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HEAVY METALS IN URBAN STREET SURFACE SEDIMENTS

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ABSTRACT.

A literature survey has been undertaken of the sources, levels and effects of heavy metal pollution in the urban street environment. Established techniques for the determination of heavy metal levels in urban dusts have been reviewed, and appropriate methods selected for use in the research project.

Spatial and temporal variations of Cd, Cu, Pb and Zn in street dust have been investigated at a number sites. Metal loadings showed stronger spatial variation than concentrations with the greatest metal loadings occurring in the gutters and kerbsides. The results have been assessed in terms of surface type and condition, traffic loadings and antecedent weather conditions.

The chemical associations of heavy metals in street dust, and their relationships to particle size have been investigated. Lead and Zn were associated mainly with carbonates and Fe-Mn oxides, whereas Cu is largely found in the organic fraction. Cadmium shows the greatest affinity for the exchangeable phase, and is therefore considered the most environmentally mobile metal studied.

In addition to the studies mentioned above levels and chemical associations of heavy metals in school playground dust contaminated by paint flakes have been investigated. The levels of Pb were much higher than those previously reported. Exchangeable Pb concentrations represented a significant hazard to children playing in the area.

The final stage of the research project involved the operation of a sampling network to establish a mass balance for Cd, Cu, Pb and Zn within a residential urban street. Metal levels in atmospheric deposition, street sediments and runoff were monitored over an eight week period. Stormwater runoff was found to remove only a minor fraction of the metal deposited in the catchment during the sampling period.

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CHAPTER 1. INTRODUCTION.

1.1. Research Context.

Over the past two decades considerable attention has been given to the levels and effects of heavy metal pollution in the urban environment. This interest has focussed predominantly on Pb, due to the scale of use and obvious toxic effects of this metal relative to other widely used metals. Initial studies were concentrated on the heavy metal content of the atmosphere, drinking water and soils. Settled dusts in urban areas are now widely recognised as being an important source of toxic metals, particularly to young children who can ingest metals by sucking their fingers and other contaminated objects. Additionally rainfall may wash heavy metals via stormwater runoff, to receiving waters where considerable pollution may result.

The role of settled dusts in the pollutant pathways and health effects of heavy metals are as yet poorly understood. A number of physical and chemical properties including the pollutant concentration, the size distribution of the metal containing particles, and the chemical form in which the metals occur are known to be important factors influencing toxicity and environmental mobility.

This research has been carried out with the following major objectives:

a) to establish a procedure for obtaining representative samples for the assessment of heavy metal levels in urban street sediments;

b) to establish detailed variations in heavy metal loadings and concentrations across selected urban road surfaces of varying composition, age and condition;

c) to determine the physico-chemical associations of heavy metals in urban street sediments;

d) to assess the relative importance of Pb based paint as a source of environmental Pb;

e) to relate metal loading rates to input and output controls, and to develop a mass balance for a typical highway dominated urban catchment.

1.2. The Metals Selected for Investigation.

The concentrations and loadings of the metals Cd, Cu, Pb and Zn in road surface sediments were investigated during this research project. It was not possible to analyse a wider range of heavy metals because of the time required for the extensive analytical methodology. Instead a selected range of metals, including those for which motor vehicles are known to be a major source in the roadside environment, were studied. Lead levels in road sediment have been reported extensively in the literature because this metal is a major vehicle derived pollutant which has given rise to much public concern. Cadmium was included in the study because it is a very toxic substance which is thought to be highly mobile in the environment.Reported cases of Cd poisoning in Japan have lead to considerable interest regarding the environmental levels of this element. Copper and Zn are widely used metals and are therefore commonly encountered pollutants. Although both metals are essential elements for plant and animal nutrition they are toxic at relatively low concentrations to many aquatic organisms. Their toxicity to humans is lower.

1.3. Thesis Content and Organisation.

The structure of the thesis and description of the research programme is outlined below. Following this introductory section, Chapter 2 provides a review of the literature which gives background information for the research project. The major sources of heavy metals in urban street sediments are identified and where possible quantified along with environmental levels, physico-chemical forms, transportation processes and critical pathways.

Although there is a considerable amount of literature on heavy metals in the urban environment, much of the published information on heavy metals in street sediments has suffered because of the problems in interpreting the data. One of the problems of interpretation is the wide range of sampling and analytical techniques which have been employed. This makes comparisons between different studies difficult. Chapter 3 reviews the sampling and analytical techniques described in the literature. Experimental work carried out to develop methods of sample collection and analysis capable of providing representative results is also described .

