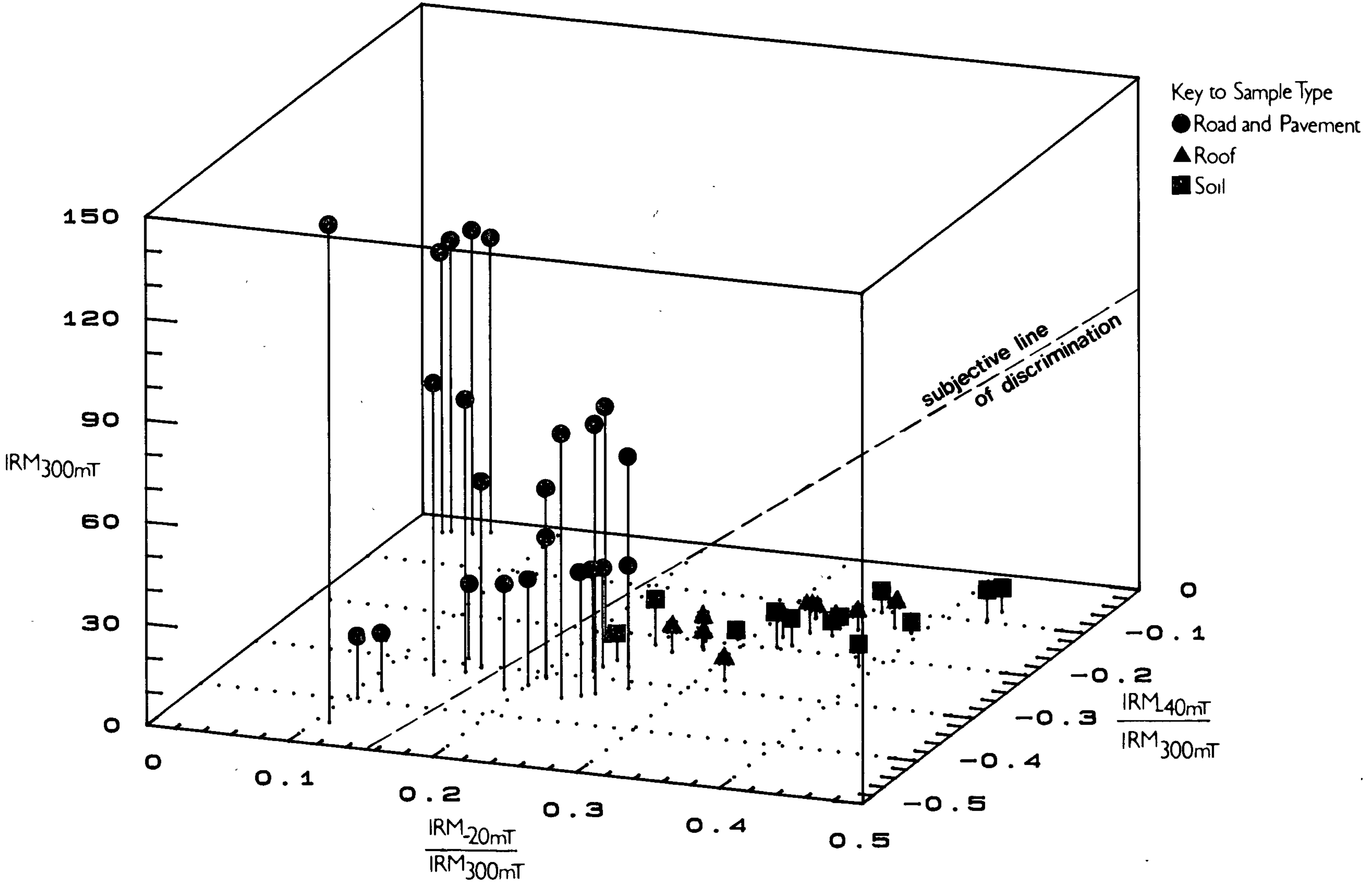


Figure 9.11 Tri-Axial Plot of Mineral Magnetic Characteristics for Source Sediments in the South Oxhey Catchment.

Table 9.5 Classification of the Results of Discriminant Analysis Carried out on Source Sediments in the South Oxhey Catchment.

Actual Group	No. of Cases	Predicted Group Membership Group 1	 Group 2	 Group 3
Group 1 (Highway Associated Sediments)	23	23 (100%)	0 (0%)	0 (0%)
Group 2 (Roof Sediments)	10	0 (0%)	5 (50%)	5 (50%)
Group 3 (Soil Sediments)	12	0 (0%)	5 (42%)	7 (58%)

There is severe difficulty in discriminating between soil and roof sediments; the distribution of samples as classified by discriminant analysis is similar to that which would be expected as a result of discrimination on a random basis, i.e. 50% in each group. It can therefore be concluded that while it may be possible to distinguish highway associated sediments from soil or roof sediments in stormwater particulates, it will not be possible to define the soil or roof sources as more than "other than highway associated sediment".

9.2.7 Relationship Between Heavy Metals and Mineral Magnetic Parameters in Source Sediments in the South Oxhey Catchment.

A strong correlation between heavy metal concentrations and magnetic mineral concentration related parameters in highway associated surface sediment samples collected in the Chilwell Gardens sub-catchment was observed (Chapter 5). The concentrations of heavy metals and concentration related mineral magnetic parameters determined on samples collected along the transects perpendicular to three roads in the catchment have been observed to decrease with distance from the road centre. It appears therefore that a strong relationship is likely to exist in relation to any area where particulates from vehicular sources are the dominant pollutant source.

Table 9.6 Correlation Coefficients for Metal Concentrations and Magnetic Mineral Concentration Related Parameters for Source Sediments in the South Oxhey Catchment.

	Cu	Fe	Pb	Mn	Zn
χ	0.68	0.86	0.71	0.47	0.94
IRM_{300mT}	0.79	0.8	0.83	0.61	0.88

(n = 26)

The results of correlation analysis indicate that there is a strong linear relationship between χ and Fe, χ and Zn, IRM_{300mT} and Cu, Fe, Pb and Zn (Table 9.6). The statistical analysis confirms the co-relationship between the metals Cu, Fe, Pb and Zn in the highway associated surface sediments and in sediments from the area adjacent to the highways. This co-relationship appears to be robust and is found in relation to all highways. The use of a simple technique such as χ determination, on highway sediments as a reconnaisance technique to identify relative variation of heavy metals associated with vehicular pollution would therefore appear to be a viable proposition.

9.3 Stormwater Particulates at the Main Catchment Outfall.

9.3.1 Hydrological Characteristics of Storm Events.

The sampling of stormwater was carried out at the outfall flume to the main parent catchment. Five storm events were captured and their hydrological properties are summarised in Table 9.7. The duration of the storm and the volumes quoted relate to the period during which sampling occurred. The float switch was set at a height of 74 mm above base line flow, equivalent to a flow of 70 l sec^{-1} and therefore only storm events that exceeded this flow were considered and monitored as runoff events (Section 4.7.3).

Table 9.7 Summary of Storm Events Recorded at Main Catchment Outfall.

Date of Storm	Storm Code	Duration (mins)	Maximum Flow (l sec^{-1})	Rainfall Volume (m^3)	Runoff Volume (m^3)
23-3-85	F1	34	244.6	-	221.8
26-3-85	F2a+b	48+>204*	171.3	11689.0	>1573.3
29-3-85	F3	25	104.4	939.3	119.3
4-4-85	F4	102	350.7	8551.5	1058.3
13-5-85	F5a+b	17+109**	246.8	5986.0	1018.0

* Two phases of storm separated by 33 minutes - the second phase continued after sampling finished.
** Two phases of storm separated by 78 minutes

9.3.2 Heavy Metals in Stormwater Particulates.

A summary of the heavy metal concentrations and loadings are presented in Table 9.8. Comparison of Tables 8.2 and 9.8 indicates that the stormwater concentrations of heavy metals associated with the particulate phase are generally greater for all metals in the samples of runoff taken at the main catchment outfall as opposed to the sub-catchment. The metal levels found in the sub-catchment runoff, as previously stated, were found to be slightly low compared to literature values. The results at the main outfall, however, are found to be fairly typical of a catchment located on the outer edge of a major conurbation despite only particulate associated metals being considered.

The metal concentrations ($\mu g\ g^{-1}$) associated with stormwater particulates are also elevated in comparison to the concentrations associated with stormwater particulates sampled at the sub-catchment. The difference is more pronounced when the overall mean concentrations (calculated from total metal loadings and runoff volumes of all storms sampled at each location) are compared (Table 9.9). The mean concentrations associated with stormwater particulates at the South

Table 9 8 Heavy Metal Concentrations and Loadings as Found in Stormwater Particulates at the South Oxhey Catchment Outfall

Storm		Cu	Fe	Pb	Mn	Zn	Suspended Solids
Particulate Stormwater Concentrations (μg l^{-1}) [Suspended Solids in mg l^{-1}].							
F1	Range	108.3-229.2	18970.4-31307.8	798-1513	1148.6-6464 0	445.0-1231.0	487.5-803.3
	Mean	180.2	28294.6	1245.2	4134	974.6	605.2
F2a	Range	58.5-102.3	11721.9-22217.4	454.6-802.8	145.8-402.7	288.8-604.8	239.6-446.0
	Mean	86.6	18995.9	696.0	299.7	473.9	368.7
F2b	Range	19.5-80.4	5086 5-14139.3	73 4-384.8	91.7-206.7	134.5-924.4	81.7-291.8
	Mean	29 6	7956.8	177.2	140.1	259	158.8
F3	Range	30.8-38.3	5094.7-5686 3	234.2-280.1	163.1-429.7	159.1-298.2	137.9-152.7
	Mean	33.2	5349	259.7	300 4	232.3	143.8
F4	Range	22.5-84.1	5234.1-15275.9	150.2-522.1	86.1-796.1	102.9-497.9	84.2-320.8
	Mean	60 5	11591.0	382 9	475.4	309.3	224.2
F5a	Range	123 8,249.2	15060.4,23100 5	703.2,1186.6	940.2,1225.9	470.7,812.5	482.9,786.9
	Mean	218.8	17871.9	1069.4	1156 7	729.6	713.2
F5b	Range	24.2-105.2	3714.7-12820.2	168.5-646.2	156.2-536.1	127 8-939.7	91.6-377.4
	Mean	59.2	7749.6	367.7	339.2	327.7	156 8
Particulate Stormwater Concentrations (μg g^{-1})							
F1	Range	184.5-436.7	37662.8-59656.6	1416.3-2883.6	2356.2-12317.1	912.8-2345.7	
	Mean	254.7	42925.6	1829.4	4837.1	1326.3	
F2a	Range	209.9-269.1	43738.5-68471.9	1684.3-2767.4	543.8-902.9	1069.4-1768.3	
	Mean	239 1	54475 2	1908.8	815.3	1283.4	
F2b	Range	129.5-386.2	32899.9-88438.4	630 0-1855.0	612.1-1152.6	1107.6-3167.8	
	Mean	188.2	51304.1	1123.8	874.3	1657	
F3	Range	202.0-231.3	34555.0-41234.8	1533.5-1952.2	1136.5-3115.8	1137.1-2077.9	
	Mean	233.2	37073.8	1752.4	2432 9	1458.6	
F4	Range	243.5-335.4	47618.1-65070.0	1604 0-2050.2	1022.5-2481.6	1174.3-1678.1	
	Mean	275.5	54940.8	1775.8	1802.9	1378.9	
F5a	Range	256.4,316.7	29356.3,31187.4	1456 3,1507.9	1557.9,1947 0	974.7,1032.5	
		286.6	30271.8	1482.1	1752 5	1003.6	
F5b	Range	256.8-388 3	33969.7-50491.9	1586.5-2232.4	1359.7-2104.1	1073.3-3330.9	
	Mean	302.6	38462.7	1856.1	1723.7	1585.5	
Total Particulate Metal Loadings (g)							
F1		39.98	6277	276.23	917.1	134.25	
F2a		20 71	4541.5	166.4	71.64	88.15	
F2b		40.47	10887.13	242.48	191 73	217 27	
F3		3.96	638 28	30 99	35 84	17.15	
F4		64 04	12266.56	405.25	503.16	237.29	
F5a		20.02	1634.75	97.82	105 8	65.24	
F5b		54.81	7180.57	340.74	314 27	80.02	

Table 9.9 Overall Mean Metal Concentrations Associated with Stormwater Particulates Sampled at Chilwell Gardens And At the South Oxhey Catchment Outfall.

	Cu (μg l^{-1})	Fe (mg l^{-1})	Pb (μg l^{-1})	Mn (μg l^{-1})	Zn (μg l^{-1})	Suspended Solids (mg l^{-1})
Chilwell Gardens	9.18	1.328	46.8	61.4	52.8	72.6
S.Oxhey Outfall	61.1	10.882	390.9	536.1	353.1	210.3

Oxhey outfall are generally an order of magnitude greater than those associated with stormwater particulates sampled at the Chilwell Gardens sub-catchment.

The concentrations (μg g^{-1}) recorded in stormwater particulates are elevated compared to metal concentrations found in highway associated sediments both in the main catchment and those of the sub-catchment. The metal concentrations associated with stormwater particulates are generally similar to the finer fractions of the highway associated sediments collected from Chilwell Gardens (Tables 6.1 and 9.8). The metals associated with stormwater particulates sampled at the main catchment generally exhibit greater mean concentrations (μg g-1) than stormwater particulates sampled at the sub-catchment. However, it is noted that the ranges of metal concentrations associated with stormwater particulates are less for those particulates sampled at the main outfall catchment. These results suggest that there is a thorough mixing of sediments from various sources in the South Oxhey drainage system with some of the source areas contributing particulates with elevated metal concentrations compared to Chilwell Gardens.

Comparing the relative metal concentrations, it is interesting to note that the predominance of Zn over Pb seen in stormwater particulates in the sub-catchment is not readily apparent in the main outfall samples, with the exception of the samples collected during the second phase of the storm event F2 (Figures 9.12-9.16). It is not clear at this point what the explanation for this might be, although it may be that the first phase of event F2 removed the majority of surface deposited particulates and the later phase reflected the atmospheric input to a greater extent. Alternatively, it could be that at the outfall of a larger catchment the stormwater particulates are dominated by scoured deposits from within the pipe. This sediment has been observed to have greater concentrations of Pb than Zn. In addition it could be that it is only in more prolonged storms that the separate sources and their characteristics can be identified.

Generally the concentrations of particulate associated heavy metals ($\mu g\ l^{-1}$) show good correlation with suspended solids. There is a good linear correlation ($r > 0.7$) between metals ($\mu g\ l^{-1}$) and suspended solids for particulates sampled during storm events F2, F4 and F5. This is not entirely unexpected as the particulates by their very nature are the suspended solids and the relationship indicates that suspended sediment concentrations during events F2, F4 and F5, exert a major influence on the stormwater particulate metal concentrations. Good linear correlations between metals and flow were found for events F1, and F4 ($r > 0.8$), and to a lesser extent between Fe, Pb and Zn for F3. For F4, correlation of metals with flow and suspended solids was equally good. It would appear that flow is more likely to co-vary with metals on short intense storms where there is a similar peak in flow and pollutants. In other storms where the flow peaks prior to the pollutants the co-variation is not as strong.

The variation of sediment metal concentrations ($\mu g\ g^{-1}$) with variations in suspended sediments was investigated (Figure 9.17-9.21) and it was found that compared to the results obtained from stormwater sampling at the Chilwell Gardens sub-catchment the relationships were less obvious.

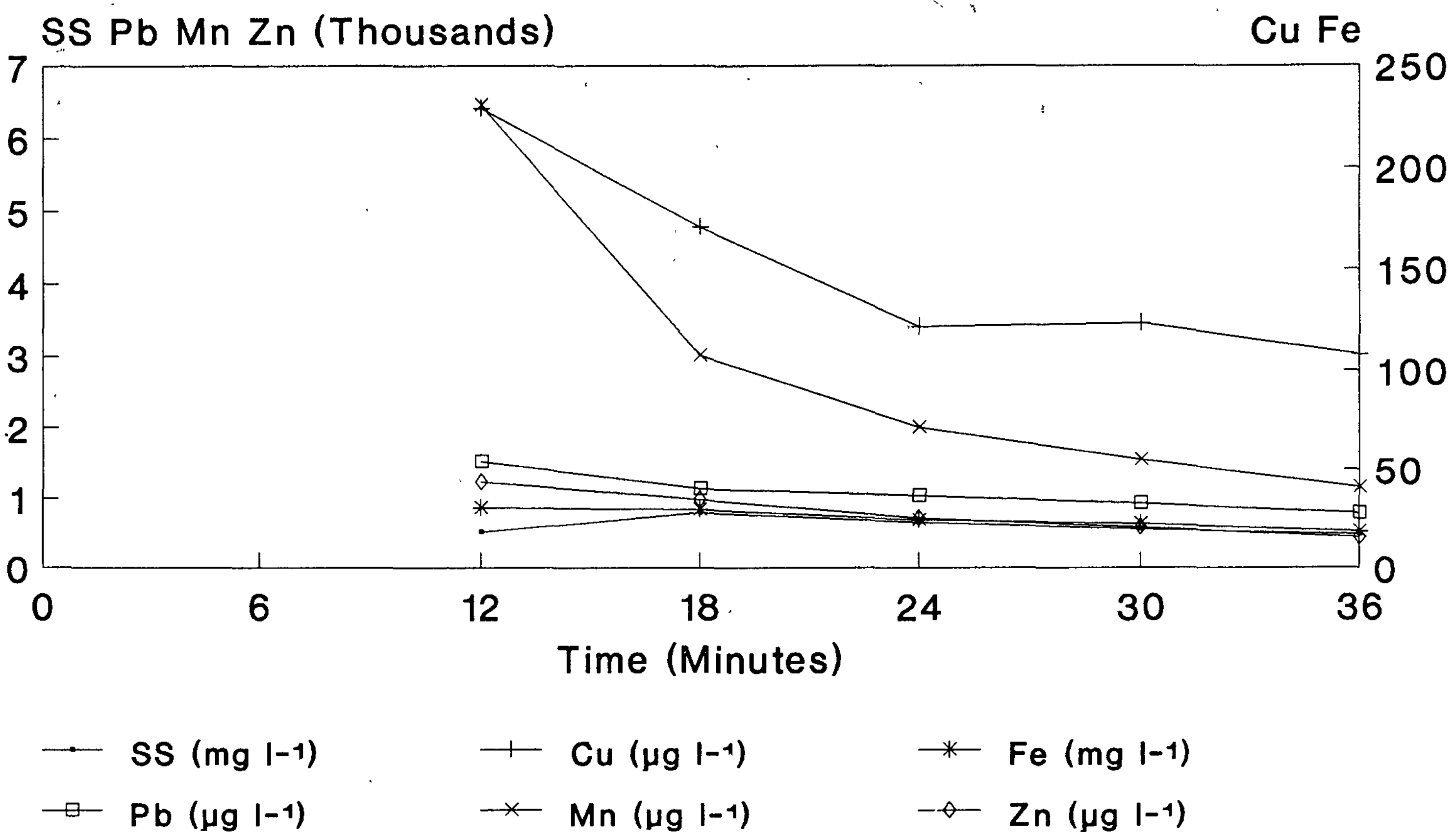


Figure 9.12 Variations of Suspended Sediment and Particulate Associated Metals over Time for Event F1.

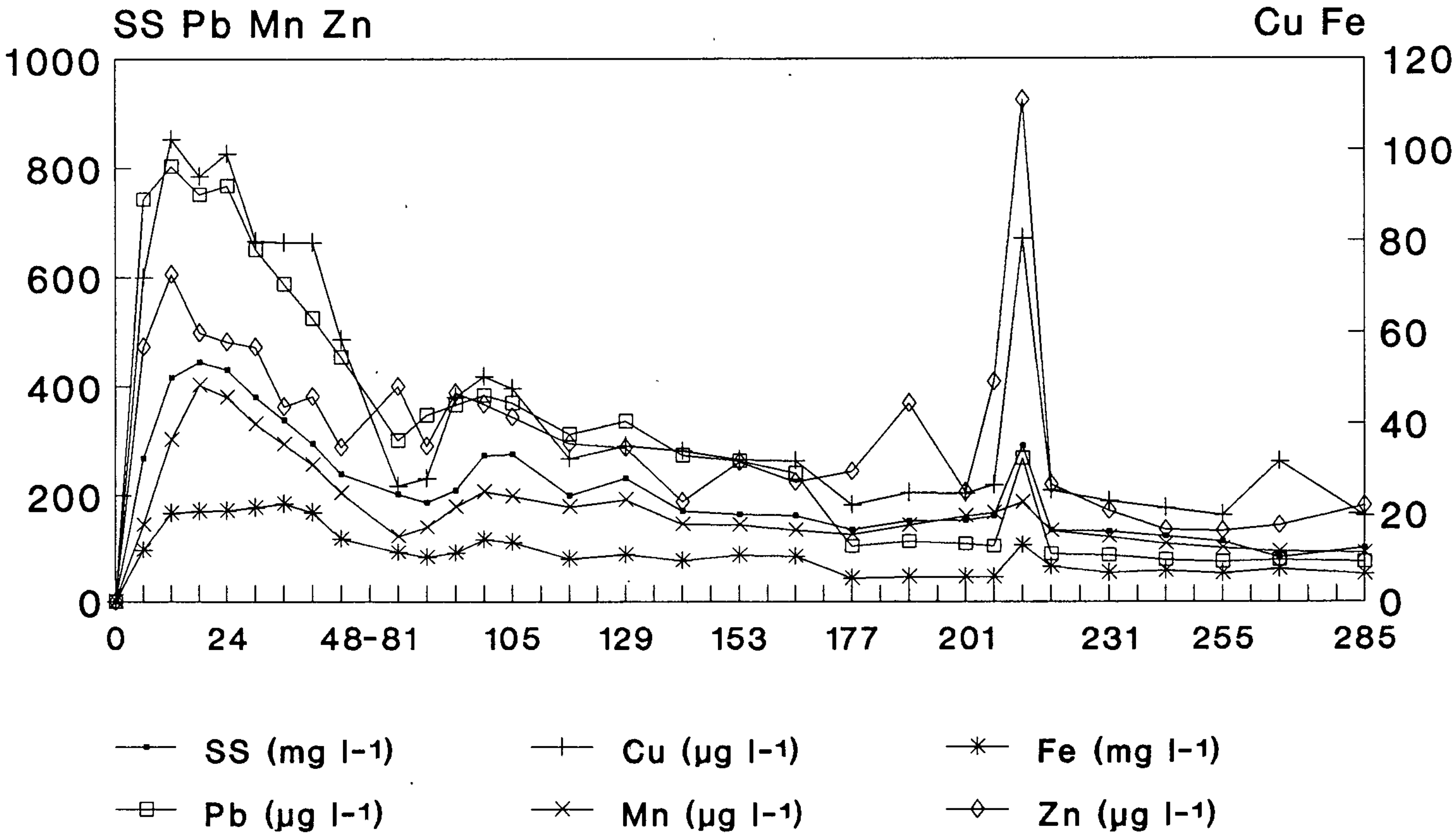


Figure 9.13 Variations in Suspended Sediment and Particulate Associated Metals over Time for Event F2.