Chapters 4 to 7 detail the four main aspects of the experimental work undertaken in the course of the research. The first of these Chapters describes an investigation into the spatial and temporal variations of heavy metals in street dust at selected urban sites. This provides information required to design a representative sampling strategy. The sites were chosen in consultation with the Air Pollution Section of the former Greater London Council (now London Scientific Services) and included; a busy trunk road, a residential side street and an estate perimeter road of medium traffic density.

An investigation into the speciation of heavy metals in street dust, and the relationship of these properties to particle size is described in Chapter 5. Chemical speciation techniques provide valuable information concerning the relative ease of release of different heavy metal pollutants from road sediments to, in particular, the aquatic environment.

The discussions presented in Chapters 4 and 5 formed part of two co-authored publications entitled 'Levels And Physico-Chemical Associations Of Cd, Cu, Pb And Zn In Road Sediments' (Hamilton et al. 1984), and 'Resuspension Of Heavy Metals From Road Surface Dust' (Hamilton et al. 1985).

Parallel to the studies reported in Chapters 4 and 5, heavy metal levels (particularly Pb) in surface dusts in a school playground have been studied. This work was carried out in conjunction with the Greater London Council and is described in Chapter 6. The aim of the work was to determine variations in metal levels while the exterior paintwork was being stripped and repainted. Additionally the dusts were analysed using the sequential extraction scheme described in Chapter 5 with a view to assessing the relative contributions of vehicle emitted Pb, and Pb from paint to the playground dust. Aspects of this work were reported in a co-authored publication entitled 'Environmental Contamination Caused By Lead Based Paint' (Duggan et al. 1986).

The development and operation of a sampling and analytical programme to establish a materials balance for heavy metals in a typical urban street are outlined in Chapter 7. This involved the instrumentation of a site at South Oxhey (near Watford) to monitor the levels of heavy metals in the atmosphere, in rainfall (soluble and particulate associated), in dustfall, in runoff (soluble and particulate associated), and in street sediments. A preliminary report on this work was presented in the paper 'Metal Mass Balance Studies Within A Small Highway Dominated Catchment' (Hamilton et al. 1987).

The concluding Chapter provides a general overview of the main conclusions and suggestions for future work, and attempts to place various components of the work into the context of the project as a whole.

CHAPTER 2. A LITERATURE REVIEW OF HEAVY METALS IN URBAN STREET SEDIMENTS; SOURCES, PATHWAYS AND EFFECTS.

2.1. Sources of Heavy Metals in the Urban Environment.

Heavy metals in street sediments may be derived from a number of sources, both natural and anthropogenic. Figure 2.1 shows the sources and pathways by which metals can reach the street surface and also be removed from it. Natural sources include fires, volcanoes and the weathering of rocks and soils. The anthropogenic contributions are of relatively recent origin, but have increased rapidly resulting in a build up of metal concentrations in many street sediments to unacceptable levels. The magnitude of some of these sources can be estimated whereas others remain unquantifiable. Furthermore in many instances there is no clear division between natural and anthropogenic sources, as many processes and pathways are involved in the environmental movement of heavy metals.

2.1.1. Natural sources.

In the uncontaminated environment, soils produced by weathering reflect the composition of underlying parent materials. A listing of some widely quoted average concentrations of the heavy metals, Cd, Cu, Pb and Zn, in soils is given in Table 2.1. In residual soils elevated heavy metal concentrations are characteristically found over metalliferrous beds. Nevertheless for the heavy metals studied here soils represent only a minor source in urban areas. A comprehensive survey of United Kingdom regional heavy metal variations has been reported by the Applied Geochemical Research Group at Imperial College, London (Webb et al. 1978).

Prior to mans' intensive use of heavy metals the major natural sources to the atmosphere were windblown dusts, forest fires, volcanoes and sea salt sprays. The total natural and anthropogenic emissions of heavy metals to the atmosphere have been estimated and compared by Nriagu (1979a). The annual anthropogenic emission of Cd and Pb exceeded the natural rates by over an order of magnitude. Current anthropogenic emissions exceed the natural rates of emission for Cu and Zn by 300% and 700% respectively.

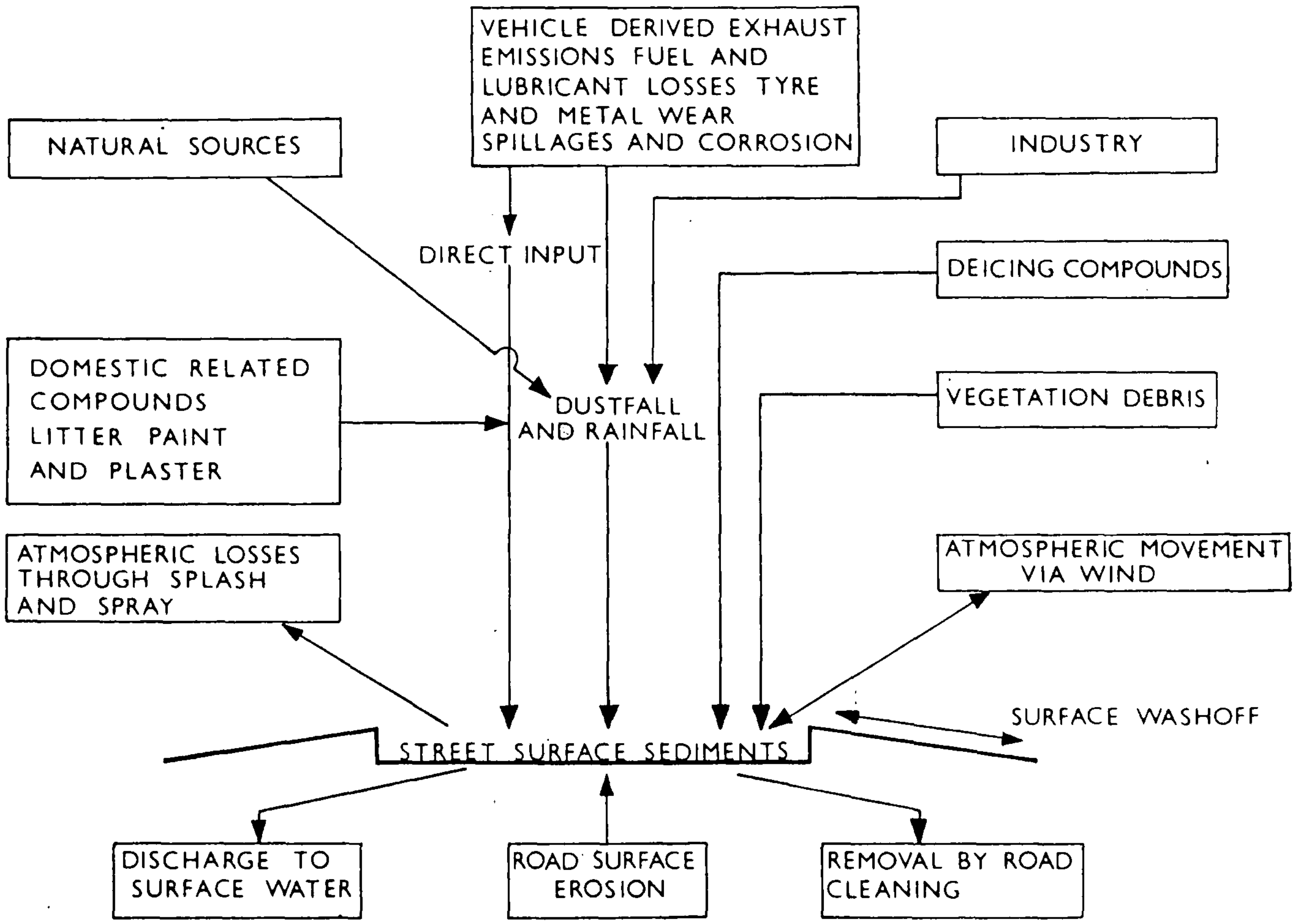


Figure 2.1. Road surface inputs and outputs of heavy metals (after Pope 1980)

Table 2.1. Concentrations of Cd, Cu, Pb and Zn in uncontaminated soils.