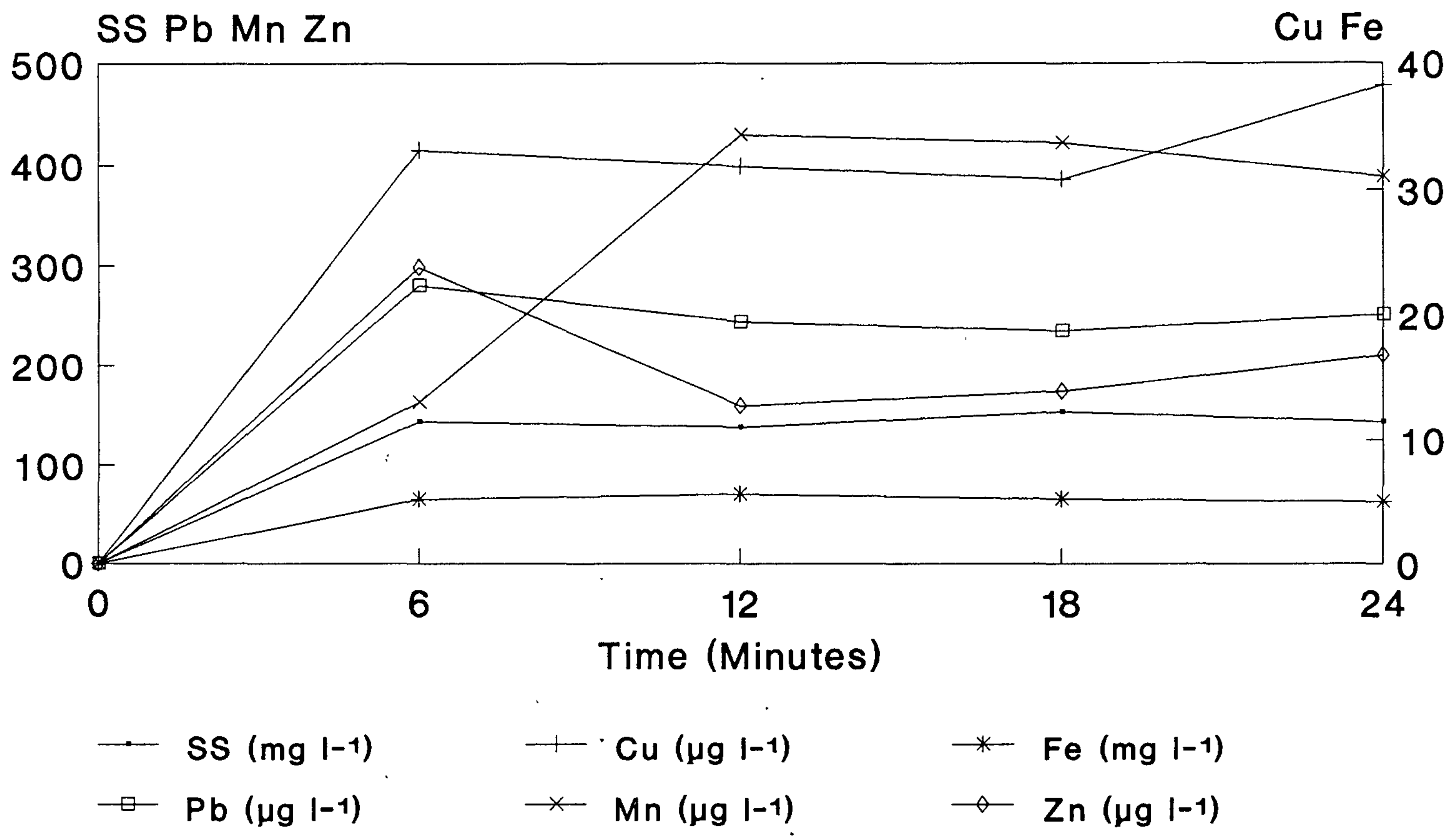


Figure 9.14 Variations of Suspended Sediment and Particulate Associated Metals over Time for Event F3.

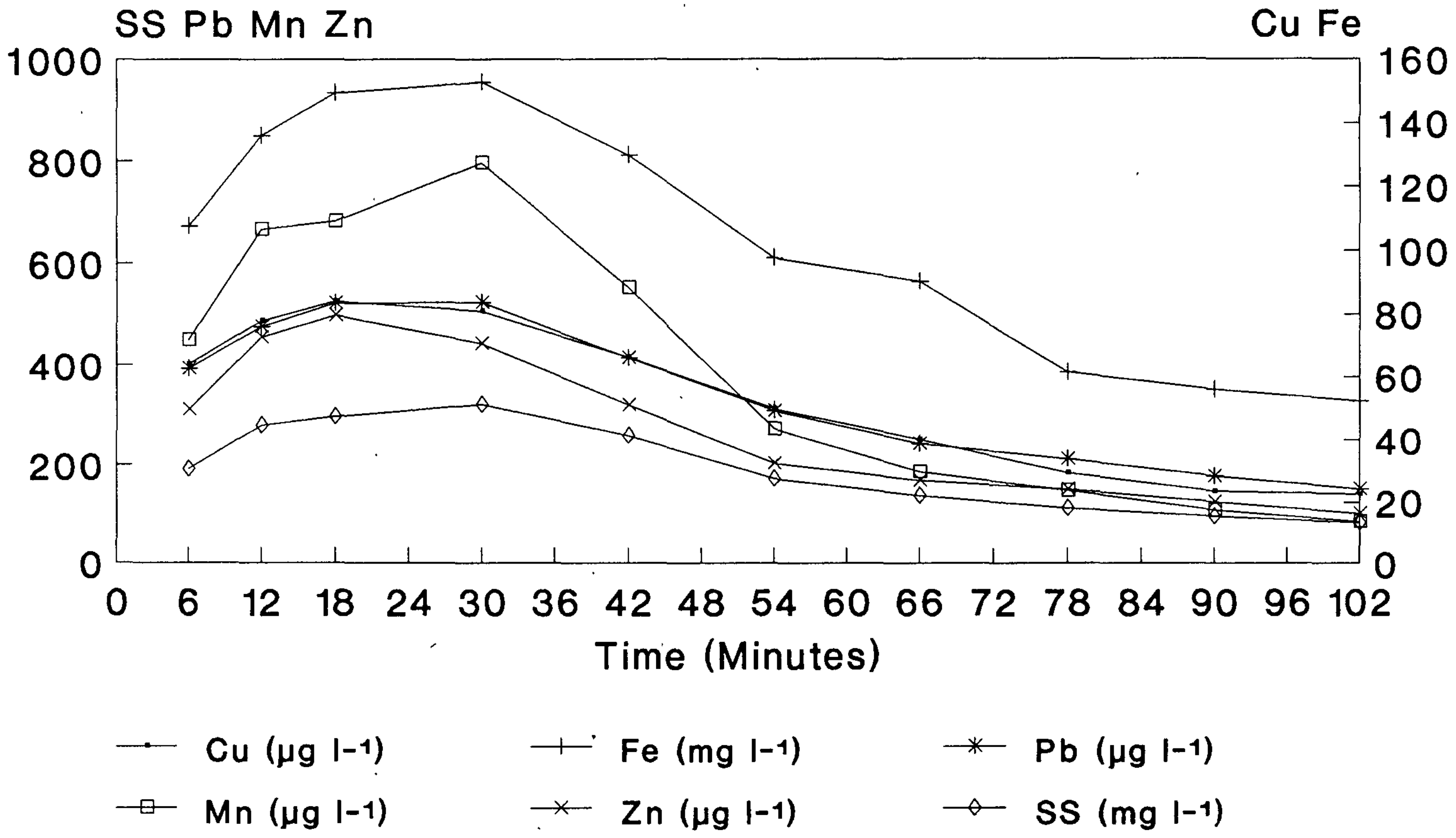


Figure 9.15 Variation of Suspended Sediment and Particulate Associated Metals over Time for Event F4.

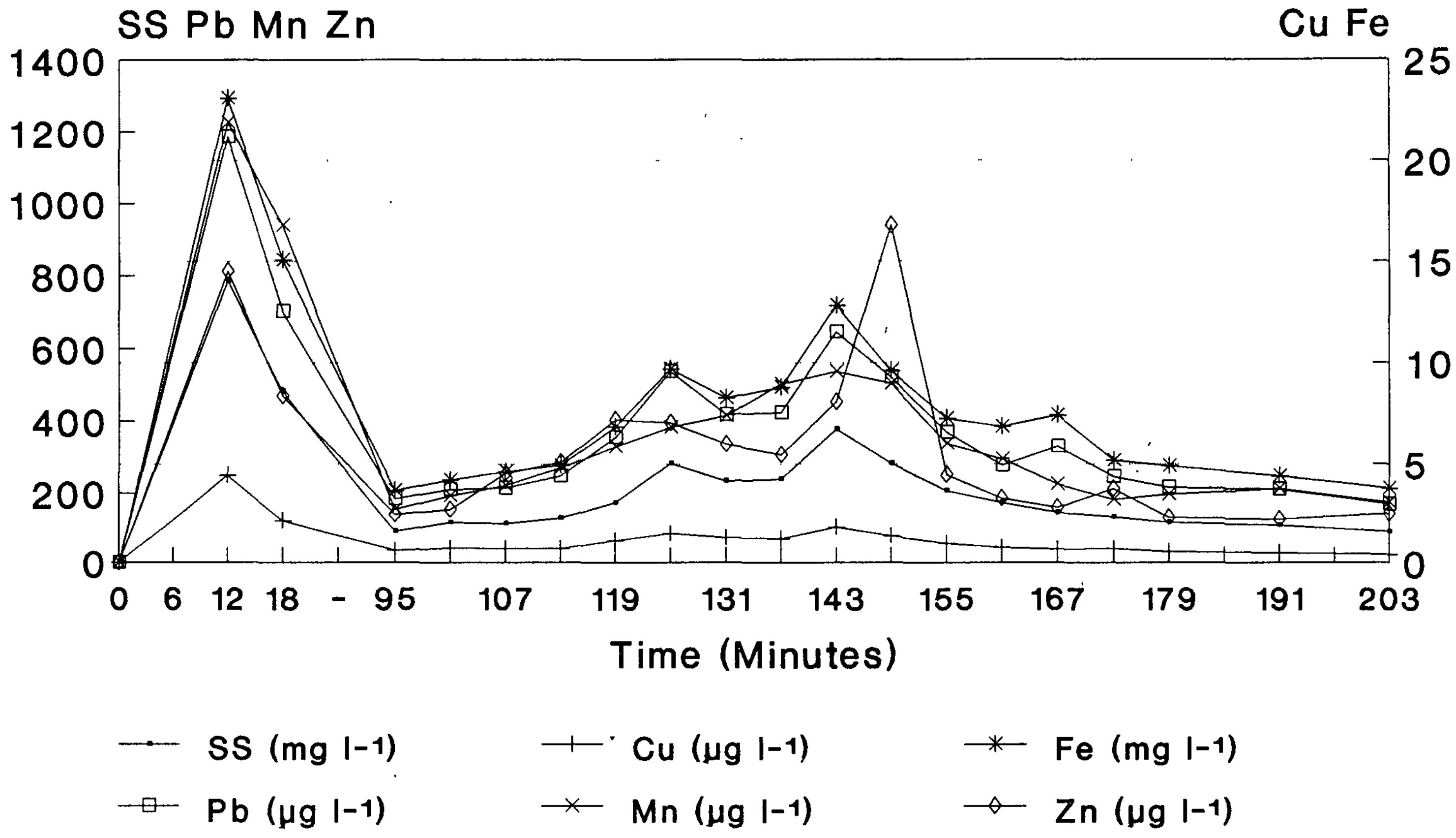


Figure 9.16 Variation of Suspended Sediment and Particulate Associated Metals over Time for Event F5.

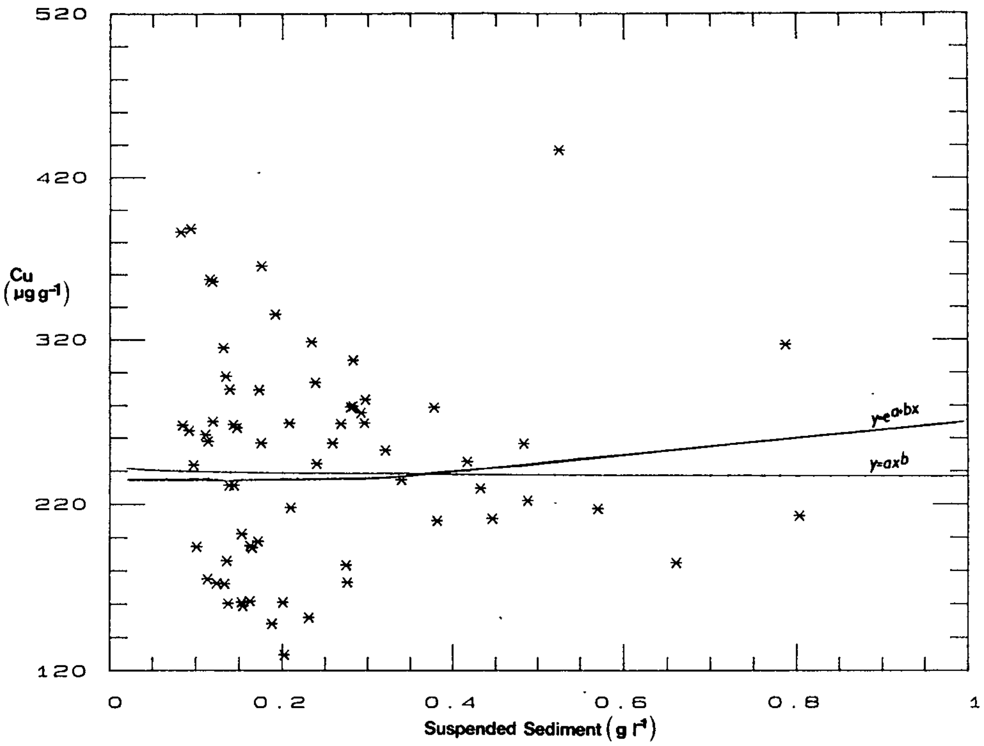


Figure 9.17 Stormwater Particulate Associated Cu Variation with Suspended Solid Concentration.

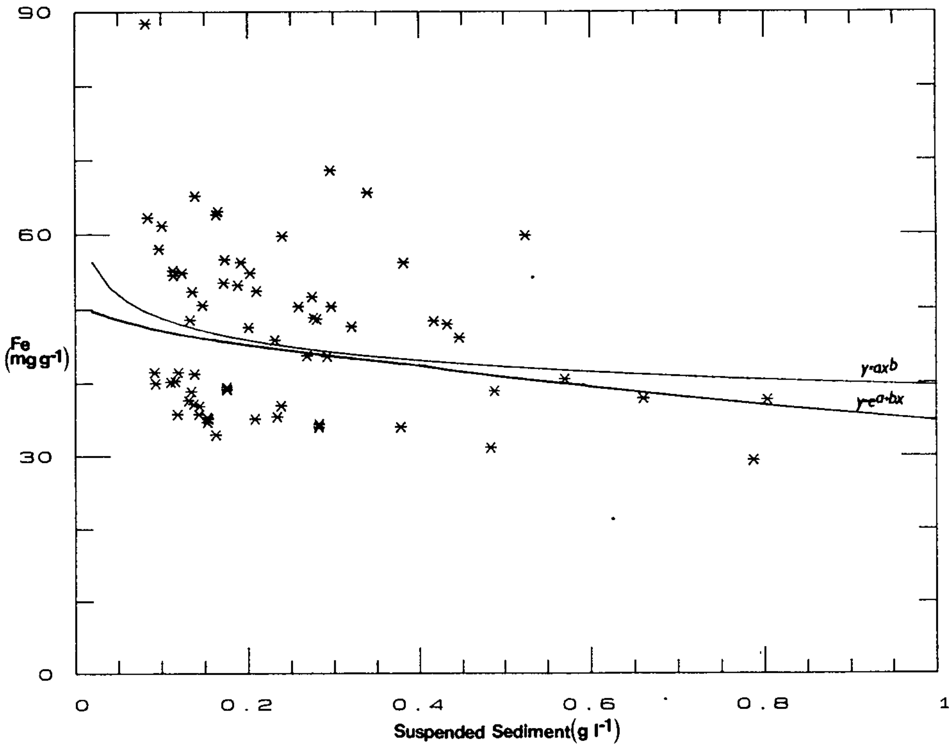


Figure 9.18 Stormwater Particulate Associated Fe Variation with Suspended Solid Concentration.

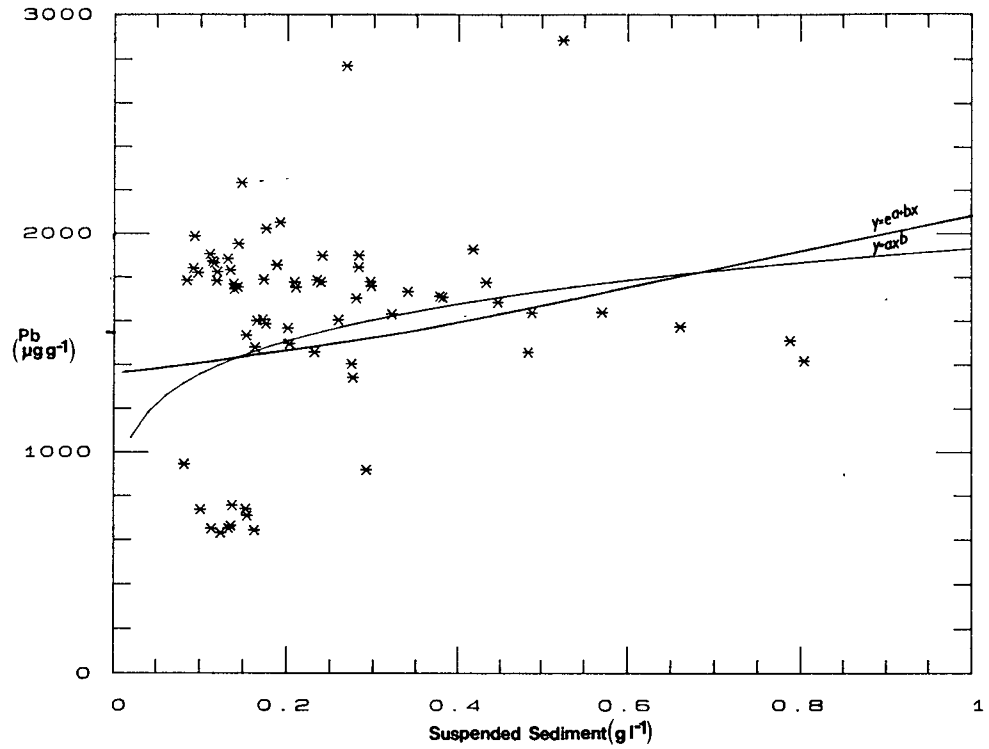


Figure 9.19 Stormwater Particulate Associated Pb Variation with Suspended Solid Concentration.

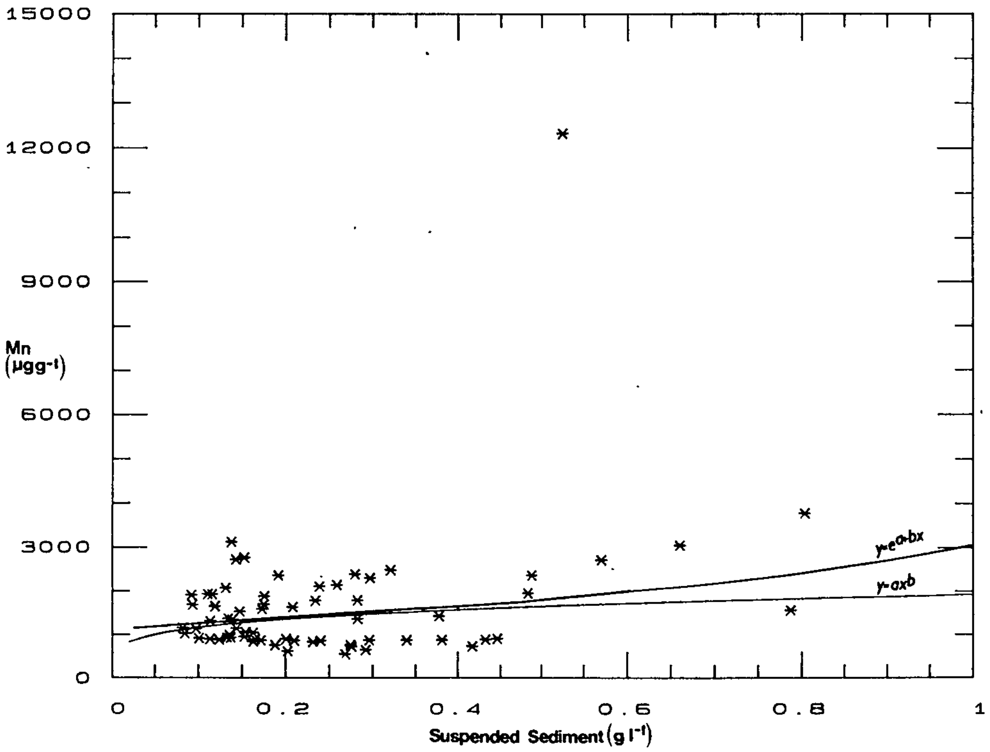


Figure 9.20 Stormwater Particulate Associated Mn Variation with Suspended Solid Concentration.

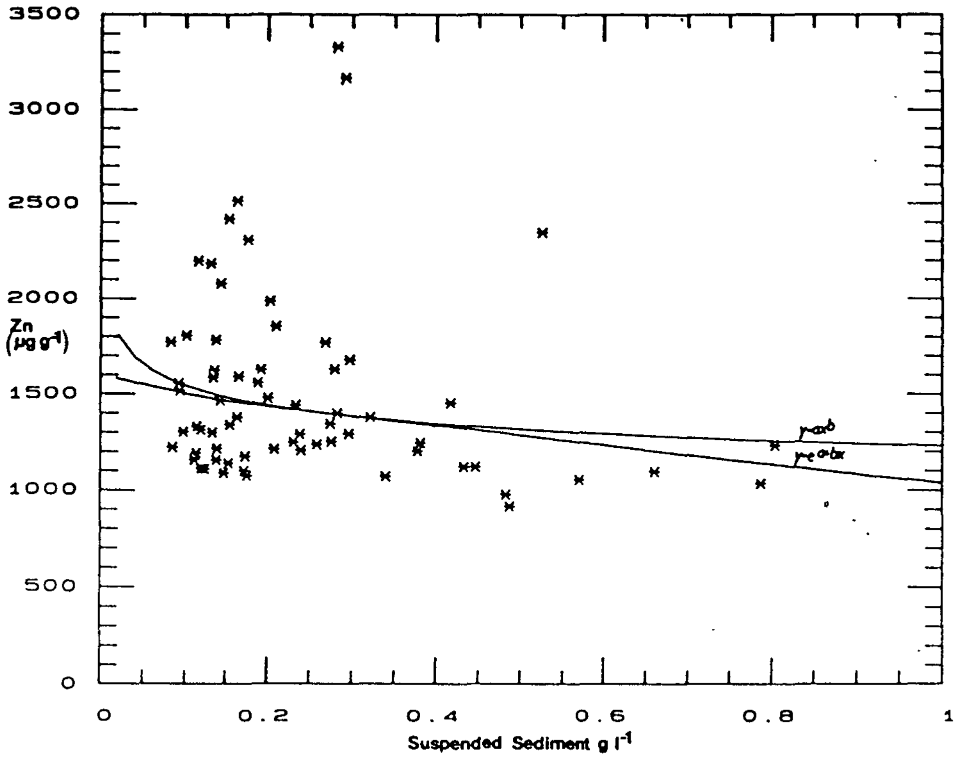


Figure 9.21 Stormwater Particulate Associated Zn Variation with Suspended Solid Concentration.

The regression equations for each model were calculated and it was found that any relationship between suspended sediment concentration and particulate associated metal was very weak. The maximum r^2 value for any equation was less than 0.1, and in the case of Pb and Mn an inverse relationship was observed indicating an increase of particulate associated metal with increasing suspended sediment concentrations (Figures 9.19 and 9.20). The approach of considering the particulate associated metal in stormwater to be mainly a function of physical sorting and surface reactions proposed by Morrison et al (1988) was based on observations on road runoff routed through a gully pot. It was suggested that where M_I values were negative or zero such as for Fe and Mn (Figures 9.19 and 9.20) then the sediment metal concentration dependence is solely ascribed to hydrodynamic sorting. In the case of the observations at the outfall to the South Oxhey catchment it would seem that the complex nature of the drain runs is liable to result in a well mixed suspended sediment. It is likely therefore that the relationship observed does reflect hydrodynamic sorting but not that of surface dusts. It is more likely to reflect the sorting of particulates by deposition and re-suspension within the sub-surface system which results in the poor relationships observed.

Metal concentrations and loadings both exhibit peak values in the first half of the storm events (Figures 9.12-9.16 and 9.22-9.26). Events F2 and F5 exhibit distinct 'first flush' phenomenon. In event F1, over 73% of the total metal loadings were discharged in the first half of the storm. Relating the metal loadings to percentage flow volume discharged indicates that while there is a positive tendency with greater percentage metal loadings discharged compared to flow volume in the first half of the storm (Figure 9.22), this is not truly a 'first flush'. In the case of the event, F2, the first 48 minutes accounted for approximately 30% of the heavy metal loading of the complete storm with greater than 63% of the total loading for the first phase being discharged only 24 minutes into the storm event. Figure 9.13 shows there is a secondary peak in concentrations at approximately 216 minutes after the start of the runoff event. There is a corresponding secondary peak in the loadings although it is not as accentuated (Figure 9.23). The storm event F3 shows least tendency to exhibit a 'first flush' or positive tendency (Figures 9.14 and 9.25). This could well be due to the brevity of the storm and the masking of variations due to sampling times which are relatively long in relation to the overall storm length. Event F4 exhibits a positive tendency towards flushing although it is not a true 'first flush'. Loadings increase gradually and peak approximately 30 minutes after the start of the storm; the flow exhibits a similar pattern. The event F5 occurred in two phases and the first of these (17 minutes duration) accounted for greater than 18% of the total heavy metal loadings; in the case of Cu it accounted for 27%. There was also a gradual increase and minor peaking of metals within the second phase of the event (Figure 9.16 and 9.26).

9.3.3 Magnetic Mineral Parameters of Stormwater Particulates Collected at the Main Catchment Outfall.

A summary of the mineral magnetic characteristics for stormwater particulates collected during the events F1, F2, F3, F4 and F5 is given

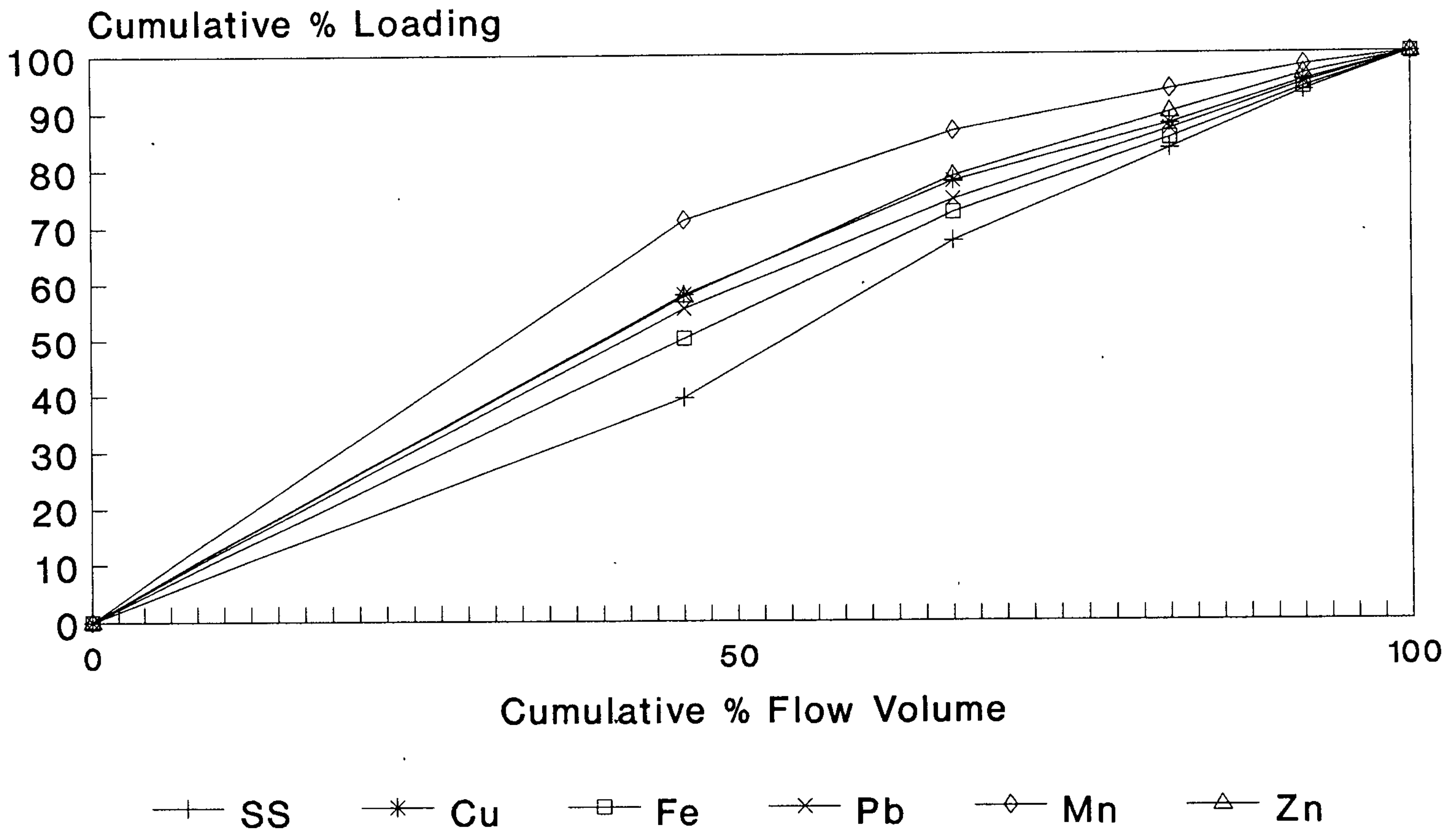


Figure 9.22 Cumulative Percentage Loadings of Flow Volume and Particulate Associated metals for Event F1.

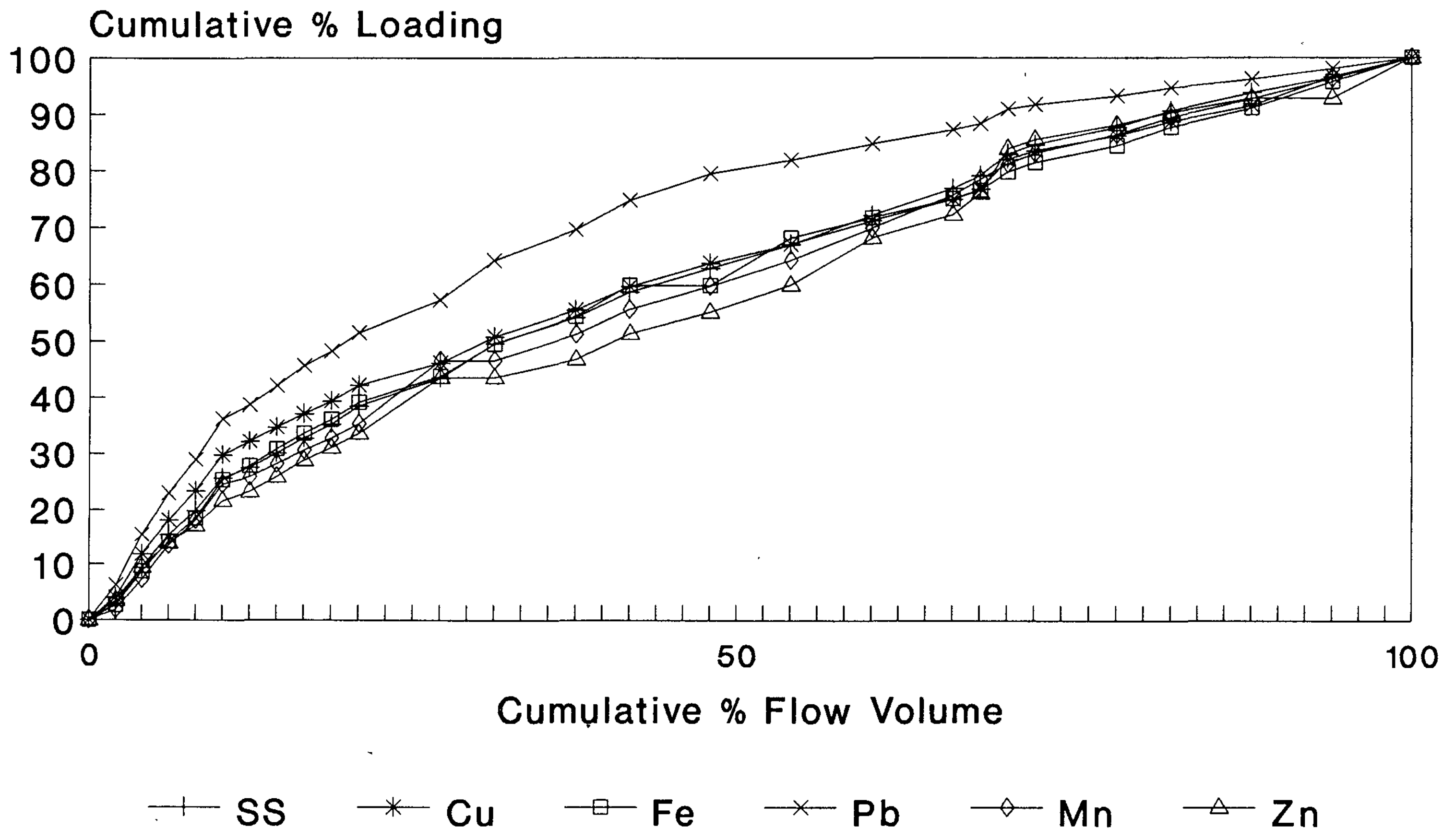


Figure 9.23 Cumulative Percentage Loadings of Flow Volume and Particulate Associated Metals for Event F2.

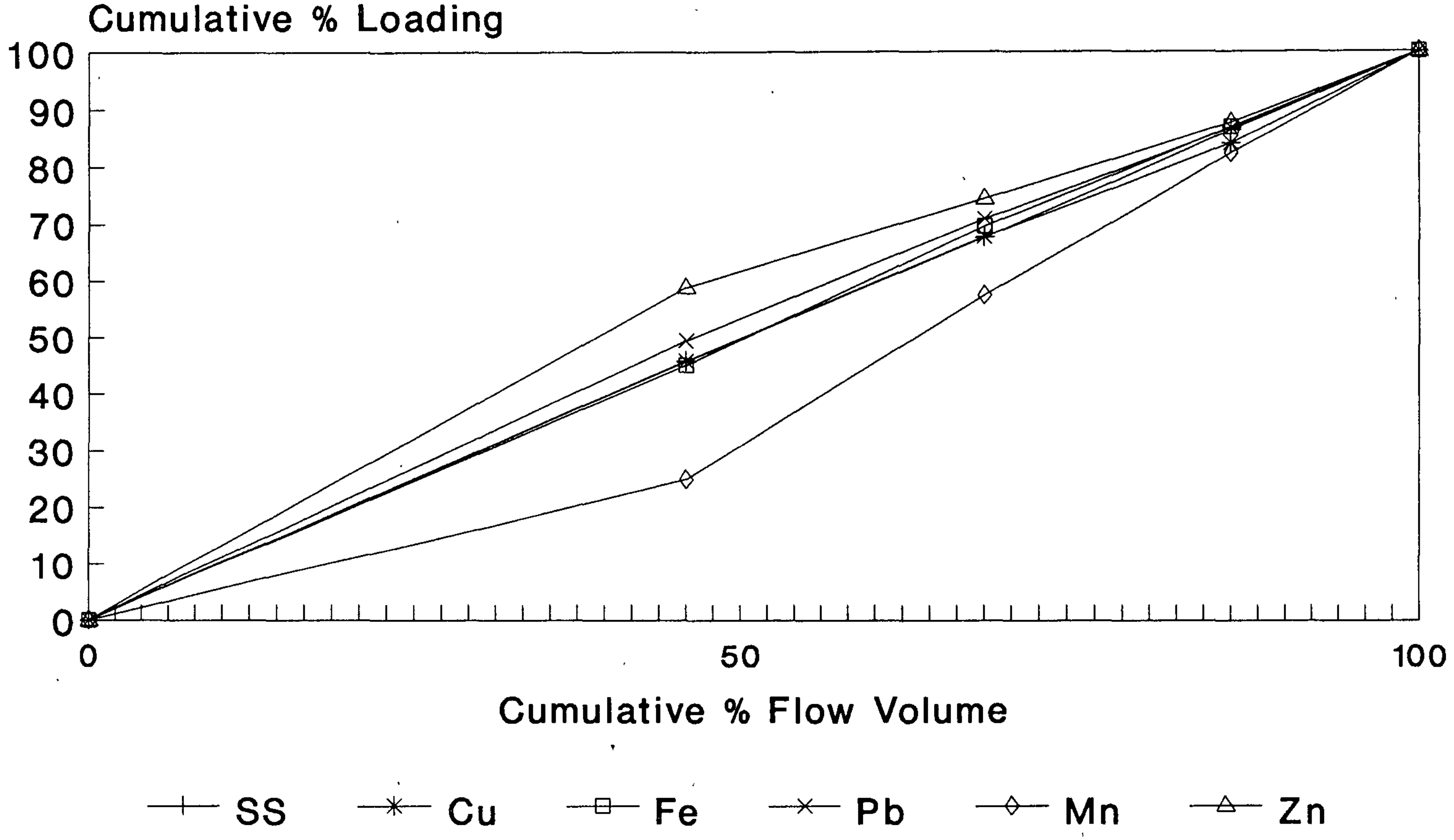


Figure 9.24 Cumulative Percentage Loadings of Flow Volume and Particulate Associated Metals for Event F3.

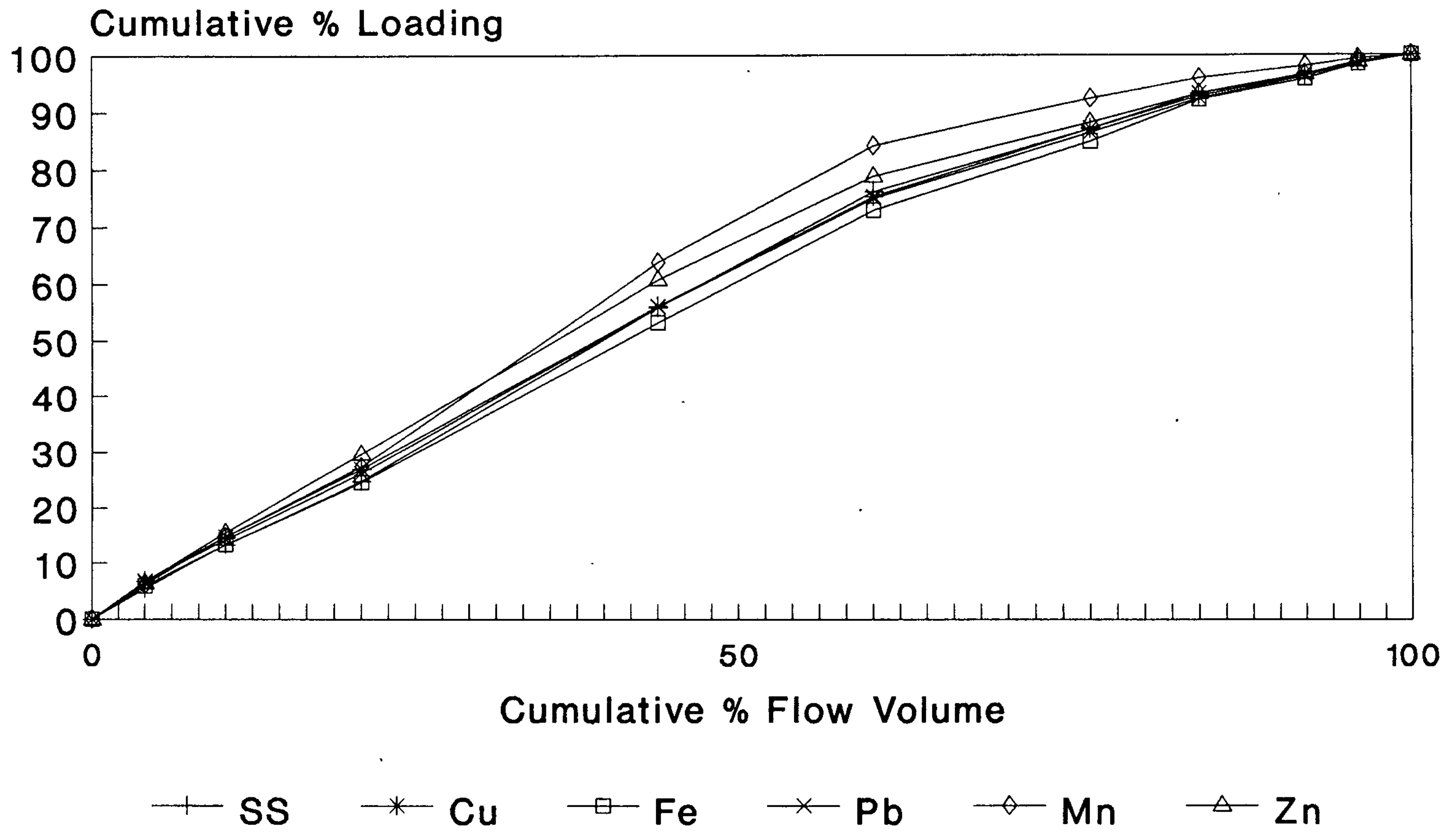


Figure 9.25 Cumulative Percentage Loadings of Flow Volume and Particulate Associated Metals for Event F4.

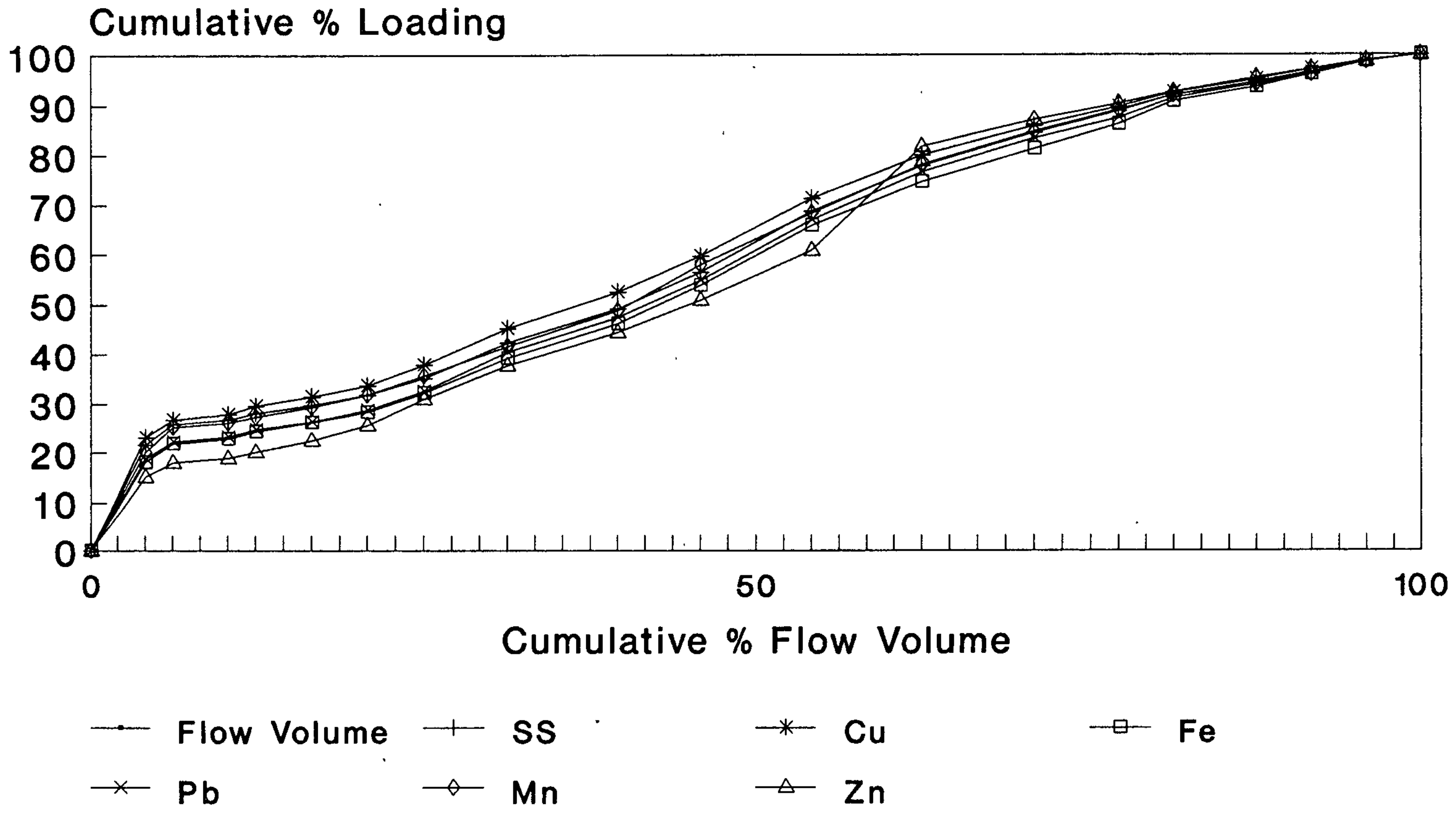


Figure 9.26 Cumulative Percentage Loadings of Flow Volume and Particulate Associated Metals for Event F5.

in Table 9.10. There is a greater similarity between storms than was found at Chilwell Gardens. The total range of values for IRM_{300mT}, IRM_{-20mT}/IRM_{300mT} and $-IRM_{-40mT}/IRM_{300mT}$ over all five events is less than the range of these parameters determined on stormwater particulates over all three storms sampled at Chilwell Gardens (Table 8.6 and 9.10). This confirms the view that the particulates in the runoff from the larger catchment are thoroughly mixed during transport through the sub-surface drainage sytem resulting in a semi-uniform stormwater suspended sediment.

Table 9.10 Mineral Magnetic Characteristics of Stormwater Particulates Collected at the Main Catchment Outfall.