	Total content µg g^{-1} (dry matter)			
	Cd	Cu	Pb	Zn
average	0.5	20.0	10.0	50.0
range	0.01-0.7	2.0-100.0	2.0-200.0	10.0-300.0

Source Baker and Chesnin (1975)

2.1.2. Industrial emissions.

Most industrial processes releasing heavy metals into the environment are controlled. However industrial processes continue to be a source of environmental damage even when constructed to the highest standards. European emissions of heavy metals from various sources are given in Table 2.2. Total United Kingdom emissions are included for comparison. Non-ferrous metal production is the largest single source of Cd, Cu and Zn. Nearly all industrial processes involving Zn are subject to the presence of Cd because both metals are associated naturally and derive from the same ores. Although Pb smelters release large amounts of Pb into the atmosphere the relative unimportance of industrial Pb compared with petrol derived Pb is shown by the data in Table 2.2. This trend is confirmed in the national emission inventory for the United Kingdom (Hutton and Symon 1986). On a local scale industrial activities can cause substantially elevated levels of Pb and other heavy metals. Contamination is usually most severe within 3 km of any stack and declines progressively in a curve until background levels are reached at about 10-15 km. The spatial distribution is usually elliptical, with the major axis extending in the direction of the prevailing winds allowing for local topography (Nriagu 1978, 1979b+c, 1980; Harrison and Laxen 1981; Ratcliffe 1981; Hallet et al. 1982).

In the immediate vicinity of smelters it has been shown that fugitive dust from trucking and hauling operations, as well as the entrainment of contaminated soils by wind gusts, are the primary sources of heavy metals in settled dusts (Schwitzgebel et al. 1983). Beyond approximately 1000 m stack emissions become the primary source (Bolter et al. 1972; Rolfe and Jennet 1975; Turner et al. 1980).

In addition to smelters and refineries, manufacturing plants such as factories, chemical plant, power stations and incinerators also release trace metals. The pollution pattern conforms to that derived

Table 2.2. Anthropogenic emissions of heavy metals to the atmosphere in Europe.

		Percent of total metal emissions			
Source		Cd	Cu	Pb	Zn
Fossil fueled power plant		3.7	8.9	0.9	1.6
Industrial, commercial and residential fuel combustion		5.7	13.1	0.7	2.3
Wood combustion		0.9	9.7	0.5	5.7
Gasoline combustion		1.1	-	60.4	-
Mining		<0.1	1.2	0.9	0.6
Primary non-ferrous metal production	Cu-Ni	22.0	50.6	7.5	3.1
	Zn-Cd	57.4	2.8	6.4	61.0
	Pb	0.3	0.8	8.5	0.2
Secondary non-ferrous metal production		0.1	0.4	0.4	4.3
Iron and steel production		2.1	11.0	11.9	12.8
Refuse incineration		3.1	1.7	0.7	7.3
Phosphate fertiliser production		1.0	0.5	-	0.3
Cement production		0.6	-	0.6	-
Total emission rate (t y^{-1})		2700	15500	123000	80000
United Kingdom emission rate (t y^{-1})		99	580	10098	3488

Source Pacyna (1984)

from smelters, being controlled by the prevailing winds, and fallout is greatest nearest any stack. Klien and Russell (1973) found a marked enrichment of Cd, Cu and Zn in soils surrounding a coal power plant. Lee (1972) investigated the surroundings of a Cheshire factory producing tetra-ethyl Pb and found the deposition was greatest within 400 m of source, but was still above background at 800 m. Similar results were obtained for a Pb battery factory in Lancashire (Ratcliffe 1975). The processing of phosphates has been found to contaminate soil with Pb and Zn to such an extent that background levels were reached only at 16 km distance from the factory (Severson and Gough 1976).

A recent report has indicated considerable pollution arising from printing presses, with Pb in dust values reaching as high as 12% (Jensen and Laxen 1985). Metal recovery and scrap yards have been identified as an important localised source of heavy metals in urban areas. Little and Heard (1978) observed Pb in dust levels up to 12000 $\mu g\ g^{-1}$ associated with scrap yards. Fugitive dust appears to be the main pathway for metal dissipation.

Table 2.2 shows that combustion of fossil fuels is a significant source of Cd and Cu. Products containing heavy metals such as batteries, paints and plastics also release metals to the atmosphere when burnt. On a global scale waste incineration is an important source of metalliferrous aerosols (Nriagu 1979a). In the United States it may be the principal source of Cd and Zn in some urban areas (Greenberg et al. 1978; Kowalcyzyk et al. 1978). In the United Kingdom the contribution of commercial combustion of municipal wastes to metal levels in urban areas is not readily quantifiable, although the D.O.E. (1980) estimate that for Cd this probably represents a minor source. Only the fine fraction of the particulate matter can remain airborne. Demuynck (1975) calculated an emission inventory which took account of the size distribution of the emissions. Only 18% of the particulate matter smaller than 10 µm originated from metallurgical industries and 33% from combustion source, compared with 50% and 21% for all particulates.