	IRM_{300mT} (10^{-3} A m^2 kg^{-1})	IRM_{-20mT} $/IRM_{300mT}$	$-IRM_{-40mT}$ $/IRM_{300mT}$	IRM_{-20mT} $/-IRM_{-40mT}$
Storm F1	10.0-20.5 (12.9)	0.374-0.412 (0.386)	0.117-0.128 (0.122)	2.93-3.67 (3.23)
Storm F2	8.7-14.1 (10.8)	0.354-0.455 (0.397)	0.08-0.5 (0.154)	0.83-5.31 (3.38)
Storm F3	10.0-11.1 (10.6)	0.384-0.409 (0.395)	0.1-0.236 (0.144)	1.68-4.07 (3.05)
Storm F4	11.3-14.2 (12.6)	0.394-0.446 (0.406)	0.1-0.165 (0.116)	2.7-4.08 (3.58)
Storm F5	10.4-16.9 (14.3)	0.212-0.442 (0.397)	0.059-0.247 (0.115)	0.86-6.83 (3.98)

Mean values in parentheses

The similarity of the characterisation of all captured stormwater particulates for the parent catchment can be seen in Figures 9.27-9.31. The majority of samples are characterised by low IRM_{300mT} values and greater backfield ratio values, resulting in the samples being plotted in the rear right hand side of the tri-axial plots (Figures 9.27-9.31). Comparison to the source sediment characterisation (Figure 9.11) indicate the samples as belonging to the roof grouping. although the IRM_{-40mT}/IRM_{300mT} values do seem to be slightly higher than the majority

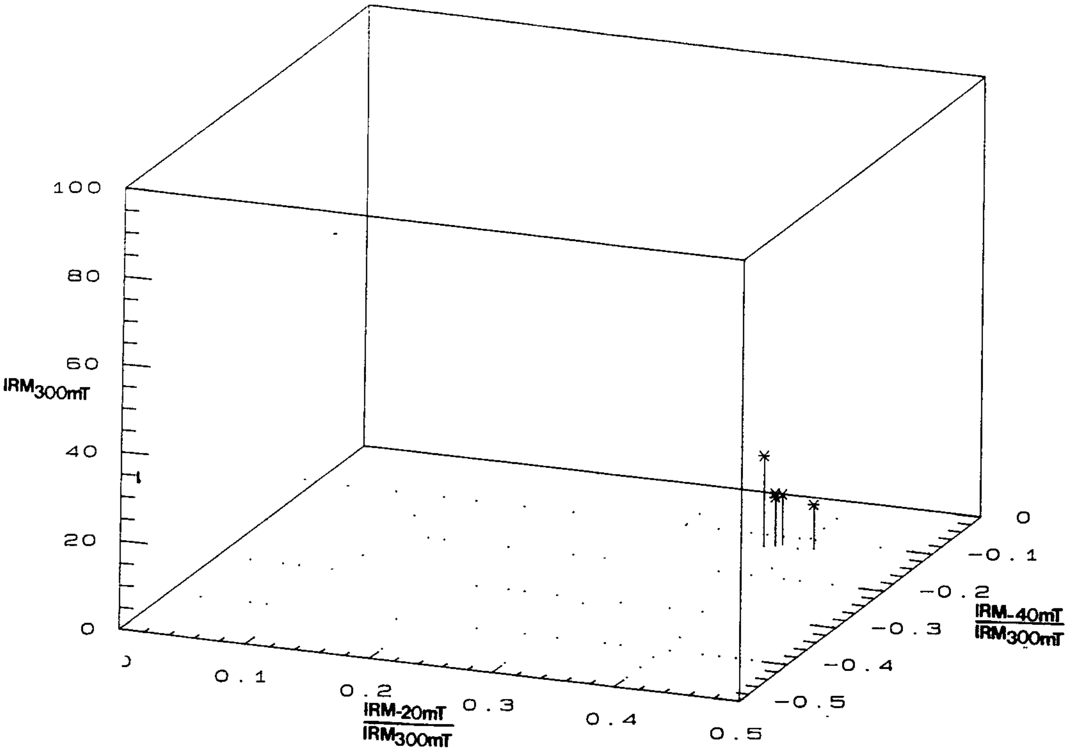


Figure 9.27 Tri-Axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event F1.

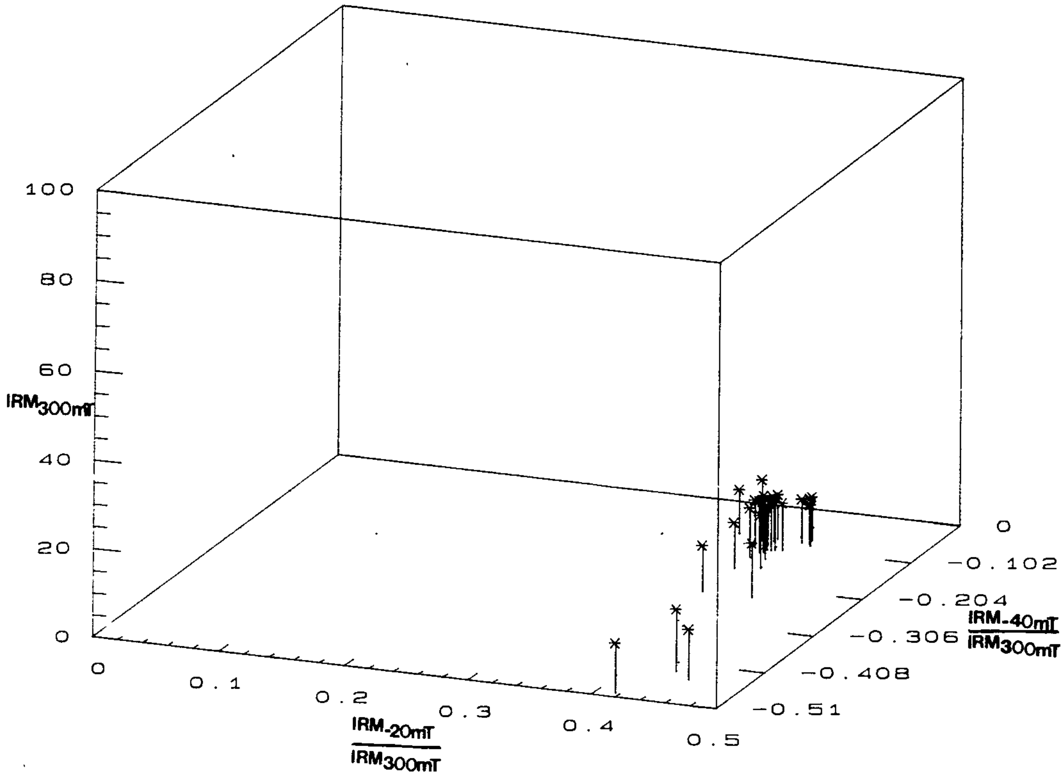


Figure 9.28 Tri-Axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event F2.

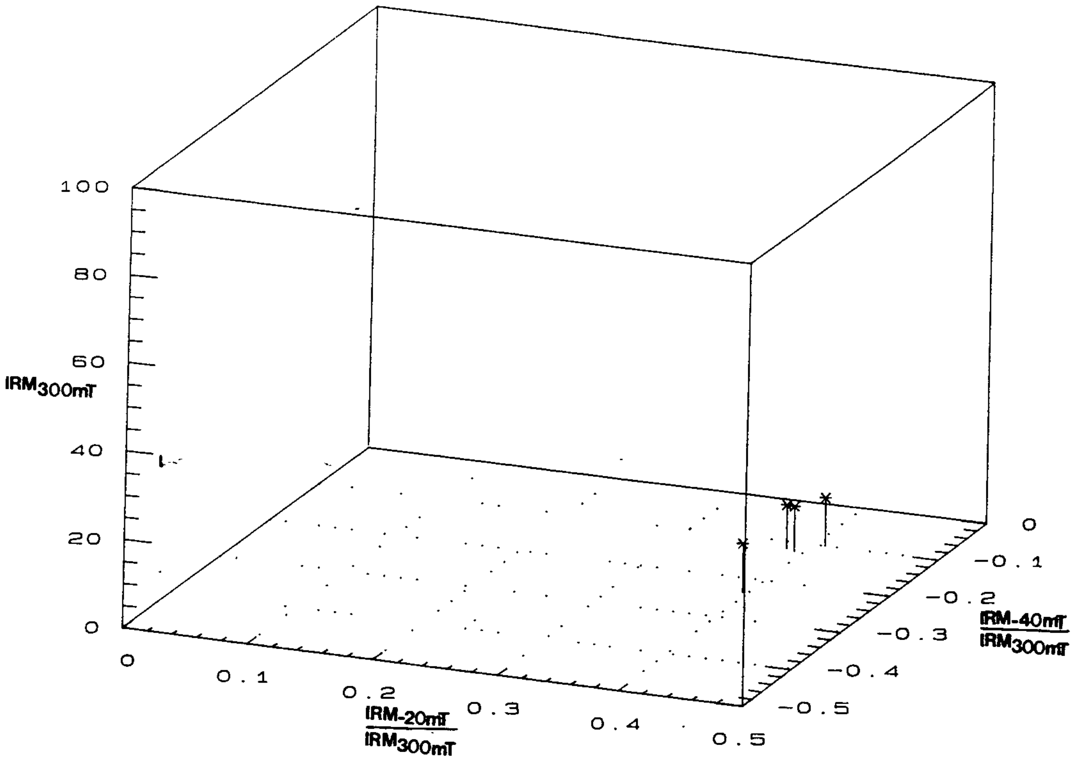


Figure 9.29 Tri-Axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event F3.

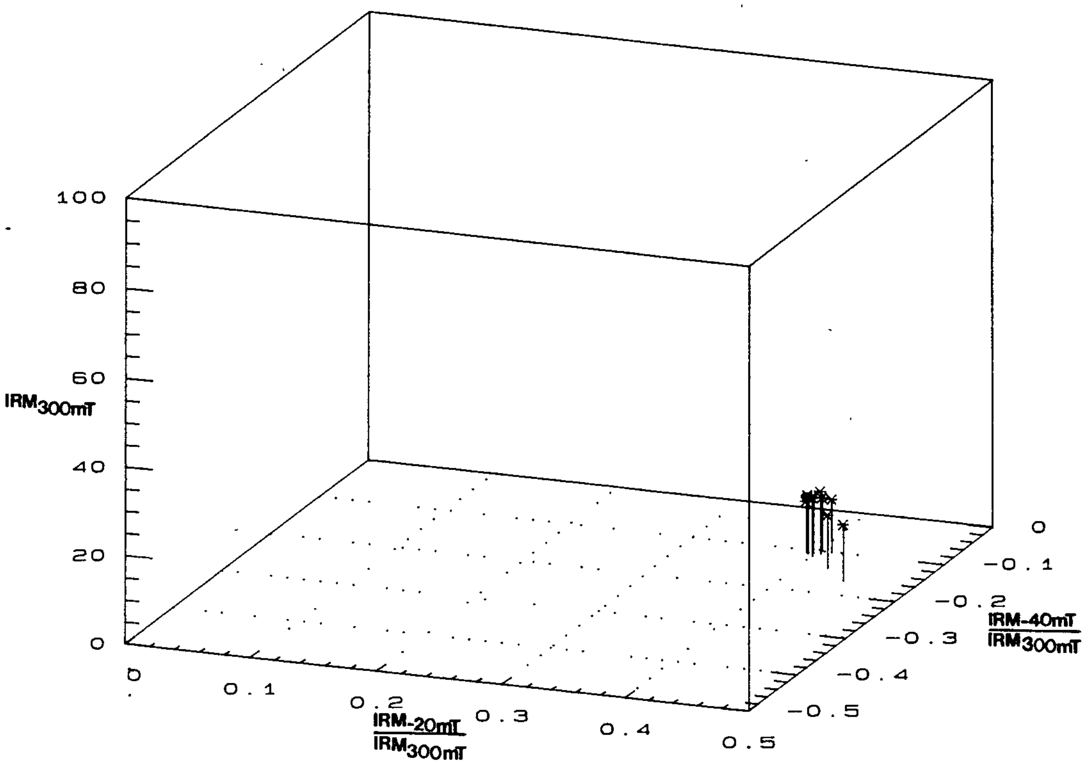


Figure 9.30 Tri-Axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event F4.

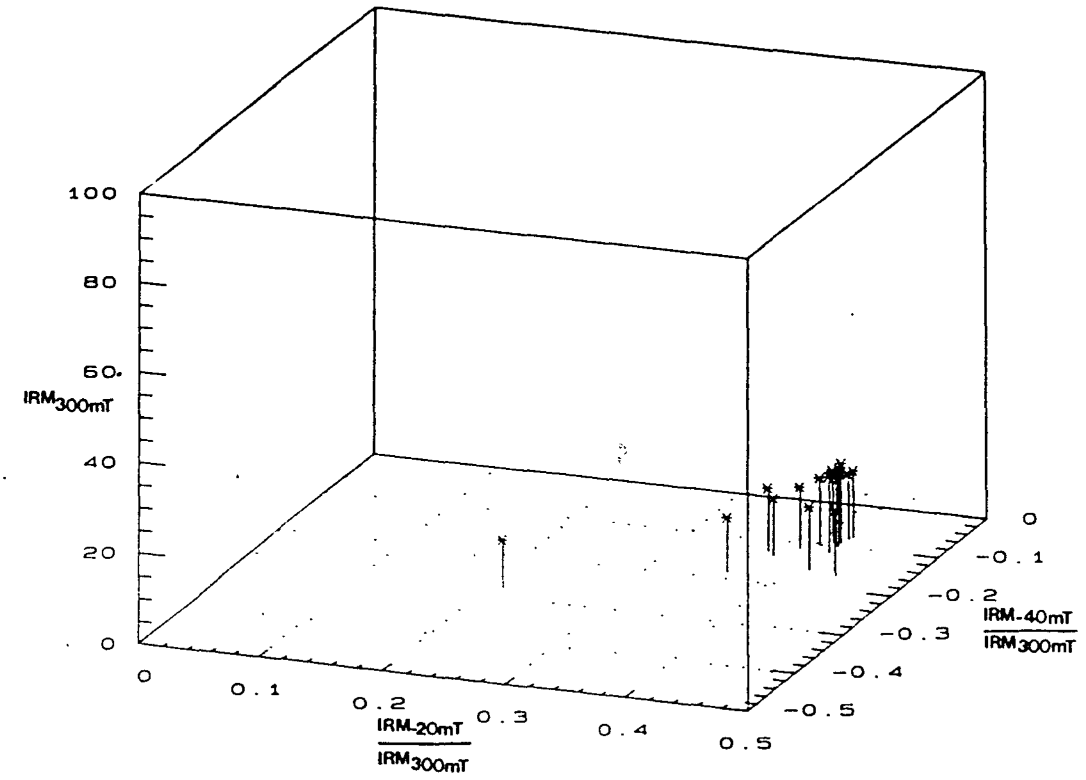


Figure 9.31 Tri-axial Plot of Mineral Magnetic Characteristics for Stormwater Particulates of Event F5.

of stormwater samples sampled at the sub-catchment.

Occasional aberrant samples with considerably lower $\mathrm{IRM}_{-40mT}/\mathrm{IRM}^{300mT}$ values were observed (Figure 9.28). These occurred at 86 minutes, 210 minutes and 264 minutes into storm event F2. Further anomalous samples were observed in the initial stages of event F3 and the second phase of event F5. In the former case this was again due to a low $\mathrm{IRM}_{-40mT}/\mathrm{IRM}_{300mT}$ value, whereas for storm F5 the outlier occurs as a result of a lower $\mathrm{IRM}_{-20mT}/\mathrm{IRM}_{300mT}$ ratio. These anomolous samples were all more magnetitic in character, that is more easily magnetised or "minerally magnetically softer". This would appear to indicate that at the times when these samples were taken the highway associated surface sources were dominating, or were making more significant contributions to the sediment supply. Owing to the fact that these incidents were rare, it is thought that these samples represent shock loadings from paved surfaces that may reflect sudden scouring by an increase in flow after sufficient rain has fully wetted surfaces. This may explain the sample collected at the start of event F3 and at the start of the second phase of the event F5. Storms F5 and C1 (Section 8.4) result from the same rainfall event and the sample at the start of the second phase of F5 mirrors the sample observed at the start of the second phase of C1 observed in the sub-catchment (Figure 8.13;Section 8.4). In contrast to storms F3 and F5 not all the anomolous samples collected during F2 occur with increases in flow. Those anomolous samples that do not occur with increases in flow may be due to the scouring and breaking up of in-pipe sediment deposits.

9.3.4 Statistical Analysis of the Magnetic Mineral Parameters of Stormwater Particulates Collected at the Main Catchment Outfall.

In order to verify the subjective observations described in the previous Section the equations Eq9.1, Eq9.2 and Eq9.3 were applied to the results of the mineral magnetic analysis of the stormwater particulates. All samples were classified with the soil grouping, with the exception of the first sample of the second phase of event F5. This singular sample was classifed with highway associated particulates. Owing to the large overlap between the soil and roof grouping in the derivation of the equations, it is not thought that this can be taken as an indication that the stormwater particulates are derived from stormwater washoff of soil particulates.

These results would indicate that application of mineral magnetic parameters to characterise stormwater particulates and the subsequent use of that characterisation to trace the source of the particulates, is not highly effective in large complex catchments. The source sediments would appear to mix within the drainage system or alternatively soil/atmospheric inputs may dominate stormwater particulates. The result is that all stormwater particulates have magnetic characteristics of soil/atmospheric particulates. The one exception is likely to have occurred as a result of a short rainfall event followed by a second longer event possessing an intense rainfall. The onset of the second phase when highway surfaces were wet and infiltration was near to capacity could possibly have resulted in high energy scouring of the highway surface particulates. Alternatively the first phase may have stirred up sediments in the gully pots and increased their suspended sediment load which was forcibly discharged into the sewer pipe at the onset of the second phase of the storm.

It is unreasonable to assume that this was the only time when highway associated sediments contributed to stormwater particulates. Their contribution at other times in this and other storm events is masked. A similar exercise to compare loadings of stormwater particulates and pollutants in terms of their sources by mineral magnetic characteristics was therefore not carried out.

Previous use of mineral magnetic parameters to aid identification of source types in urban catchments was restricted to taking high SIRM values as indications of scouring and transport of toxic particulates from the street surface (Revitt et al, 1982). Using this approach the sample identifed as being derived from highway associated sediments would be incorrectly classified as it has an IRM_{300mT} value below the average for the storm event. Consideration of only IRM_{300mT} values would also result in a larger number of samples characterised as derived from highway associated sediments which isnot the conclusion when the complete mineral magnetic character of the suspended particulates is taken into account. While a simple interpretation based on IRM_{300mT} could be effective for a small sub-catchment (Section 8.4.2) it seems that conclusions based on such an interpretation for more complex catchments may be misleading unless concentration independent characteristics are considered.

9.3.5 Relationship Between Heavy Metal Levels and Mineral Magnetic Parameters in Stormwater Particulates Collected at the Main Catchment Outfall.

The relationship between heavy metal concentrations ($\mu g\ l^{-1}$) and IRM_{300mT} values expressed in terms of volume, (10^{-3} * A m^{2} l^{-1}) is very good with correlation coefficients generally greater than 0.9, and well within the 95% confidence limits as derived from calculation of the "t" statistic for all storms except F3. Poor correlations were seen for F3 with none being within the confidence limits. In a similar manner to the inter-metal correlations, metal-IRM_{300mT} correlations is a function of suspended sediment concentration. The sediment related IRM_{300mT} concentrations (10^{-3} A m^{2} kg^{-1} do not exhibit similar consistently strong correlations with metals. There is a strong relationship, however, between IRM_{300mT} and the all metals for F1, between IRM_{300mT} and only Pb for F2, between IRM_{300mT} and Mn and Zn for F4 and finally between IRM_{300mT} and Cu, Fe and Pb for F5. This suggests that any relationship between metals and IRM_{300mT} (expressed in terms of weight) is not robust and is likely to be modified by transport of particulates through the drainage system. This may result from the changes of metal concentration on particulates due to solubilisation or adsorption during transport.

The concentrations of magnetic minerals therefore appear to vary in a similar manner to those of particulate associated heavy metals in stormwater. The correlations of IRM_{300mT} and heavy metals in paved surface sediments were limited to Cu, Fe, Pb and Zn with Mn not exhibiting a consistent strong linear relationship. It would, therefore, seem likely that the cause of the strong linear relationship in stormwater particulates is not derivation from a similar source. A probable cause of these apparent metal-metal and metal-IRM_{300mT} relationships is the controlling factors with respect to distribution of particulate associated metals and IRM_{300mT} in stormwater such as flow or suspended solid concentration, but particularly the latter.

Investigation of the application of mineral magnetic parameters to the tracing of pollutants through the drainage system of the main catchment has been shown to have severe limitations. Mineral magnetic methods can be used to highlight the shock loadings of sediment from highway associated surfaces. In a complex catchment, however, this is only valid in extreme cases and generally the amalgamated samples will bear the characteristics of the dominant sediment supply which apppears to be atmospheric and soil derived in origin. The application of mineral magnetic parameters to characterise stormwater sediments captured at a sub-catchment and at the outfall of the parent catchment does give firm indications in terms of both range of magnetic mineral concentration dependent parameters and characteristic backfields that thorough mixing of source sediments occurs within the sub-surface drainage system. It is likely, therefore, that with increasing size and complexity of drainage systems the sequencing of pollutant sources becomes less discrete and less significant in determining the quality at the outfall.

CHAPTER 10 CONCLUSIONS.

10.1 Summary of Major Findings.

a) A review of the relevant literature indicates that in a non-industrialised urban catchment heavy metals are contributed to the aqueous environment by atmospheric, domestic and vehicular sources. The metals are transported through a series of environmental compartments, leaving the urban catchment by a combination of re-suspension, cleaning practices and runoff/washoff processes.

b) Previous applications of mineral magnetic parameters indicate that providing there is a significant contrast between source sediments or particulates, mineral magnetic parameters can be used to type and trace sediments in atmospheric, marine, estuarine, fluvial and soil particulates or sediments.

c) A suitable sampling and analysis scheme of source sediments in a non-industrialised suburban catchment has been designed. This scheme included trials on the acid digestion method resulting in the use of HNO_3:$HClO_4$ and separation of sediment residue from digestate by centrifuge techniques for analysis of source sediments.

d) The variations of heavy metals across the highway associated surfaces of a small suburban sub-catchment have been established. The concentrations of Cu, Fe, Pb and Zn generally increase with proximity to the road centre. Cadmium and Mn exhibit a tendency to decrease with proximity to the road centre. Seasonal variations were also noted with Cu, Fe, Pb, Mn and Zn concentrations generally greater in the summer than the winter months. Cadmium did not exhibit such seasonal distributions.

e) Concentrations of Cu, Pb, and Zn in roof sediments were less than those of the road centre sediments, although similar to pavement or road gutter sediments. Cadmium concentrations were similar to those of pavement sediments while Mn concentrations exhibited greatest similarity to road centre sediment concentration levels. Iron concentrations refect the roofing construction materials and were elevated compared to highway associated sediment concentrations.

f) The heavy metal concentrations in sub-surface sediments tend to reflect the immediate source sediments, with the possible exception of Cd which exhibited unusually high concentrations in sub-surface sediments.

g) Heavy metal loadings in highway associated sediments and roof gutter sediments were dominated by the sediment loadings, with maximum loadings of highway associated sediments occurring in the summer months.

h) Magnetic mineral concentration related parameters, such as χ and IRM_{300mT}, exhibit similar spatial and seasonal variations to the metals Cu, Fe, Pb and Zn.

i) Mineral magnetic characterisation of the sediments was achieved with almost complete discrimination being achieved between highway associated sediments and roof sediments. Statistical analysis allowed the derivation of discrimnatory equations based on mineral magnetic parameters to type unknown sediments. Use of these equations indicated that generally gully pots were assigned to the highway associated sediment grouping while in-pipe deposits in the roof drain were assigned to the roof grouping. The in-pipe deposits below the confluence of the sewer drainage system of the highway and roof areas were categorised with the highway associated sediment grouping with the exception of one sample and this was shown to be close to the discriminating plane of the two sediment types.

j) Strong linear relationships between the metals, Cu, Fe, Pb and Zn, and magnetic mineral concentration related parameters, χ and IRM_{300mT}, are observed and these relationships are generally stronger when solely highway associated sediments are considered.

k) Variations in heavy metals with particle size were investigated. The metal concentrations generally increased with decreasing particle size. Differences in the distribution of metals with particle size were concluded to result from preferential removal of fine particulates from the road centre to the road gutter, possibly in combination with solubilisation processes which leach surface adsorbed metals. The spatial variations were similar to those of the bulk sediments. Sediment mass is the dominant control on metal loadings.

l) Magnetic mineral concentration related parameters did not increase with decreasing particle size, although they did vary with spatial location in a similar manner to Cu, Fe, Pb and Zn. The overall discrimination based on fractionated sediments was found to be poorer than that based on bulk sediments. Improved discrimination was achieved by consideration of the fractionated road centre and roof sediments only.

m) Investigation of potential sources of metals and magnetic minerals was carried out. Metallic and magnetic mineral parameters indicate that vehicle derived particulates and atmospheric particulates are likely to be the dominant source particulates, with a possible minor contribution from soils.

n) Stormwater particulate associated metal concentrations and loadings at the sub-catchment were found to be similar to other studies carried out on small non-industrial residential catchments. Concentrations and loadings exhibit positive 'flushing' behaviour. There is some indication that the distribution of particulate associated metal ($\mu g\ g^{-1}$) with suspended solids concentration ($mg\ l^{-1}$) results from a combination of physical sorting and surface reactions. The concentration at which the dominant process changes is linked to the experimentally determined solubility of metals in stormwater and street sediment particulates. The overall dominant parameter controlling particulate associated metal concentrations in stormwater is the suspended solid concentration and this is indicated by strong correlations between particulate associated metals ($\mu g\ l^{-1}$) and suspended solids ($mg\ l^{-1}$).

o) The variation of mineral magnetic parameters in stormwater particulates can be used to categorise the dominant souce of particulates at the time of sampling. Sediments from the roof grouping appear to be the overall dominant source. This is thought to be an indication of the importance of atmospheric deposition on stormwater quality. The importance of the source characterisation of the initial phase of storm events in establishing the dominant sediment source for the whole event was noted. Estimations of sediment and particulate supply emphasise the importance of the influence of atmospheric particulates and scour of in-pipe deposits on ultimate stormwater quality.

p) The investigation was widened to include the main parent catchment. Similar relationships between metal concentrations, loadings and magnetic mineral parameters to those seen in the sub-catchment were observed.

q) Discriminant equations based on highway associated sediments, roof sediments and soils were derived from the results of analysis of the samples. Good discrimination between highway associated sediments and both of the other two groupings was achieved. However, there was a large overlap between roof and soil groupings. Discrimination of soil sediments from roof sediments by mineral magnetic parameters was not possible.

r) Stormwater particulate associated metal concentrations were generally greater than those of the sub-catchment with a lesser range of values. This was concluded to result from thorough mixing of source sediments in the sub-surface drainage system.

s) Mineral magnetic characterisation of stormwater particulates by statistical methods indicated that all samples were categorised with the soil grouping with the exception of one sample. This one sample is thought to represent a shock loading of highway associated sediments, possibly already present in the drainage system as gully pot sediments or in-pipe deposits, from the fully saturated catchment. The thorough mixing of sediment prior to being discharged at the outfall limits the ability of the mineral magnetic methodology to characterise the stormwater particulates. The results suggest, however, that it is likely soil and/or atmospheric/roof particulates make a major contribution to stormwater particulates discharged at a non-industrialised suburban catchment.

10.2 Implications for Future Use of Mineral Magnetic Parameters in Source Sediment Typing and Tracing and as a Reconnaissance Method for Heavy Metals.

The most important implication of the research findings is that mineral magnetic techniques exhibit a high potential as rapid, non-destructive and economic reconnaissance techniques for the evaluation of heavy metals on highway and associated impermeable surfaces. The strong correlation between magnetic mineral concentration related parameters and metal concnetrations has been found for samples taken from a number of road types with Cu and Pb tending to exhibit the strongest relationships.

In extending the use of mineral magnetic techniques to tracing and typing particulates in the sub-surface system it was found that the methodology had limitations. Heavy metals and mineral magnetic parameters are subjected to different reactions in an aqueous environment. Heavy metals are adsorbed onto the surface of particulates,and are solubilised at varying rates dependent on reactions with humic acids and other complexing agents. Mineral magnetic parameters reflect the inherent nature of the mineralogy of the particulate and not its surface chemistry. As a result the non-conservative changes in heavy metals are not paralleled by mineral magnetic parameters and as a result the relationship between mineral magnetic parameters and heavy metals is weakened in the aqueous environment. The degree to which the relationship is weakened will depend on the reactivity of the surface adsorbed metals and the chemical characteristics of the runoff in which the particulates are suspended.

The initial studies in a small, well defined catchment indicate that mineral magnetic parameters can be used to successfully type sediment sources in such an environment. The results of the investigations at the outfall of the larger parent catchment however, indicate that thorough mixing of suspended sediments takes place during transport of particulates through the drainage system. This is thought to result from the sequential contributions of a large number of sub-catchments at differing intervals throughout the storm. Even at the parent catchment outfall shock loadings of particulates characterised with highway associated surface particulates can be identified as occuring, probably related to immediate runoff from fully wetted surfaces.

Despite these limitations there is definite scope for the use of mineral magnetic techniques in urban hydrology to further the understanding of sequencing of sediment supply from a variety of source sediments.

10.3 Recommendations for Further Work.

Given the positive indications of a strong linear relationship between magnetic mineral concentration related parameters and a variety of metals, further investigation of the application of mineral magnetic techniques on the evaluation of heavy metals for a variety of road types and surfaces is recommended. This work has already been initiated and the preliminary results concur with the results of this study (Beckwith et al, *in prep*).

This research was carried out with the intention of aiding the understanding of the routing of heavy metals and sediments through a residential catchment. The use of mineral magnetic parameters has given such indications in terms of dominance of sources and the sequencing of sources during storm events. There are many further areas of trace investigation of sediment sources in urban catchments however, that can be carried out. These include the addition of manufactured magnetic particulates and the artificial enhancement of naturally occurring sediments. The man-made particulates would result in a tracer of uniform characteristics whereas the enhanced source sediments will be characteristic of the sediments available for transport. The type of tracer used will depend upon the investigation to be carried out. Tracing by these methods could be compared with the use of coloured sand as a cross-check of the methodology.

Initial magnetic typing of source sediments has been carried out in this study but there is scope for distinguishing source sediments by further analysis. This includes defining the mean Curie point of sediment source types, and by such means definitively identifying the magnetic minerals present in the particulates. Other aspects of typing sampled stormwater particulates that could be applied in future studies would be to compare collected samples to artificial samples formed as a result of mixing quantities of source sediments. By such means a semi-quantitive methodology can be formed to estimate the relative contributions from each source (Oldfield et al, 1979).

The investigation carried out in the Chilwell Gardens sub-catchment indicated that sediment supply was theoretically dominated in terms of overall mass by atmospheric deposition, although the magnetic mineral signatures of source sediments were dominated by vehicular derived particulates. The investigation of sequencing of suspended solids in solely highway runoff may provide useful information on the contribution of atmospheric deposition to metal levels in highway runoff. Additionally, this research has highlighted the contribution of roof runoff to pollutant levels in stormwater. Roof runoff should be included as an important source of metals in any future study of metals in the urban environment.

The quantity of lead added to petrol has been reduced and lead free petrol is now available. However, with increasing traffic there is still a considerable quantity of lead emitted to the environment by automobiles. In addition large quantities of other metals, such as Zn from tyre wear, are produced. Accordingly the rates of production, the transport and transformation, and the total environmental impact of vehicle derived particulates, including brake particulates and the products of attrition of engine and exhausts, requires further investigation..

As a result of samples investigated in this study it would appear there is a potential for the use of mineral magnetic parameters in identifying the sources of polluting particulates in inner cities and discriminating between particulates derived from petrol-engines, diesels and industrial emissions. Continuing political pressure is being applied to produce cleaner inner city environments and mineral magnetic techniques may be useful in establishing the main cause of building soiling and pollutant accumulation.

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APPENDIX A.

The following co-authored papers were published in advance of the thesis based in total or in part on data derived from the research project:

A2-A10 Beckwith, P R., Ellis, J.B., Revitt, D.M. and Oldfield, F. (1984a) Identification of pollution sources in urban drainage systems using magnetic methods. In: Balmer, P., Malmqvist, P.A. and Sjoberg, A. (Edits) Proc. 3rd Int. Conf. Urban Storm Drainage, Vol. 4, Göteborg, Sweden, June 4-8, 1984, Chalmers University of Technology, pp. 1313-1322.

A11-A16 Beckwith, P R., Warren, R.S. and Harrop, D.O (1984b) The behaviour of sediment associated heavy metals within an urban surface runoff drainage system. In: Proc. Int. Conf. Environmental Contamination, London, 1984. CEP Consultants, Edinburgh, pp. 785-790.

A17-A19 Beckwith, P R., Ellis, J.B. and Revitt, D.M. (1985) Particle size distribution of Cu, Pb and Zn across a road surface. In: Proc. Int. Conf. Heavy Metals in the Environment, Athens, 1985. CEP Consultants, Edinburgh, pp. 174-176

A20-A28 Beckwith, P R., Ellis, J.B., Revitt, D.M. and Oldfield, F. (1986a) Heavy metal and magnetic relationships for urban source sediments. Physics of Earth & Planetary Interiors, 42, pp. 67-75.

A29-A39 Ellis, J.B., Revitt, D.M., Harrop, D.O. and Beckwith, P.R. (1987) The contribution of highway surfaces to urban stormwater sediments and metal loadings. Sci. Tot. Environ., 59, pp. 339-349.

IDENTIFICATION OF POLLUTION SOURCES IN URBAN DRAINAGE SYSTEMS USING MAGNETIC METHODS

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ABSTRACT

Magnetic methods have been used recently as a tracer technique for sediment sources. This paper examines the feasibility of utilising such techniques in the identification of pollution sources within urban catchments. Magnetic parameters used for this investigation include magnetic susceptibility (X), isothermal remanent magnetisation induced in samples in a field of 300mT, and other magnetic ratios. Samples were obtained from both surface and subsurface sources within a small, well defined, separately sewered residential catchment.

Good discrimination between paved surface sources is provided by X, $\text{IRM}_{300\text{mT}}$ and backfield ratios; the latter also being distinctive for roof sources. The relationship between the measured magnetic parameters and magnetic properties of the sediments is discussed. The backfield and $\text{IRM}_{300\text{mT}}/\text{X}$ ratios provide information on the magnetic mineralogy and magnetic grain size of the sediments, and X and $\text{IRM}_{300\text{mT}}$ are indicative of the relative concentration of ferrimagnetic minerals. The mixed nature of subsurface sediments is reflected in their varied and non-specific magnetic values. However, the results indicate that magnetic parameters may provide a useful "fingerprint" of urban surface source sediments even when, as for the moment in the present case study, their mineralogical implications are uncertain.

Keywords: magnetic methods, pollution sources, urban sediments.

INTRODUCTION

Although the contributing sources to storm runoff pollution are readily identifiable within urban catchments, it is a much more difficult problem to quantify their relative contributions to total pollutant loadings. Indeed a major deficiency in stormwater modelling procedures is the uncertain quantification of the various contributing sources to outfall quality.

A number of studies have indicated that atmospheric deposition can contribute substantial baseline loadings, particularly of heavy metals to urban runoff water (Huber et al 1979, Malmquist and Svensson 1975, Goettle, 1978, Randall et al, 1978, Ellis, 1982). Some research has been undertaken on the enhanced contributions that roof surfaces can potentially add to background atmospheric loadings and it is known, for example, that substantial concentrations of copper and zinc can be derived from corrosion of roofing materials (Malmqvist, 1983) which can make up 45 to 80% of the total outfall loadings; the roof surface in addition can be a major source of inert solids (Waller, 1972).

It is now widely accepted that road and paved surfaces contribute large quantities of solids, organic loadings, heavy metals and hydrocarbons to the subsurface sewer system (Ellis and Harrop, 1984; Harrop, 1983). A 1975 Swedish study reported typical wearing rates for bituminous surfaces of 50 to 70 tonnes of solids per kilometre per million vehicles (TFD, 1975); surface wetting and salting will substantially increase these rates of erosion. Metal removal rates associated with these eroded solids can vary from 1 to 40 mg day^{-1} with metal enrichment occurring in size fractions less than 63 microns (Harrop et al, 1984).

There is finally the contribution that below ground sources make to total outfall quality. The limited data available on roadside gully pot liquors indicate that substantial quantities of solids, nutrients and metals can be stored in and routed through these subsurface chambers (Mance and Harman, 1978; Fletcher et al, 1978).

The heterogeneous nature and multiphase origins of urban stormwater sediments do not make it a simple task to discriminate and identify between the specific contributing sources in the composite sewer or outfall sample. This paper examines the use of a range of rapid and non-destructive magnetic measurements as source identification techniques. Previous work has demonstrated that mineral magnetic methods can be diagnostic of particulates within a river system. Oldfield et al (1979) and Walling et al (1979) have developed these techniques for characterising source sediments within part of the River Exe catchment and in the identification of sediment sequences from contributing areas during storm events. Magnetic methods have also been successfully employed in studies of atmospheric pollution sources (Hunt et al, 1984). Recent work has also demonstrated apparent relations between magnetic parameters and heavy metal concentrations in separately sewered storm discharges (Revitt et al, 1981) and industrial effluents in the marine environment (Scoullos et al, 1979 and 1981). The development and application of these techniques which allow determinations to be made non-destructively on natural sediment suggest they may provide rapid, inexpensive and reliable methods of identifying and tracing contributing pollution sources within urban catchments.

DEFINITION OF PARAMETERS

Magnetic Susceptibility (X); this is the ratio of induced magnetization to the applied field. It is a measure of "magnetizability" or the degree of attraction of the sample to a magnet. X is approximately proportional to the volume concentration of ferrimagnetic minerals in the sample and is not strongly affected by magnetic grain size (Oldfield et al, 1978).

Isothermal Remanent Magnetization (IRM); this is the magnetization induced in and retained by a sample after it has been placed in a magnetic field. IRM increases non-linearly with applied field strength until saturation IRM, or SIRM, is reached (Oldfield et al, 1978). Maximum field strength used in this study was IRM_{300mT}, (the IRM induced by a magnetic field of 300mT) and like SIRM this is also indicative of the volume concentration of magnetic minerals in a sample. SIRM is dependent to a greater extent than X on magnetic grain size and mineralogy (Thompson and Morton, 1979) and IRM_{300mT} has been interpreted in a similar manner.

Discriminating Backfields; these parameters are obtained by placing a sample that has been exposed to the peak magnetic field, IRM_{300mT}, in a particular reverse field or series of fields and calculating the ratios of the resultant IRM's to the peak field value. These normalised parameters vary according to magnetic mineral type and grain size assemblages present and are indicative of the relative remanent "hardness"; that is the degree of resistance a magnetized sample possesses to magnetization in the reverse direction.

IRM_{300mT}/X; as both IRM_{300mT} and X reflect changing concentrations of magnetic minerals, this ratio can be viewed as a normalised parameter that is independent of concentration and therefore is indicative of magnetic minerals present in a sample and of magnetic grain size variations.

EXPERIMENTAL

The sampling area of $533.09m^2$ is a separately sewered highway catchment situated in a post-war housing estate on the north-west margins of Metropolitan London. The highway surfaces are drained by two gully pots located directly opposite each other; additional runoff from roof surfaces being routed directly into the subsurface drainage system at a point below the gully pots. The residential gardens do not contribute directly to surface drainage as they are at a level below that of the road surface. The pavement surface is rolled tarmacadam and the road surface is tarmacadam faced with coarse stone chippings. There is no grass verge between the pavement and the road. Roofing tiles in the area are made of a sand cement mix and the roof guttering is made of iron.

Sediment samples from the pavements, road gutters and middle of the road were collected using vacuum techniques along a transect approximately 10m above the gully pots. Roof samples were collected, using a plastic dust pan and brush, from a house in line with the transect. Gully pot samples and weir plate samples from the drain monitoring point were collected using a plastic scoop.

The collected sediment samples, which are 20-40% organic, were dried overnight at 105°C and sieved through a 1mm stainless steel sieve.

Magnetic susceptibility was measured using a Bartington Instruments meter and dual frequency sensor. Isothermal remanent magnetisations were induced using a Molspin pulse magnetiser and measured on a portable Minispin fluxgate magnetometer.

RESULTS AND DISCUSSION

The ranges of values for magnetic parameters measured over a six month period for the sediments sampled from the varying catchment sources are listed in Table 1. It can be seen that the ranges of magnetic parameters provide an initial identification of surface sediment sources, although occasional overlaps are evident as occur between X values for the road gutter and pavement samples and between IRM_{300mT} values for roof gutter and roof surfaces.

Figure 1 shows a strong linear relationship between IRM_{300mT} and X for each source, enabling the former to be used as a reasonably reliable magnetic concentration parameter. There is, however, some minor deviation from linearity exhibited by the pavement sediments.

The ratios of discriminating backfields to IRM_{300mT} also provide ranges which are characteristic of source types (Table 1). Comparison of concentration related and normalized parameters suggests that maximum concentrations are associated with relatively higher backfield ratios. This could point either to differing magnetic grain size assemblages or to a relatively higher haematite:magnetite ratio in the most magnetic samples.

Greater discrimination between source types can be achieved by consideration of the relationship between magnetic parameters (Figures 2 and 3). Inspection of Figure 2 shows that the IRM_{-20mT}/IRM_{300mT} ratio provides a clear separation of the paved surface sources as well as the roof surface. The middle

Table 1. Magnetic Parameter Ranges for Sampled Sediments.

Sample Area	X $(10^{-6}m^{3}kg^{-1})$	IRM_{300mT} $(10^{-6}Am^{2}kg^{-1})$	$\frac{IRM_{-20mT}}{IRM_{300mT}}$	$\frac{-IRM_{-100mT}}{IRM_{300mT}}$
Pavement	0.87-2.06	41209-10535	0.08-0.13	0.85-0.87
Road Gutter	1.73-3.16	21462-39991	0.14-0.23	0.80-0.84
Road Centre	3.44-7.25	41209-105235	0.27-0.30	0.82-0.83
Roof Surface	0.76,0.95	7502,8310	0.33,0.38	0.75,0.75
Roof Gutter	0.80,0.83	7319,9473	0.26,0.28	0.77,0.78
Gully Pots	1.32-1.65	11872-24011	0.20-0.25	0.76-0.85
Weir Plate	0.93,1.80	11526,24087	0.13,0.24	0.79,0.86

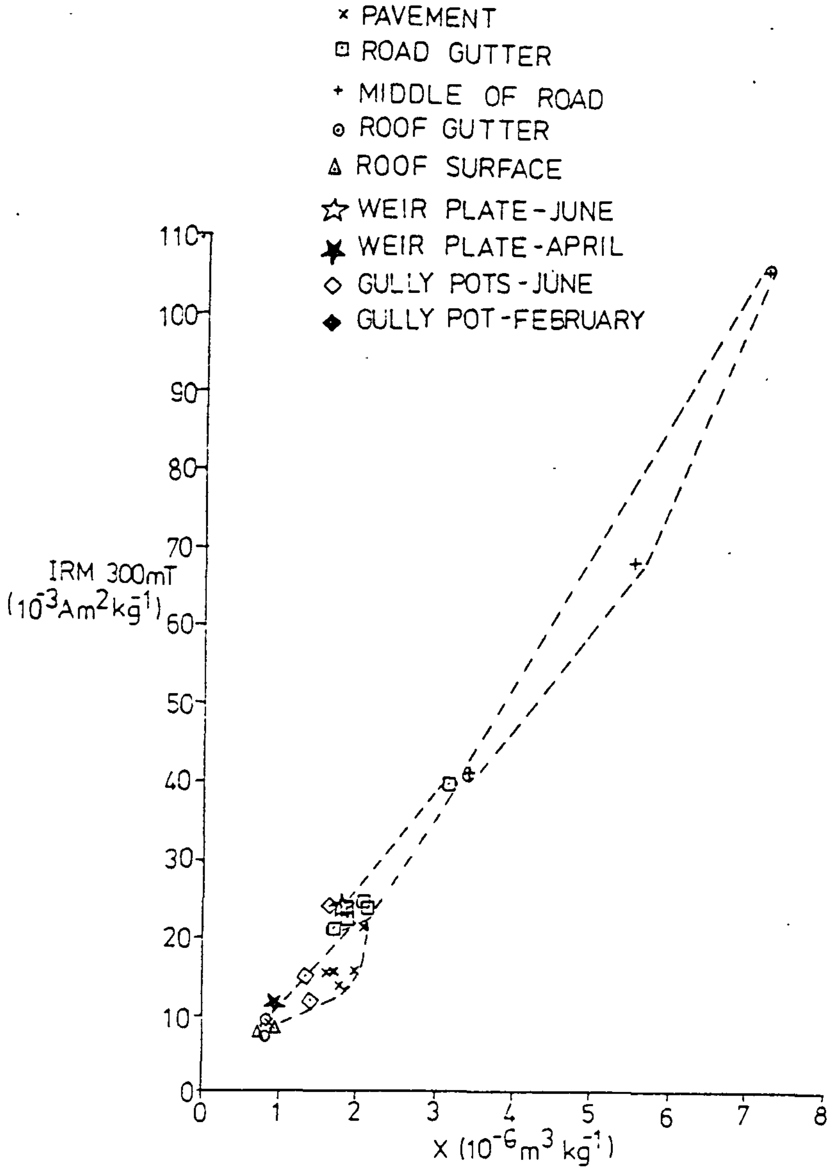

Figure 1. Sediment Discrimination using IRM_{300mT} versus X.

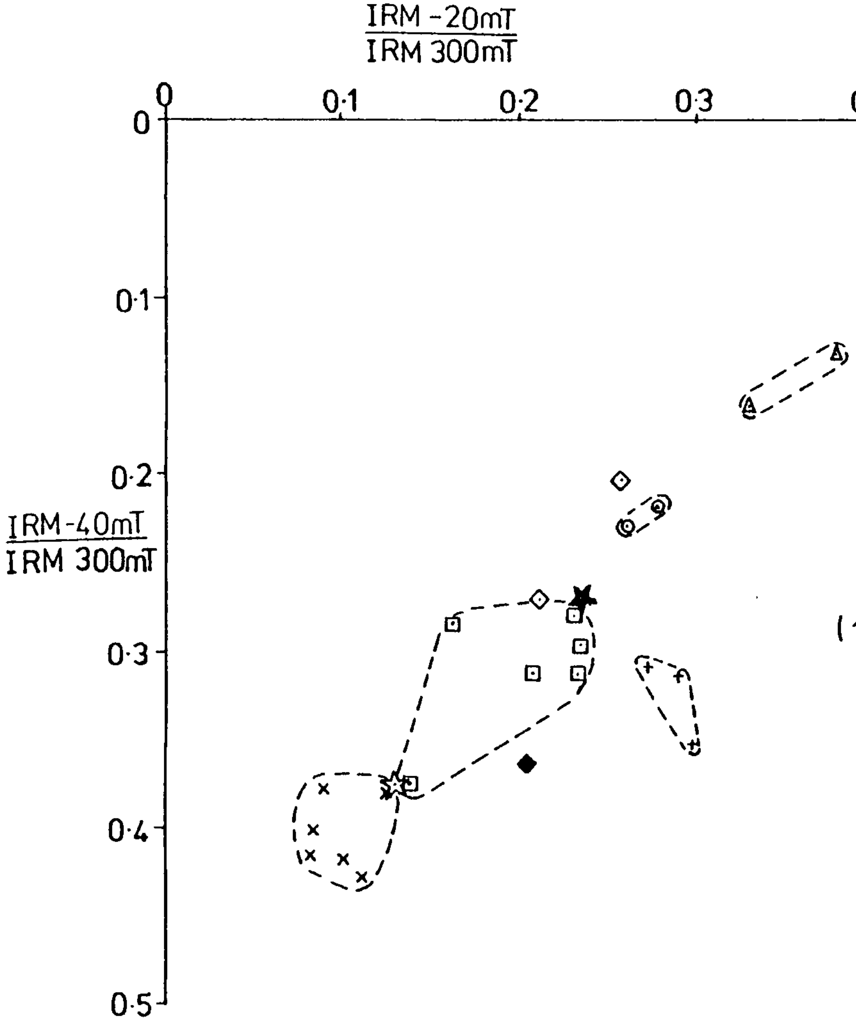

Figure 2. Sediment Discrimination using Backfield Ratios.

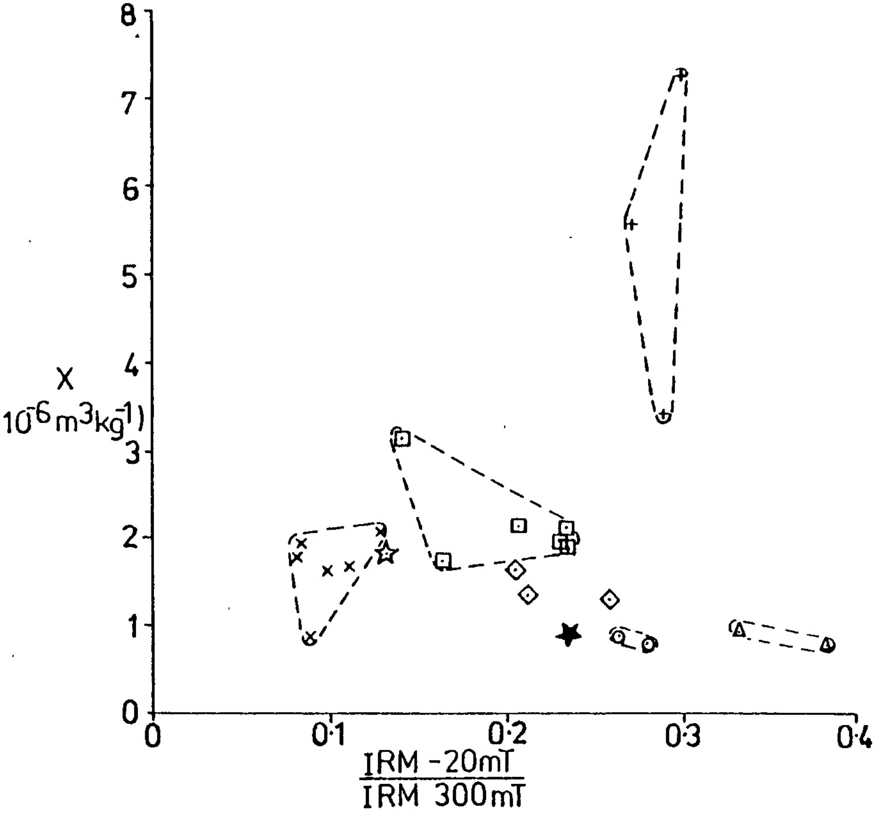

Figure 3. Sediment Discrimination using X versus IRM_{-20mT}/IRM_{300mT}.

of the road and roof gutter sediments can be distinguished by reference to the IRM_{-40mT}/IRM_{300mT} ratio. The flexibility of magnetic parameters in identifying source type is further illustrated in Figure 3 where the use of X against a backfield ratio provides a more distinct separation of the road centre sediments. Although the use of X does not permit the clear differentiation of roof surface and roof gutter that was previously apparent in Figure 2, the value of using a variety of magnetic parameters to characterise or "fingerprint" potential sources within the catchment is clearly illustrated by the diagrams.

Subsurface sediments are not distinguished by any of the graphical plots. The weir plate samples fall at the extreme ranges of the backfield plots for road gutter samples whilst the gully pot samples appear relatively randomly distributed although there is some tendency for a grouping near to the road gutter samples. This spread is not unexpected considering the varying origins of the gully pot sediments.

Table 2. Summary of Magnetic Characteristics and Concentrations of Roof and Roadway Sediments.

Parameter	Relative Remanent "Hardness"	Relative Concentration of Ferrimagnetic Minerals
IRM_{-20mT}/IRM_{300mT}	RFS>RFG,MRD>RDG>PMT	
IRM_{-40mT}/IRM_{300mT}	RFS>RFG>MRD,RDG>PMT	
IRM_{-100mT}/IRM_{300mT}	RFS>RFG>MRD,RDG>PMT	
IRM_{300mT}		MRD>RDG>PMT ≫RFS,RFG
X		MRD>RDG>PMT ≫RFG,RFS

Abbreviations:				
	PMT	Pavement	RFG	Roof Gutter
	RDG	Road Gutter	RFS	Roof Surface
	MRD	Middle of Road		

Table 2 summarises the hierarchy of the road and roof sediments in terms of their magnetic characteristics. The table shows that consideration of the backfield ratios as well as X and IRM_{300mT} indicates that there is a direct relationship between the relative remanent "hardness" and the concentration of ferrimagnetic minerals. The pavement sediment therefore appears to have a lower concentration of more exclusively ferrimagnetic minerals, whilst the sediment in the road centre has a higher concentration of less exclusively ferrimagnetic minerals; the road gutter being intermediate, possibly reflecting contribution from both source areas.

Inspection of X values for the weir plate samples and their position in Figures 1 and 3 implies that they have ferrimagnetic concentrations similar to those of the pavement samples although the June sample falls within the overlap of the pavement and road gutter. These low concentrations may arise as a result of roof inputs diluting the overall input of ferrimagnetic minerals from the road surfaces. The IRM_{300mT}/X ratios, are similar to or lower than the road surface sediments. The gully pot sediments have ferrimagnetic concentrations which vary in character between those of the pavement and the road gutter samples. The IRM_{300mT}/X ratios for gully pot sediments are spread throughout the range of IRM_{300mT}/X values for paved surface sediments, possibly reflecting both changes in mineralogy and grain sizes. The variation in magnetic concentrations,mineralogy and magnetic grain sizes for subsurface samples make it difficult to quantify the levels of source input.

To obtain a greater insight into the relative contributions of sources further work is needed. Magnetic measurements of artificial assemblages created by the mixing of collected sediments and comparison of values found to those of subsurface sediments collected may allow a semi-quantification of source supply. Greater clarification of pollutant sediment sources will be achieved from analysis of larger sample sets and more detailed exploration of magnetic mineralogy and grain size. However, the work has indicated the feasibility of identifying urban pollutant sources using magnetic methods.

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THE BEHAVIOUR OF SEDIMENT ASSOCIATED HEAVY METALS WITHIN AN URBAN SURFACE RUNOFF DRAINAGE SYSTEM

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ABSTRACT

The relative enhancement in concentration with respect to particle size fractionation in sediments washed from the road surface to the stormwater pipe, has been investigated for the metals Cd, Cu, Fe, Mn, Pb and Zn. Elevated concentration levels of the toxic metals Cd, Cu, Pb and Zn were found in the gully-pots and in-pipe compared to the road surface sediments. The pattern of enhancement varied between the two gully-pots studied. Variations in metal concentration levels cannot be explained simply in terms of the more efficient removal from the above ground surfaces of the more toxic fine particles. The results for toxic metal levels in gully-pot sediment and their subsequent displacement by storm runoff events give cause for concern regarding the effectiveness of the chamber as a sink for surface washed metal pollutants.

INTRODUCTION

Roadside gully-pots are known to be active contributors to and important regulators of pollution loads to stormwater runoff (refs 1, 2,3). Nevertheless very little work has been undertaken to evaluate the nature and behaviour of sediment associated heavy metals discharged to storm sewers via roadside gully-pots.

The principal purpose of the gully-pot is to act as a settling chamber for particulate (and organic) material transported from the highway surface in stormwater runoff. However, gully-pots have been found to be ineffective in removing all but the larger particles. Recent research has shown that for sediments less than 1mm in diameter, the mass of sediment washed through the gully-pot greatly exceeds that retained (ref 4). The mass of particulates removed from the road surface has been found to be dependent on rainfall-runoff characteristics, and site characteristics (refs 3,5). A comparison of heavy metal levels in adjacent road surface sediments with those in sediments entering gully-pots has shown enhancement of the toxic metals Cd, Cu, Pb and Zn in the latter (ref 6). This has been attributed to the preferential removal of the more polluted fine particles from the road surface by stormwater runoff. This is supported by the higher metal levels which are generally observed in the fine fractions of road surface sediments (ref 7).

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The aim of the present study is to investigate more fully the relative enhancement in metal concentrations, with respect to particle size, of surface sediments discharged to storm sewers via roadside gully-pots.

SITE CHARACTERISTICS AND EXPERIMENTAL METHODS

The sample area studied is a 0.05ha highway catchment situated within a 247ha separately sewered housing estate on the north west margins of Greater London. The highway surface camber effectively defines two distinct drainage areas (Site A and Site B) of almost equal size, each drained by a roadside gully-pot.

To collect the sediment washed from the road surface a nest of nylon sieves, from 2000 to 63μm mesh size was placed in the inlet of each gully-pot chamber, at sufficient depth to avoid surcharging. Grab samples of basal gully-pot and in-pipe sediments were collected using a plastic scoop, the latter collected downstream of the confluence of the gully-pot drainage pipes. Vacuum techniques were used to collect road dust samples from the gutter adjacent to each gully-pot.

Metal analysis was carried out on both total and size fractionated sediment samples which had been dried overnight at 105°C. Representative subsamples were digested in concentrated nitric acid, and the metal concentrations were determined by flame atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

The total metal concentrations for non-size fractionated sediments are given in Table 1. Observed metal concentrations for road surface sediments are consistent with previous work carried out in this catchment (ref 6) and in other Outer London urban/residential area studies (ref 7,8). Surface metal levels for both road gutter lines are similar particularly for Cu and Fe, although there is a considerable disparity for Cd and Pb. The two gully-pots show obvious differences in the variation of concentration levels for the metals Cd, Cu, Fe and Zn, although with the notable exception of Fe, both chambers show a definite enhancement in concentrations from road surface levels. For gully-pot B, sediment entering the chamber exhibits distinctly higher metal concentrations which may be a reflection of the more effective hydrological scouring mechanisms in the removal of pollutants from the associated road drainage surface. Basal sediment in gully-pot A compared to sediment entering the gully-pot shows elevated Cu, Fe, Pb and Zn concentrations, implying these sediments are a more efficient sink for these metals. Nevertheless for both chambers, basal sediment metal concentrations for Cd and to a lesser degree for Cu, Pb and Zn emphasis the limitations of the chamber in its inability to retain toxic metals washed from the above ground, prior to discharge to the below ground pipe system. This would seem to confirm recent work suggesting that gully-pots are unsatisfactory as settling chambers for pollutants contained in stormwater runoff (ref 9).

TABLE I

METAL CONCENTRATIONS IN THE TOTAL SEDIMENT ($\mu g.g^{-1}$)

Sample	Cd	Cu	Fe ($mg.g^{-1}$)	Mn	Pb	Zn
<u>Drainage Area A</u>						
Road surface dust	0.1	48.3	24.0	306.5	573.3	218.4
Sieve solids	3.4	49.8	13.6	382.2	568.1	286.5
Basal sediment (gully-pot)	2.2	59.7	17.9	363.5	570.6	399.3
<u>Drainage Area B</u>						
Road surface dust	0.9	45.9	20.8	567.6	285.0	281.5
Sieve solids	5.0	122.3	14.1	562.2	635.0	532.0
Basal sediment (gully-pot)	2.4	59.9	26.0	377.0	378.7	423.0
Roof gutter solids	1.2	17.3	49.6	579.3	322.6	211.5
In-pipe sediment	1.1	52.3	44.4	351.0	396.7	398.8

Below ground in-pipe sediments are shown to have increased concentrations of the toxic metals Cd, Cu, and Zn compared to the road surface. Concentrations of Fe are also enhanced relative to the road surface due to the input from roof guttering solids (49.6 $\mu g.g^{-1}$) draining directly to the below ground system. Mn shows no consistent pattern in the variation of concentrations through the system.

The heavy metal levels in the size fractionated samples are summarised in Table II. Generally the metal concentrations increase as sediment grain size decreases, although this trend is less evident for Fe. A notable exception to this mattern is shown by Cu, Pb and Zn in the basal sediment of gully-pot A.

For Site A no Cu concentration enhancement from road surface to sieve to basal sediment was found in the fine fractions (< 250um) although this is observed in the coarser grain sizes. Pb and Zn show this concentration enhancement in both the fine and coarse grain sizes. The greater concentration elevations for these metals shown by the coarse fraction suggest that aggregation of the fine Pb and Zn containing particles is taking place, particularly within the gully-pot itself. The overall dominance of the coarse fractions in the sediment distributions result in a considerable elevation in the metal content of the total sediment (see Table I). Cu, Pb and Zn show distinctly different trends in the pattern of concentrations enhancement through surface, sieve and basal sediments at site B when compared to site A. The levels are greater for both size fractions in the sediment captured at the gully inlet compared to the road surface sediment. The metal levels with the exception of Pb in the fine fraction, then show a marked decline between the sieve sediment and the basal sediment. The relative enhancement in the metal levels between the road surface and the gully-pot, particularly for the coarser fractions, suggests that particle aggregation also takes place at this site during the transport of sediment from the road surface. Previous work on the catchment indicates that the road surface sediment found at site B has a higher proportion of organic matter than that at site A (ref 5). Differences in surface flow characteristics between the two drainage areas have also been noted and result in the more effective removal of sediment material at site B (ref 5,6). The combination of these two factors may be responsible for the distinct increase in Cu, Pb and Zn concentration levels for sediment entering gully-pot B (see Table I). It is well known that Cu shows a high affinity for the organic fraction of sediments and that this tends to increase as particle size decreases (ref 8). The combination of higher organic content and the more effective removal may thus explain the considerably enhanced levels of Cu observed in the fine sediment fraction entering gully-pot B. A comparison of the sediment size distributions at site B with those at site A shows a depletion in the proportion of fine particles in the basal sediment at the former. This suggests that particles entering the system are more readily washed through gully-pot B, or are being completely broken down within the gully-pot itself.

At both sites Cd shows similar trends in the pattern of concentration enhancement between the above and below ground phases which are also similar to those exhibited by Cu, Pb and Zn at site B. Cd demonstrates a greater tendency to be associated with the fine fraction, which suggests that it is more readily removed by surface

TABLE II

METAL LEVELS FOR THE COARSE AND FINE SEDIMENT GRAIN SIZES ($\mu g.g^{-1}$)

Sample	Size Category (μm)	Cd	Cu	Fe $mg.g^{-1}$	Mn	Pb	Zn	Sediment Weight (g)
Drainage Area A								
Road Surface dust	>250	0.2	38.4	20.1	550.1	119.1	145.9	193.9
	<250	1.1	84.3	20.8	733.3	496.1	305.9	53.8
Sieve solids	>250	2.9	44.0	12.9	555.4	310.3	263.1	460.8
	<250	4.8	73.0	15.8	620.5	629.9	398.5	129.3
Basal sediment (gully-pot)	>250	2.2	65.7	16.3	331.1	744.3	416.4	55.4
	<250	2.9	66.7	29.2	401.1	675.8	410.5	17.3
Drainage Area B								
Road surface dust	>250	0.7	46.0	18.9	475.1	227.6	234.1	112.0
	<250	1.7	80.4	22.3	642.8	657.9	546.6	37.0
Sieve solids	>250	4.5	96.0	13.4	614.3	521.3	506.4	373.2
	<250	6.7	200.5	16.6	717.4	709.3	626.2	117.1
Basal sediment (gully-pot)	>250	1.6	61.5	27.7	287.7	378.7	384.0	54.5
	<250	2.4	91.7	24.9	423.5	744.0	596.1	8.6
In-pipe Sediment	>250	0.7	47.7	48.4	280.7	185.4	260.6	159.5
	<250	1.6	69.4	48.8	455.3	480.4	480.4	26.3

runoff, this is particularly noticable at site B. Concentrations of Cd, Cu, Pb and Zn in all size fractions of the in-pipe sediment are generally lower than in the basal sediments of both gully-pots. This depletion is greatest in the case of Cd and follows the order Cd>Pb>Zn>Cu, which is in agreement with the relative availability of these metals to the soluble phase of stormwater runoff (refs 7,8). Nevertheless, the in-pipe sediment levels of these metals are generally elevated relative to the road surface for both fractions. Fe and Mn concentration levels decline in both size fractions of the sediment captured at each gully-pot compared to the road surface sediment. However, while the Mn concentrations continue to decrease in the below ground system the Fe concentrations are enhanced. This enhancement of Fe has already been commented upon and is due to the direct input of Fe to the sewer from roof guttering. The percentage Mn and Fe content shows overall similarity with the percentage sediment distributions for both size fractions, which provides evidence of a natural input of these metals to the system.

The evidence provided by these results suggest that variations in the levels of sediment associated heavy metals within an urban surface drainage system cannot readily be explained in terms of the preferential removal of the more toxic fine particles by stormwater runoff. The hydrological characteristics and the nature of contributing sediments at individual sites are important influencing factors. The elevated levels of toxic metals in gully-pot sediments, and their removal by storm runoff events give cause for concern over the effectiveness of the chamber as a sink for surface washed metal pollutants.

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PARTICLE SIZE DISTRIBUTION OF Cu, Pb AND Zn ACROSS A ROAD SURFACE

Paul R Beckwith, J Bryan Ellis and D Michael Revitt

ABSTRACT

The relationship between metal levels and particle size distribution across a residential road over a 6 month period has been investigated. The results show a gradual increase in metal sediment concentrations towards the centre of the road and a higher affinity of heavy metals for the smaller particle sizes. The concentration patterns and sources of Cu, Pb and Zn are discussed and inferences drawn as to their transport across the road surface.

INTRODUCTION

Metal levels in street dusts have been widely reported and have been shown to be closely related to traffic density (refs 1 and 2). The sources of vehicle derived metals have been identified as exhaust emissions, tyre wear and corrosion processes. The spatial metal distribution patterns, in terms of both concentrations and loadings have been investigated within different highway environments (ref 1) but have not taken into account the importance of particle size. By emphasising this important aspect, this paper discusses the movement of Pb, Cu and Zn from vehicular sources within the confines of a relatively quiet residential road.

SITE CHARACTERISTICS AND EXPERIMENTAL METHOD

The sampling area is a residential road situated in a housing estate in NW London, UK. Sediment samples were collected from the paved surfaces using vacuum techniques. Automobile-derived particulates were obtained directly using a stiff plastic brush with repeated samples being taken from two different family saloon cars. Samples were dried overnight and sieved using stainless steel sieves of aperture sizes from 38 µm to 1000 µm. Metal analyses were carried out by extracting with a 9:1 mixture of concentrated nitric and perchloric acids followed by flame atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

The Cu, Pb and Zn concentrations of the bulk samples collected from a transect across the road were generally found to increase from pavement to road gutter and from road gutter to road centre. This trend was most obvious for Pb and least consistent for Cu with Zn occupying an intermediate position. This pattern reflects the expected increase in metal concentration with closer proximity to the vehicular source.

Analysis of Pb levels with respect to particle size indicates that for this metal the highest concentrations were found to be consistently

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associated with the smaller particle sizes, specifically those finer than 250 µm. These are therefore seen to be the most important sizes for controlling Pb distribution across the road.

The highest source Pb particulate concentrations have been found in in-pipe exhaust samples (~ 100000 ug g^{-1}) and particle size analysis reveals that only ~24% of these samples are in the 38-125 µm range with 59% in the <38 µm range. It might therefore be expected that the <38 µm fraction of the highway sediments would exhibit consistently greater Pb concentrations than other size ranges. This is not apparent for the road centre sediments (Table 1) and therefore it is probable that much of this finest fraction is rapidly dispersed by resuspension and washoff processes.

	Pavement	Road Gutter	Road Centre	Road Gutter	Pavement
BULK	127.3	321.0	481.2	335.2	111.0
500-1000 µm	228.3	95.0	305.7	232.3	57.0
250-500 µm	61.0	222.3	517.8	263.3	126.2
125-250 µm	162.3	310.0	1316.9	444.4	163.7
63-125 µm	301.5	872.8	3133.9	830.4	256.4
38-63 µm	600.8	1087.3	2312.7	1097.9	358.5
<38 µm	1440.3	1260.4	1851.0	1653.9	468.7

TABLE 1: Average Pb concentrations (µg g^{-1})

The considerably higher concentrations found in the >38 µm size ranges of the road centre compared to the road gutter and pavement sediments suggests that a proportion of the finest particulates aggregate or adhere to the larger particles already present on the road surface (ref 3). This process will also contribute to the lower Pb concentrations in the <38 µm size fraction.

For the road gutters there is again an overall trend for Pb concentration to increase with decreasing particle size which continues to the finest fraction (Table 1). This suggests that the <38 µm particles are more readily trapped by the greater bulk of material which collects in the road gutter compared to the road centre. There is a natural division of road gutter sediment fractions into two size groups; one of size range <38-125 µm, possessing higher Pb concentrations (830-1654 µg g^{-1}) and the other of size range, 125-1000 µm, with lower Pb concentrations (95-444 µg g^{-1}). Comparison of these groupings with the road centre sediments reveals that for these samples equivalent higher Pb concentration size ranges extend from <38 to 250 µm (Table 1). This suggests that the 125-250 µm particulates are less readily transported to the road gutter by runoff processes than the 38-125 µm particulates.

The pavement sediments, while displaying a tendency for Pb concentration to increase with decreasing particle size, do not show such a distinct concentration differentiation. These sediments exhibit lower concentrations than the road gutter sediments suggesting a lower input of Pb containing particulates and additionally efficient removal of particles to the road gutter.

Cu exhibits less distinct trends than Pb with respect to both bulk sediments and particle size. Brake wear is the dominant source of Cu in this environment with disc brake particulates having been found to have Cu concentrations of 17680 µg g^{-1}. Brake wear is a less consistent source mechanism than exhaust Pb particulates which are emitted continuously although in varying amounts according to driving mode. This may explain the reduced definition of trends in the case of Cu.

The road centre sediments exhibit an increase in Cu concentration with decreasing particle size in the 500-63 µm range although the Cu concentration decreases for the finer particle size. This suggests that the <38 µm, and a considerable proportion of the>38 µm particles are rapidly dispersed. Particle size analysis of brake wear dusts has revealed that ~58% occurs in the<38 µm size range which is similar to that observed for the in-pipe exhaust particulates. However, unlike exhaust particulates the remaining 42% of brake dust is distributed evenly across the 38 to 250 µm size range which may partly explain the less distinct particle size concentration trends compared to Pb.

There is a general increase in Cu concentrations with decreasing particle size in the road gutter sediments and the levels are generally less than those found for the road centre. Peak gutter sediment concentrations occur in the 38-63 µm size range suggesting that the trapping efficiency for Cu associated particulates (<38 µm) is lower than that for the similarly sized Pb particles. However, further details of the nature of the source particulates and their tendency to agglomerate is needed before precise reasons for the differences between the behaviour of the Cu and Pb associated particulates can be given. As in the case of Pb there is evidence to support the less ready removal of the 125-250 µm sizes by wash off processes. Although there is some indication of a trend for Cu concentrations to increase with decreasing grain size of pavement sediments this trend is not well defined and Cu concentrations are generally low with an overall mean of 62.8 µg g^{-1}.

Zn concentrations generally exhibit an increase with decreasing particle size although unlike Cu and Pb there is no distinct partition of particle sizes into groupings of higher and lower concentrations. Zn has been found to occur in high concentrations (185 000 µg g^{-1}) in particulates collected from the outside of galvanised exhausts which occur predominantly in the larger particle size ranges (>125 µm). Zn is also known to originate from tyre wear with tyres having been found to contain 7300 µg g^{-1} (ref 4). The particulates emitted from tyres have been found to range in size from 0.01 µm to >30 µm with the larger particles dominating the total mass (ref 5). The presence of these two different sources of Zn particulates may be responsible for the observed lack of distinct concentration patterns for Zn with particle size.

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Heavy metal and magnetic relationships for urban source sediments

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A major problem in urban hydrology is the assessment of the relative contributions of different pollution sources within urban drainage systems. This paper examines the use of magnetic techniques for the identification of pollution sources and the possible relationships between heavy metal levels and several magnetic parameters

The characterisation of pollution sources by the use of magnetic methods is consistent with previously published results. Surface constructional materials and directly derived vehicular particulates have been analysed and compared with sediments sampled from within a highway catchment. The results of this analysis indicate that automobiles are the major source of metal pollution; this is consistent with the results obtained for metal analysis of the sediment types.

Strong linear relationships are observed between the metals (Cu, Fe, Pb and Zn) and ferrimagnetic concentration related parameters. The implications of these results regarding the use of magnetic techniques for the identification of pollution sources are discussed.

1. Introduction

Significant advances have been achieved in urban hydrology research over the past decade but despite this progress, one of the major issues remains the problem of pollution source identification in urban drainage systems. In addition, interest in pollutional aspects of urban runoff has been extended from conventional constituents to persistent toxic priority substances such as hydrocarbons and heavy metals. One of the outstanding needs at present is to identify the accumulation and movement of priority pollutants from specific sources and to assess their relative contributions to outfall loadings (Delleur and Torno, 1983).

Tracer techniques have had little application in urban hydrology apart from dilution gauging and the use of non-degradable chlorinated benzoic acids in sanitary sewers to evaluate times of concentration. However, magnetic tracer methods have been utilised in a variety of alternative aquatic environments to characterise source particulates (Dearing et al., 1981) and to determine sediment contributions, routing and sequencing during storm runoff (Oldfield et al., 1979; Walling et al., 1979; Arkell et al., 1983). However, all of these studies have been conducted within rural catchments which are characterised by relatively unpolluted waters. The purpose of this investigation is to assess the ability of magnetic methods to provide a diagnostic 'fingerprinting' of source sediment types as a preview to determination of temporal sequencing during storm events within separately sewered urban catchments.

Stormwater sewers route large quantities of solids and metals, often in close mutual associa-

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tion, through urban catchments to receiving streams with the majority of the solids loading being within the 20–3000 micron size range. Peak sediment removal rates of 60 g day^{-1} have been recorded for highway surfaces (Ellis and Harrop, 1984) with metal loadings reaching 22 and 24 mg day^{-1} for zinc (Zn) and lead (Pb), respectively (Harrop et al., 1983). The highest Pb concentrations for road surface sediments have been shown to be associated with median particle sizes of ~ 350 μm (Ellis and Revitt, 1982) which indicates considerable aggregation of the fine exhaust emitted Pb particles.

Atmospheric deposition is known to contribute substantial baseline heavy metal loadings to those already existing on the paved surface (Mance and Harman, 1978; Randall et al., 1978; Ellis, 1982), and it is also known that roofing materials can considerably enhance background atmospheric loadings (Malmqvist, 1983; Beckwith et al., 1984a). The below ground phase of the stormwater drainage system also plays a significant role in storing and routing solids and metals. Roadside gully pots and below ground conduits serve as effective sediment and pollutant sinks. They also regulate the nature and strength of anoxic liquors flushed through the system.

A number of studies have indicated potential relationships between heavy metals and magnetic mineral concentration dependent parameters for both aquatic (Scoullos et al., 1979; Revitt et al., 1982) and atmospheric environments (Hunt et al., 1984). These studies indicate the possible existence of linear correlations between metals and magnetic parameters. Therefore, previous work suggests that magnetic methods might well provide a rapid, cheap and non-destructive approach to typing urban source sediments and also provide a useful reconnaisance method for determining their heavy metal distributions. This paper investigates the relationship between magnetic parameters and heavy metals in source sediments within a small residential catchment.

2. Experimental

The sampling area used in this study is a 0.05 ha separately sewered highway catchment situated within a post-war housing estate on the northwest margins of Metropolitan London. The highway surface is effectively divided into two drainage areas by the road camber; each area being drained to a roadside gully pot. Additional runoff from adjacent house roof surfaces is routed directly into the subsurface drainage system. The housing is typical of the estate and consists of terraced blocks of four houses all of similar design, construction and roof material. The pavement surface is composed of rolled tarmacadam and the road surface is tarmacadam dressed with coarse stone chippings. The roofing tiles are made of a sand-cement mix and the roof guttering material is cast iron.

Sediment samples were collected from the paved surfaces using vacuum techniques. Roof samples were collected from one of the houses adjacent to the catchment by the use of a plastic dust pan and brush. Grab samples were taken of the basal gully pot sediments and of in pipe sediments using a plastic scoop. Samples of road chippings were taken from local stock piles; one exposed to the urban environment for 2 weeks, the other for ~ 1 y. Automobile-derived particulates were directly obtained using a stiff plastic brush; repeated samples being taken from a standard family hatchback vehicle. Samples were stored in plastic bags prior to analysis. Plastic sampling equipment and storage bags were used to avoid any possibility of sample contamination. All samples were dried overnight at 45°C; this temperature prevented any premature enhancement of mineral magnetic parameters. Samples were sieved through a 1 mm stainless steel sieve to remove extraneous particles such as pull rings from discarded cans which could result in anomalous, unrepresentative results for both mineral magnetic parameters and heavy metal determinations.

Magnetic susceptibility was measured using a Bartington Instruments meter and sensor. Isothermal remanent magnetisations were induced using a Molspin pulse magnetiser and measured on a portable Minispin Fluxgate magnetometer.

Metal analyses were carried out by digesting replicate samples with a 9 : 1 mixture of nitric and perchloric acids, followed by evaporation to dryness and dissolution of the residue in 2% hydrochloric acid. The nitric/perchloric acid mixture was chosen for sample digestion in an attempt to extract all adsorbed metals other than those retained in the crystalline lattice. The perchloric acid oxidises the organic fraction of the samples, which in the case of copper is the most significant phase of metal concentration in street dusts (Hamilton et al., 1984). Metal concentrations were determined using flame atomic absorption spectrophotometry. The precision of the analysis was better than ±10% for all samples.

3. Discussion

3.1. Magnetic properties of source sediments

A preliminary characterisation of source sediments from the catchment by use of magnetic methods has been presented previously (Beckwith et al., 1984b). This more comprehensive study confirms the general findings of the previous work in identifying strong linear relationships between isothermal remanent magnetisation at 300 mT (IRM_{300mT}) and specific magnetic susceptibility (X). In addition, the ratios of the discriminating backfields to IRM_{300mT} provide ranges which are characteristic of the various source types (Fig. 1). However, with the increased number of samples in this study the backfield plots show a greater tendency to overlap for the specific source areas; particularly pavement and road gutter, and roof and road gutter. The hierarchy of ferromagnetic mineral concentrations remains such that the middle of the road sediments have the greatest concentration, the pavement and roof sediments have the lowest concentration and the road gutter sediments are intermediate.

The magnetic characterisation of subsurface sediments is not as immediately apparent as that of surface sediments. Gully pot and in pipe sediments tend to fall within, or close to, the ranges of the road gutter sediments. This might be expected in the case of the gully pot sediments since the road gutter sediments are the immediate source sediment for the gully pot chamber. The observed overlap of the gully pot and road gutter sediments would indicate that, despite the strong biochemical reactivity associated with the former sink, the magnetic parameters appear to be relatively unaltered.

The differentiation between gully pot sediments and roof sediments is also not readily apparent. There is some tendency for the former to contain slightly higher concentrations of ferrimagnetic minerals and to have a greater relative remanent "softness". This difficulty in discriminating between these source sediments will certainly cause problems in enabling a definitive characterisation of loadings from each respective source to be taken during runoff events. However, the sediments from the road centre with their inherent high ferrimagnetic mineral concentrations, may be washed selectively through the system, and appear as peak concentration measurements during storm runoff.

Revitt et al. (1982) observed such peak concentrations during storm runoff from urban catchments and categorised them in terms of the scouring and transport of highly magnetic toxic particulates from the street surface. The sediments from the road centre, with their inherently high ferrimagnetic mineral concentrations, may therefore be washed selectively through the system and so enable some characterisation of sequential loadings during runoff events.

The possible source or sources of the magnetic minerals within the catchment can be identified as:

(1) atmospheric deposition;
(2) soil particulates;
(3) automobile derived particulates; and
(4) surface constructional materials.

Atmospheric deposition can be assumed to be generally constant throughout the catchment and although it may contribute substantial amounts of pollutants, it would not solely account for the high concentration of magnetic minerals found uniquely in the sediments collected from the road centre.

Soil particulates are not considered to be a major source in this catchment, since the drainage of the gardens immediately adjacent to the road is directed away from the highway. If soil particulates were a major source, then the highest concentrations of ferrimagnetic minerals might be expected to occur at sampling points close to the

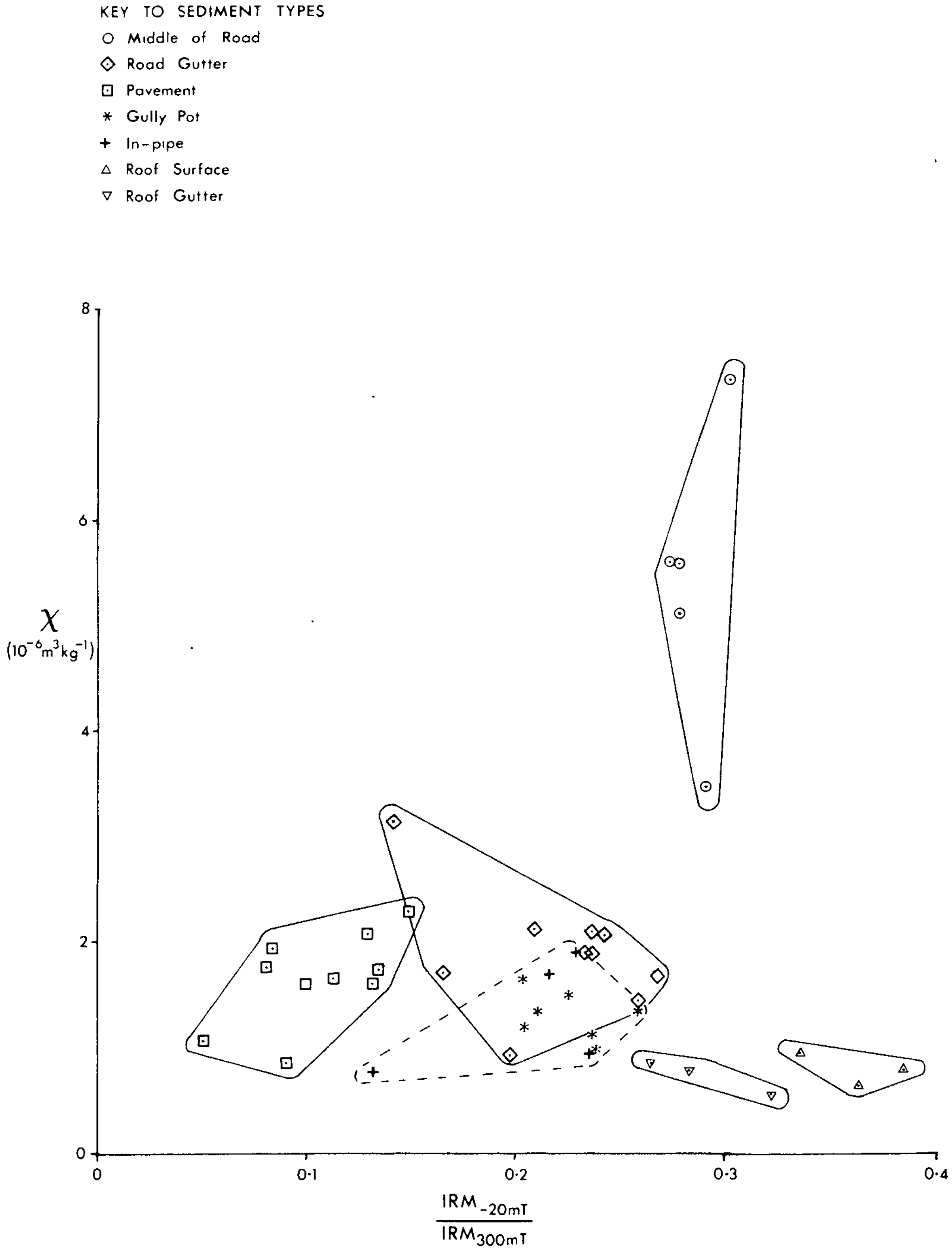

Fig. 1. Sediment discrimination using X versus $\mathrm{IRM}_{-20\mathrm{mT}}/\mathrm{IRM}_{300\mathrm{mT}}$.

gardens, such as in pavement sediments.

To assess 'in situ' and vehicle emitted contributions to the road surface magnetic levels, samples of road dressing and automobile-derived particulates were obtained and analysed. Table I summarises the ranges of magnetic measurements as well as selected metal concentrations measured for these particulates.

The Mount Sorrel granite road chippings which were > 1 mm in diameter possessed ferrimagnetic mineral concentrations lower than those determined for samples taken from the middle of the road. In the case of road chippings < 1 mm in size there is overlap with the lower end of the middle of the road range (Table I). All of the automobile derived particulate samples, with the exception of that taken from within the exhaust pipe, have greater concentrations of ferrimagnetic minerals than those of the sediments collected from the road centre.

Comparison of the concentration independent ratios shows that the IRM_{300mT}/X ratios of the larger size fractions of road chippings are similar to those of the middle of the road. The particulates collected from the outside of the exhaust pipe, and from the corroded paintwork sample exhibit values of IRM_{300mT}/X, which is slightly greater than those of the road centre sediments. The IRM_{-20mT}/IRM_{300mT} ratio values for road chippings are much greater than those of the road centre sediments; the corroded paintwork sample having the greatest similarity in value to the ranges yielded by the road centre sediments.

To suggest that paint and corroded bodywork are the main sources of magnetic minerals on the road would undoubtedly be an oversimplification but it is highly probable that vehicular rust particulates contribute greatly to the IRM_{300mT} and X values of the road centre sediments.

3.2. Heavy metal concentrations and sources

The range and means of metal concentrations determined for the various source sediments within the catchment are given in Table II.

The values are comparable to those found in previous studies within the catchment (Harrop et al., 1983). The Cd, Cu, Pb and Zn concentrations are generally higher in sediments associated with the paved surfaces and the subsurface drainage system than they are in roof samples. The road centre sediments consistently exhibit the highest concentrations of Cu, Pb and Zn whereas the maximum Cd concentrations occur in the pavement samples. The high values of Cu, Pb and Zn in the middle of the road sediments are consistent with the elevated values of these metals which are found in vehicle derivatives (Table III). A similar trend can be seen for Fe although the highest concentrations of this element are found in both types of roof sediment and for the in-pipe sediments. This relationship between the high Fe values can be explained by the direct input of Fe which occurs from roofs to the subsurface system which by-passes the gully pots. Mn levels are relatively constant between all sediment types in-

TABLE I

Magnetic parameter values for source materials and road centre sediments

	IRM_{300mT} ($10^{-3}Am^2\ kg^{-1}$)	X ($10^{-6}\ m^3\ kg^{-1}$)	IRM_{-20mT}/IRM_{300mT}	IRM_{300mT}/X (kAm^{-1})
ROAD CHIPPINGS				
8 mm	27.0–30.0	2.36–4.42	0.42–0.69	6.6–13.1
4–8 mm	20.0–37.9	2.83–4.97	0.42–0.62	7.1–12.6
2–4 mm	25.8–34.7	2.95–3.08	0.45–0.62	8.4–11.8
1–2 mm	19.8–24.6	3.12–5.34	0.54–0.57	4.6–6.3
1 mm	32.9–67.7	1.49–3.77	0.45–0.55	18.0–22.1
CAR DERIVATIVES				
Exhaust particulates				
Inside	23.0	3.99	−0.13	5.8
Outside	119.2	6.32	0.46	18.9
Wheel hub particulates	177.7	273.32	0.46	1.02
Corroded bodywork	1225.5	64.67	0.25	19.0
ROAD CENTRE SEDIMENTS	41.2–105.2	3.45–7.28	0.27–0.3	11.9–14.5

TABLE II

Heavy metal concentration ranges and means for sampled source sediments

	Cd(μg g^{-1})	Cu(μg g^{-1})	Fe (mg g^{-1})	Pb (μg g^{-1})	Mn (μg g^{-1})	Zn (μg g^{-1})
Pavement	0.5–5.8	11.8–65.5	12.0–29.7	56.9–225.2	479.1–780.6	131.6–293.5
	(2.2)	(40.4)	(22.9)	(134.0)	(626.5)	(186.1)
Road	0–1.7	35.6–78.6	15.3–31.5	146.6–1076.3	283.3–647.1	141.1–403.4
gutter	(0.7)	(50.6)	(22.0)	(452.1)	(480.5)	(292.6)
Road	0.1–0.7	26.6–190.2	26.1–35.5	295.2–2843.5	444.7–589.9	302.6–849.8
centre	(0.4)	(87.8)	(31.6)	(1041.1)	(592.9)	(499.8)
Gully pot	0–3.2	38.2–101.2	11.5–29.6	242.6–1448.3	340.8–502.1	282.6–616.9
	(2.0)	(67.4)	(19.5)	(608.1)	(413.7)	(490.4)
In pipe	1.0–2.0	13.0–92.4	29.6–43.8	235.8–908.5	370.5–590.8	335.3–499.8
	(1.5)	(50.5)	(39.5)	(472.2)	(459.2)	(415.4)
Roof	0–2.1	28.3–31.8	31.2–41.0	308.6–480.1	429.2–644.3	3340–438.1
surface	(1.3)	(30.3)	(35.8)	(419.4)	(549.1)	(375.8)
Roof	0–1.2	17.1–33.8	37.1–49.6	319.5–579.3	322.6–468.1	211.5–355.3
gutter	(0.7)	(26.8)	(41.7)	(418.7)	(380.3)	(289.3)

Mean values in brackets.

dicating its major occurrence as a natural background source element.

The metal levels found in the stockpiled road chippings (Table III) are low compared to levels found in the source sediments (Table II) although the metal concentrations of the chippings do increase with decreasing grain size. A comparison of the Tables shows that, with the exception of Cd and Cu the observed peak concentrations of the road chippings fall close to the lower ranges of the source sediments. In the case of Cd and Cu the values for the finest fraction are well within or exceed those recorded for the surface sediments. The relative enrichment of these source sediments must imply that breakdown and wear of the highway constructional material cannot of itself explain their observed sediment associated pollutant levels. It is apparent from a consideration of the concentrations that the major heavy metal source to the paved surface comes from directly derived automobile emissions and corroded particulates. This conclusion is in full agreement with the earlier inferences made on the basis of mineral magnetic measurements.

TABLE III

Heavy metal concentrations for source materials

	Cd (μg g^{-1})	Cu (μg g^{-1})	Fe (mg g^{-1})	Pb (μg g^{-1})	Mn (μg g^{-1})	Zn (μg g^{-1})
ROAD CHIPPINGS						
8 mm	N.D.	6.1–9.5	2.8–3.9	1.8–3.3	48.9–71.3	11.9–37.2
4–8 mm	N.D.	8.1–10.3	3.6–4.6	0.7–4.1	66.9–92.1	14.0–28.0
2–4 mm	0.0–0.2	15.9–21.6	11.2–14.1	7.0–8.1	182.9–241.7	38.6–50.1
1–2 mm	0.0–0.2	18.8–33.3	12.6–19.1	13.4–17.8	214.3–269.0	60.3–78.6
1 mm	0.3–1.1	40.0–73.6	16.7–21.9	9.6–121.5	248.3–378.2	96.7–267.0
CAR DERIVATIVES						
Exhaust particulates						
Inside	4.8	57.7	80.8	119420.1	103.0	8105.3
Outside	5.6	68.1	116.8	1991.8	630.2	186612.1
Wheel hub particulates	N.D.	14476.4	286.7	7426.3	2253.4	10720.1
Corroded bodywork	0.2	55.1	236.0	32.3	636.2	6611.1

N.D. Not Detected

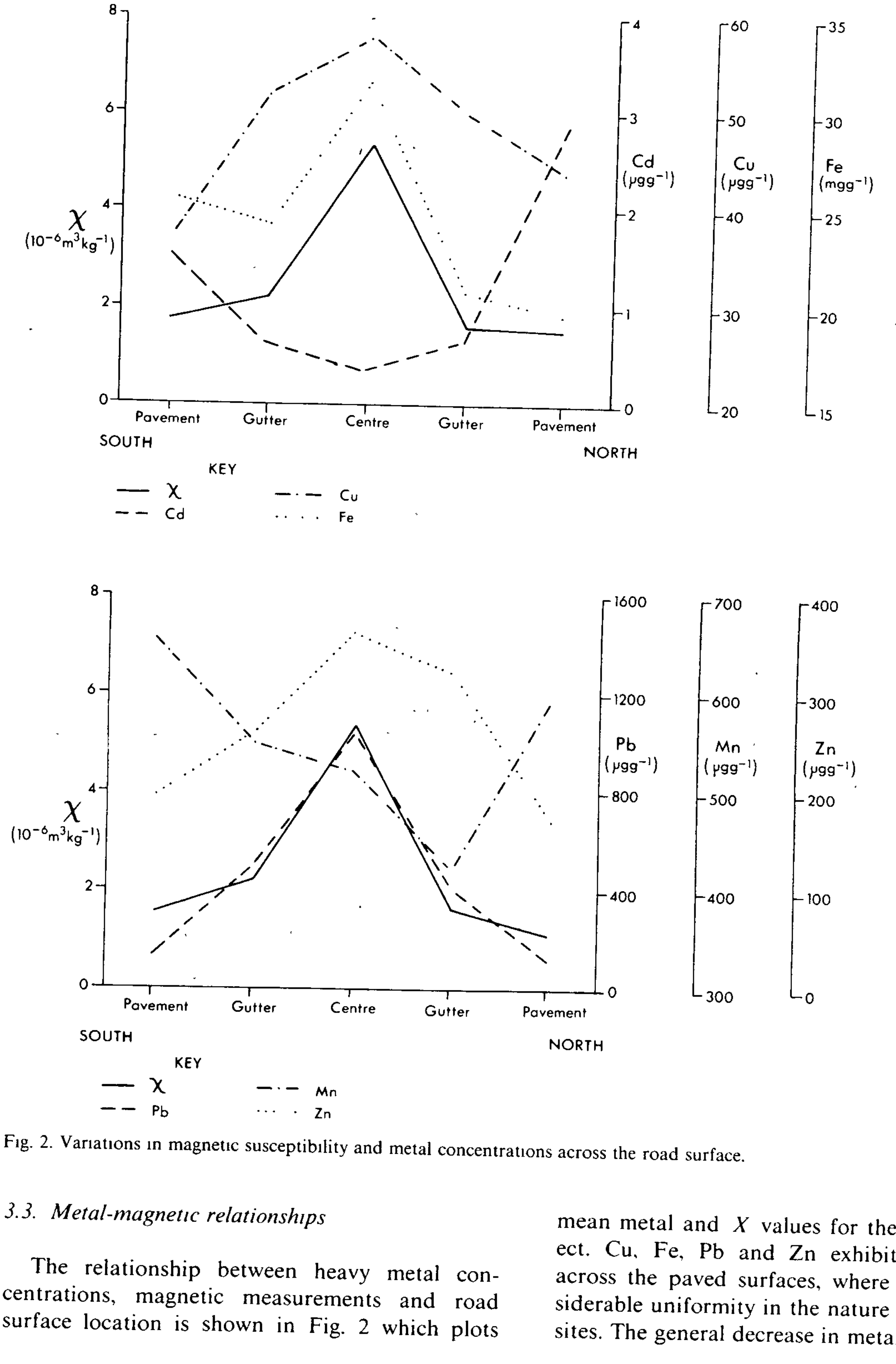

Fig. 2. Variations in magnetic susceptibility and metal concentrations across the road surface.

3.3. Metal-magnetic relationships

The relationship between heavy metal concentrations, magnetic measurements and road surface location is shown in Fig. 2 which plots mean metal and X values for the highway transect. Cu, Fe, Pb and Zn exhibit similar trends across the paved surfaces, where there is a considerable uniformity in the nature of the sampling sites. The general decrease in metal concentrations from road centre to pavement is paralleled by the ferrimagnetic concentration related magnetic measurements. Cu, Fe, Pb and Zn show good correlations with both X and $\mathrm{IRM}_{300\mathrm{mT}}$ providing 30–50% explanation of the co-variance. The correlations noted for the ferrimagnetic concentration dependent parameters are, however, not evident when backfield ratios are used in the analysis. Cd exhibits a tendency towards a negative relationship with magnetic mineral concentration; whilst Mn displays no obvious pattern.

If all sediments, irrespective of their source, are considered there is no obvious observable pattern to the metal-magnetic relationship. This perhaps is not unexpected as the inputs to and the processes working within each discrete source are significantly different. The roof sediments are dependent upon both constructional material and atmospheric inputs; the former regulates the Fe levels yielded from this source and this could provide a distinctly different magnetic mineral constitution from that of the paved surface sediments. This constitutional difference is diagnosed by the characterisation provided by the respective backfield ratios (Fig. 1).

In the case of the subsurface sediments, these are subject to complex biochemical processes involving leaching, complexation, bacterial mobilisation and potentially rapidly changing redox conditions. All these can affect the metal speciation state and thus affect the metal concentration values but do not appear, however, to have any substantial effect upon the mineral magnetic properties. There is also the additional distraction caused by the direct input of roof sediments, with their differing mineralogy, into the sewer system.

4. Conclusion

Magnetic methods have been shown to consistently identify surface source sediments within a small urban catchment although the characterisation of subsurface sources remains problematic. Both metal analyses and magnetic methods identify the major pollutant source to the highway environment to be automobile derived particulates. For a given impermeable surface type and conditions, there is a distinct linear relationship observable between metals (Cu, Fe, Pb and Zn) and ferrimagnetic concentration related parameters.

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THE CONTRIBUTION OF HIGHWAY SURFACES TO URBAN STORMWATER SEDIMENTS AND METAL LOADINGS

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SUMMARY

A 0.05 ha highway subcatchment located within a larger 243 ha separately sewered residential estate in NW London has been investigated to evaluate the relative pollutant contribution of highway surfaces to total urban runoff discharges.

Mass balances for both solid and soluble metal loadings for the subcatchment are 'scaled-up' to estimate the potential impact of rooftop, road surface and roadside gullypots on stormwater loadings discharged to the receiving stream from the parent catchment. The scaling-up procedure predicts a 46%, 78%, 47% and 13% contribution of total Cd, Cu, Pb and Zn loadings respectively from road runoff with ratios of soluble to insoluble metal being 4.0, 1.8, 0.2 and 3.0 respectively for these metals.

The analysis confirms the importance of belowground, in-pipe processes in modifying the inherent geochemical characteristics of road runoff quality as well as highlighting the potential deleterious effect of uncontrolled highway discharges on receiving stream quality.

INTRODUCTION

Stormwater runoff from highway surfaces can present a serious water quality problem to receiving waters particularly if they may be subsequently utilised as sources of potable water supply. Although a wide range of materials are found in highway runoff, particular concern has been expressed at the significant amounts of solids and heavy metals which are associated with road drainage systems (refs. 1,2,3,4,5). It has been suggested that between 35 to 75% of the total receiving stream metal budget might be derived from such highway runoff (refs. 6,7,8,9,10) and that the stream chemistry can on occasion become dominated by the input road drainage water (ref. 11).

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The majority of toxic materials entering surface runoff are inert, occurring in association with inorganic particles or rubber, bitumen and other organics found on the impermeable surface. However, once this material is entrained during a storm event and removed from the surface via the roadside gutter into the subsurface drainage system, considerable phase transformations can occur which affect the pollutant form and strength. There have been relatively few studies identifying the specific source contributions of various impermeable surfaces to final outfall loadings and few attempts have been made to define the belowground modifications superimposed on the characteristics of incoming surface runoff quality. It is these aspects of highway runoff quality which are addressed in this paper.

POLLUTANT SOURCES AND PATHWAYS

The work described in this paper was undertaken on a 0.05 ha asphalted highway surface located within a larger 243 ha residential housing estate on the north west fringes of Greater London. The highway and paved surface drainage empties via conventional gullypot chambers to the subsurface sewer system where the flows are augmented by roof discharges. Full details of the monitoring instrumentation and data acquisition system for the highway subcatchment are given elsewhere (ref. 12), whilst the parent catchment and its separately sewered outfall are described, together with the analytical methods employed in the study, in Harrop (ref. 13).

The pollutant removal rates from the discrete subcatchment are used to predict loadings at the parent catchment outfall for comparison with observed values. The degree of agreement noted between these loadings are then used as a basis for identifying the changes in pollutant loadings occurring within the belowground sewer system which is inherently difficult to study experimentally.

The conventional urban drainage system provides a number of temporary reservoirs intercepting and retaining pollutants following their introduction to and deposition upon the impermeable surface (Fig.1). In this lightly trafficked, residential highway the contaminated fine particulate is preferentially retained near the centre of the road, whilst the greater mass of coarse sediments with their reduced metal concentrations accumulate against the kerb face in the roadside gutter channel.

There is a considerable enhancement of all solid associated metals washed into the gullypot from the source gutter sediments. This enrichment, which is particularly noticeable for Cd and Cu, has been explained by a preferential hydrodynamic mechanism which selectively removes the

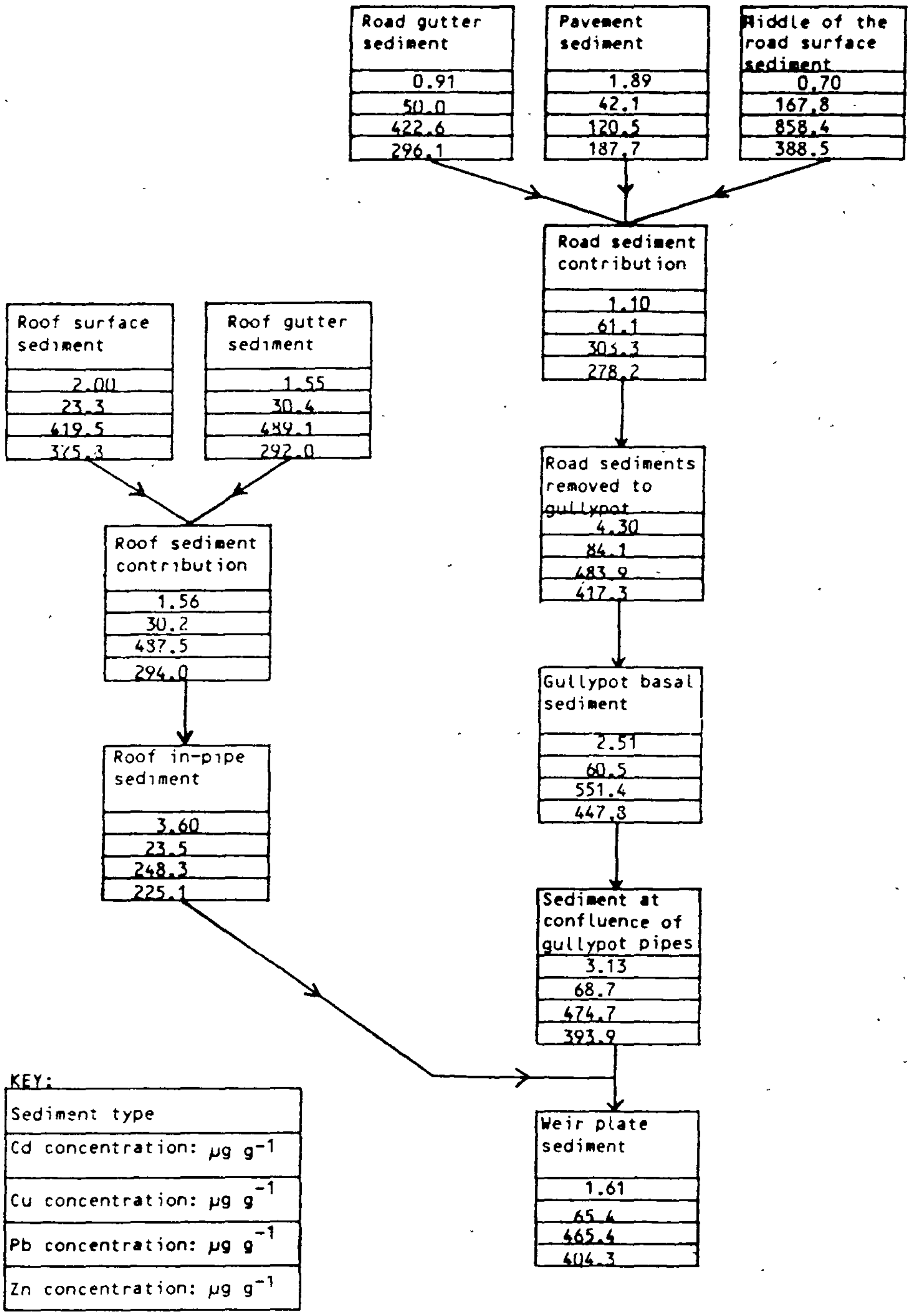

Fig. 1. Solid associated metal pathways through a 0.05 ha sub-catchment

contaminated fines from the road surface (refs. 4,11). This process is particularly noticeable during low flow events.

Figure 1 expresses a long term balance in terms of the pollutant routing and shows that excess concentrations of Cd, and Cu to a lesser extent, are removed from the gullypot chamber whilst the chamber sediments evidently act as a storage reservoir for both Pb and Zn. With the exception of Cd, roof runoff has a dilution effect on sediment metal levels discharged from this impermeable source, although the additional metal input from such rooftop sources does not lead to any observeable increase in the solid associated metal concentrations in the sewer sediments trapped behind the weir plate inserted into the pipe. Indeed, considering the variety of impermeable surfaces included in the experimental programme, and therefore the potential variability in source metal levels, there is not that much difference in the solid associated metals at entry to and within the early belowground stages of the drainage system. This might suggest that an equilibrium is established over a period of several days between solid and dissolved metal phases with metal saturation levels achieving a steady state condition in the belowground sewer sediments.

RUNOFF VOLUMES

The surface runoff for the entire catchment during the sampling period varied between 33.7 and 73.6% for a total annual rainfall of 78.09 cm (ref.13). The average percentage rainfall-runoff value of 56.4% compares with a value of 46% obtained by Wilkinson (ref. 14) for the same catchment when the housing development and consequently the impervious area was less extensive. The rainfall losses cannot, however, be attributed entirely to pervious area infiltration, as recent work (ref. 15) has shown that the assumption that road surfaces are totally impervious is not valid. Surface runoff losses can occur through seepage at the road/pavement joints, infiltration, from spray processes due to vehicle movement, gullypot bypassing and road surface depression storage in conjunction with evaporation. The effective storage capacity of the catchment is 1.61 mm which is at the top end of the 0.13 to 1.5 mm range quoted for other European urban catchments (refs. 16,17).

The predicted annual runoff volume for the total catchment calculated from the annual runoff depth (44.08 cm) and the impervious area (54.9 ha) is 241,811 m^3. The contribution of highway and roof surfaces to this annual discharge is 60.4 and 39.6%, respectively. This compares favourably with water balance studies carried out for the sub-catchment which showed that between 25 and 77% of the directly received sewer flow is from the highway surface with an average of 45% being derived from roof surfaces (ref. 12).

SOLIDS LOADINGS

The analysis of the runoff from 34 storm events at the stormwater outfall pipe has shown that the event mean concentrations of dissolved and suspended solids were 156 g m^{-3} and 194 g m^{-3}, respectively. The latter value is identical to the annual average suspended solids concentration of 193.6 g m^{-3} observed by Wilkinson (ref.14) which corresponded to an annual suspended material loading of 17161 kg. This total is considerably lower than the annual suspended solids loading of 46911 kg which would be expected on the basis of the present data and the 2-3 fold increase in sediment delivery is indicative of the increase in anthropogenic activities which has occurred within the catchment during the last 30 years. Not only will the suspended solids themselves create a detrimental effect on the receiving waters but additionally the sediment-associated toxic pollutants, such as heavy metals, may become available for release to the soluble phase. It is, therefore, important to assess the source loading contributions of both solids and metals to the stormwater outfall and in the case of metals to attempt to determine the distribution between the dissolved and particulate associated phases.

The sediment removal rate for road and pavement surfaces within the sub-catchment has been found to be 1217.1 mg m^{-2} (cm runoff)$^{-1}$ (ref. 15) which is equivalent to a total loading at the parent catchment outfall of 17,772 kg $year^{-1}$. The contribution from roof surfaces can be calculated from the measured average roof runoff suspended solids level for 27 storms at the sub-catchment of 274 g m^{-3} (ref.13). Given the annual estimated runoff from roof surfaces for the total catchment of 95757 m^3, the total annual mass loading would be 26237 kg. When this is combined with the highway surface contribution, a total solids loading at the outfall of 44009 kg is predicted. This figure, which is based on the measured surface sediment removal within the sub-catchment, is close to the expected outfall suspended solids loading of 46911 kg and suggests that the behaviour of this particular pollutant within the small catchment is representative of the total catchment. The shortfall in the solids audit can be attributed to the scouring effect of in-pipe sediment which can contribute some 20% of the total mass discharge (ref.18).

METAL LOADINGS

The annual loading levels of each of the metals Cd, Cu, Pb and Zn (Table 1) have been determined from the mean event concentrations for both the dissolved and the solid associated phases as monitored at the catchment outfall (ref.19) combined with the annual estimated runoff from all impervious surfaces (241,811 m^3).

TABLE 1

Average concentrations and annual loadings of metals at the catchment outfall

	Average metal concentration in the soluble phase (gm^{-3})	Annual metal loading in the soluble phase (kg)	Average metal concentration in the suspended solid phase (gm-3)	Annual metal loading in the suspended solid phase (kg)	Total annual metal loading (kg)
Cd	6×10^{-3}	1.45	2×10^{-3}	0.48	1.93
Cu	45×10^{-3}	10.88	61×10^{-3}	14.75	25.63
Pb	17×10^{-3}	4.11	393×10^{-3}	95.03	99.14
Zn	169×10^{-3}	40.87	298×10^{-3}	72.06	112.93

Using the computational approach previously outlined for suspended solids, these annual metal loadings for the overall catchment (Table 1) can be compared with those predicted by a consideration of pollutant removal behaviour from the impervious surfaces in the sub-catchment. The removal rates of solid associated pollutants from road and pavement surfaces to the receiving gullypots have been measured over a 9 month sampling period (ref.15) and are given in Table 2 together with an estimation of the resulting outfall loadings based on an annual runoff depth of 44.08 cm and a total road and pavement impervious area of 331250 m^2. Such an extrapolation of the data necessarily assumes that the sub-catchment is representative of the whole catchment in terms of pollutant removal characteristics from the impervious surface area.

The soluble metal contributions to the gullypot have been estimated from a detailed study carried out by Morrison (ref.20) on a gullypot in a similar urban catchment in Göteborg, Sweden. The collection and analysis of road runoff entering the gullypot has shown that typical metal distributions between the solid and dissolved phases can be established (Table 2) and these have been used to estimate annual soluble metal loadings that might be expected at the outfall.

TABLE 2

Predicted dissolved and suspended solid associated metal loading contributions to the catchment outfall from highway surface runoff.

	Average metal removal rates to the gully-pot $\mu g\ m^{-2}$ $(cm\ runoff)^{-1}$	Estimated loading of particulate associated metal from highway surfaces (kg)	Ratio of soluble to insoluble metal in road run-off.	Estimated annual loading of soluble metal from highway surfaces (kg)	Estimated annual loading of total metal from highway surfaces (kg)
Cd	4.80	0.07	4.00	0.28	0.35
Cu	92.15	1.35	1.75	2.36	3.71
Pb	370.0	5.40	0.23	1.23	6.63
Zn	347.8	5.08	3.00	15.24	20.32

A major problem to be considered when extrapolating the loadings of metals from surface sources to the stormwater outfall is to account for the transformations which occur within the below-ground system where physical and biochemical processes can combine to change the metal distribution between the soluble and solid associated fractions. Very little work has been undertaken to evaluate in-pipe quality mechanisms although recent gullypot studies (ref.20) have shown that large changes in the associations of some metals can occur between entering and leaving the gullypot system. In the case of Pb, an analysis of several discrete storm events has shown that on average the dissolved metal increases by 49% and the suspended solid associated metal can increase by 200%. Loading enhancements through the gullypot system were also shown by Cd and Cu with the reverse situation being true for Zn. This effect of the gullypot on changes in metal loadings is clearly shown by a comparison of Tables 2 and 3.

TABLE 3

Predicted metal loading contributions to the catchment outfall from gullypot outflow pollutants.

	Estimated annual loadings of metals from gullypot outflow (kg)		
	Solid associated	Dissolved	Total
Cd	0.09	0.30	0.39
Cu	2.85	8.14	10.99
Pb	16.20	1.83	18.03
Zn	4.93	2.59	7.52

In addition to highway surfaces, roof surfaces, which exhibit a fast rainfall-runoff response time, have been shown to make considerable metal contributions to stormwater pollution (ref.21). The annual loading of suspended solids from roofs within the total catchment has already been estimated to 26237 kg and if this is combined with the average metal concentrations for roof sediments, it will enable a computation of the annual roof surface contribution to the solid associated metal loading (Table 4). The metal concentrations used in this calculation are those for roof gutter particles finer than 250 µm since this is the size fraction expected to be most readily removed as suspended solids. Soluble metal loadings in roof runoff have been estimated using the soluble/insoluble metal ratios relevant to road runoff from Table 2. The resulting total metal loadings derived from roof runoff are shown in Table 4 below.

TABLE 4

Predicted metal loadings at the catchment outfall from roof runoff

	Average Concentration of metal in <250 µm roof gutter sediments (µg g^{-1})	Estimated annual loadings of metals from roof surfaces (kg)		
		Solid associated	Dissolved	Total
Cd	3.36	0.09	0.36	0.45
Cu	41.9	1.10	1.92	3.02
Pb	629.6	16.52	3.80	20.32
Zn	474.9	12.46	37.38	49.84

SOURCE CONTRIBUTIONS TO CATCHMENT LOADINGS

Combination of the predicted contributions to catchment outfall loadings from highway, gullypot and roof surfaces enables a comparison to be made with the observed annual loading values obtained from the measured average metal concentrations at the outfall (Table 1). This data is summarised in Table 5 together with the estimated percentage contributions from highway and roof surfaces for each of the 4 metals.

TABLE 5

Comparison of predicted with observed annual loadings at the catchment outfall.

	Predicted annual metal loadings from road and roof surfaces (kg)	Percentage contriubtion from roads	Percentage contribution from roofs	Percentage predicted of observed metal loading at the outfall.
Cd	0.84	46.4	53.6	43.5
Cu	14.01	78.4	21.6	54.7
Pb	38.35	47.0	53.0	38.7
Zn	57.36	13.1	86.9	50.8

The contributions to the predicted loadings from the highway surfaces, except in the case of Cu, are substantially lower than might have been expected given the expected inputs from vehicular sources. Beckwith et. al (ref.22) have found Pb levels of up to 119.4 mg g^{-1} in exhaust particulates, Zn levels of up to 186.6 mg g^{-1} in external exhaust pipe particulates and Cu concentrations of up to 14.5 mg g^{-1} in wheel hub particulates, all of which will contribute substantial metal loadings to highway surfaces. However, in the case of Pb which has a high affinity for the solid phase, the highway contribution will be balanced to a certain extent by the higher sediment contribution (60%) provided to the outfall loadings by roof surfaces. The large proportion of Zn predicted in the analysis from roof surfaces is consistent with the higher atmospheric deposition values which have been measured for this metal compared to Pb at sites through Europe (refs.23,24). Thus it is possible that Zn is distributed more evenly over impervious surfaces throughout the catchment and that the more rapid response of roof surfaces forces the higher loadings through the drainage system from this source.

It is considered that the measured pollutant removal rates (Table 2) represent lower range values with regard to the overall highway contributions as the vehicle movement within the sub-catchment is typical of the lowest traffic densities exhibited by the parent catchment. Metal levels in stormwater runoff from highways have been reviewed (ref.4) and clearly show an increase in the sequence rural, urban/residential, motorway type locations. In a specific study of runoff from a 0.448 km^2 section of a major highway (>100,000 vehicles day^{-1}) in Rhode Island, USA, Hoffman et.

al., (ref.10) found metal loading factors of 2715, 11460 and 36 g km^{-2} cm $rain^{-1}$ for Cu, Pb and Cd, respectively. Incorporation of these values into our model, produces predicted highway contributions to the catchment outfall loadings of 70.2 kg Cu, 296.5 kg Pb and 0.93 g Cd. Comparison of these values with the data given in Table 2 indicates, particularly in the case of Pb, the considerable influence that increased vehicular activity can have on the predicted metal loadings.

The percentage predicted to observed metal loadings at the outfall (Table 5) are much lower than the same ratio for the sediment which reflects the extent of potential changes to which metals are subjected as they are routed from the above ground phase through the sewer system to the outfall. The metals will be subject to adsorption, precipitation, deposition and solubilisation processes due to changes in ambient oxic/anoxic conditions and pH levels and the influence of biochemically mediated reactions. Thus, Morrison (ref.20) has shown that the dissolved levels of Cd, Cu, Pb and Zn increase in the gullypot liquor between storm events and are potentially available for flushing out at the onset of the next storm event. Examination of the pathway diagram for the sub-catchment (Fig.1) shows that the sediment associated metal levels show little change in the early part of the below ground system. However, it is in the later, downpipe sections of the oversized sewer system that deposition and re-mobilisation of toxic sediments will most affect metal partitioning and transfer between the soluble and solid phases. Previous work in this catchment (ref.19) has clearly demonstrated that the particulate associated metal concentrations at the outfall are considerably enhanced when compared to surface derived solids. The role of sediment/water interactions in sewers is poorly understood and the transformation of pollutants as they travel through conveyance systems to receiving waters has been clearly identified as a future research need in the field of urban runoff pollution (ref.25). Despite this lack of knowledge, it is evident that highway runoff can present problems of long term, chronic toxicity to receiving streams. Where road drainage discharges to a public sewer as in the case of the subcatchment investigated, there is no requiring consent under existing legislation and therefore there would not appear to be any mechanism that might force remedial action against the chronic pollution situation. Where highway drains are not connected to the sewer system, as is often the case with motorway drainage, proposed legislation under Section 32 (1) of the Control of Pollution Act 1974 can invoke Section 103 of the 1959 Highway Act and subject the offending drain to full consent provisions.

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