2.1.3. Domestic and allied sources.

The ubiquity of Pb in and around domestic premises is well known. In addition to the occurrence of Pb in paint and house dusts, excess Pb and other heavy metals have been found in printed matter, paper, textiles and plastics. The metals fulfil a variety of uses such as heat and light stabilisation, mold inhibition and durability improvement (Lagerwerff and Specht 1970; Bogden and Louria 1975; Royal Commission on Environmental Pollution 1983).

Old paint has been identified as a particularly important source of adventitious Pb (D.H.S.S. 1980). Pre-1930 paints and primers contain substantial quantities of Pb pigments and primers. Lead in paint can be transferred to soils and dusts by natural weathering, by sanding and scraping, or by burning off the old paint prior to repainting. Sturges and Harrison (1985) using microscope techniques determined that in some residential street dusts up to 20% of the Pb content may be derived from paint sources. Very high Pb concentrations have been found in soils and dirt in the immediate vicinity of houses, particularly where paintwork is deteriorating and where houses are of wooden construction. However, even where reparation of surfaces has been carried out, the levels fall off rapidly with distance away from the source (Ter Haar and Arnow 1974; Jordan and Hogan 1975; Bogden and Louria 1975).

Cadmium, Cu and Zn are also used in paints although very little work has been carried out to determine levels of these metals in the environment derived from this source. In the United States, Solomon and Hartford (1976) analysed paint and paint dust for Cd and found maximum levels of 50 µg g^{-1} and 6-8 µg g^{-1} respectively. In the same study Cd in dust levels as high as 105 µg g^{-1} were measured in some homes. These high levels were attributed to dust produced by abrasion of the rubber backing used on carpets. A random sample of this material exhibited a Cd concentration of 2000 µg g^{-1}. In a survey of British homes this material was found not to be a source of Cd (Harrison 1979).

In addition to paints other construction materials may contain heavy metals. Berman (1980) suggests that plaster and putty on window frames may be possible sources of Pb. Lead is also used in weather protective strips and flashings on buildings, erosion of which can result in considerable metal build up in adjacent dusts (Table 2.3).

Table 2.3. Metal levels in dust adjacent to weather protective flashings.

Metal	Cd	Cu	Pb	Zn
Concentration µg g^{-1}	12	602	29993	605
Loadings mg m^{-2}	0.2	9.3	464.9	9.4

Source Warren (1983)

2.1.4. Traffic related sources.

Traffic related sources within an urban area contribute a broad range of pollutants in a number of different ways. The contributions are difficult to quantify but have been categorised as follows (Sartor and Boyd 1972):

a) leakages of fuel, lubricants, hydraulic fluids and coolants;
b) fine particulate wear from tyres, clutch and brake linings;
c) particulate exhaust emissions;
d) dirt, rust and decomposing coatings from vehicle underbodies;
e) vehicle components broken by vibration or impact.

In an attempt to quantify these traffic related deposits, Shaheen (1975) measured pollution deposition rates at a number of sites. It was found that only 5% by weight of the deposits originated directly from motor vehicles. These pollutants are potentially the most toxic and include Pb, which is introduced principally through the use of tetra-alkyl Pb compounds in petrol as anti-knock agents. The maximum permissible Pb content of petrol in the United Kingdom has been progressively reduced over the past decade from 0.84 to 0.15 $g\ l^{-1}$. Despite the lower Pb content, increased consumption of petrol has served to maintain the total emissions of Pb close to the 1971 level (Royal Commission on Environmental Pollution 1983). Some of the emitted Pb is lost by evaporation and some passes through the engine uncombusted. However, only low levels of tetra-alkyl Pb compounds are found in the atmosphere (Harrison et al. 1974; De Jonghe and Adams 1982).

The major portion of the Pb in exhaust emissions occurs as particulate associated inorganic compounds. The emission rate is dependent on the mode of operation. Higher engine speeds and loads result in increased Pb emission rates (Hirschler and Gilbert 1964; Ter Haar et al. 1972 and Habibi 1973). During city driving, as little as 7% of the input Pb may be exhausted the remainder is deposited in the engine and exhaust or retained in the engine oil (Ter Haar et al. 1972). Deposited material is re-entrained in the exhaust gas, and over 2000% of the input Pb can be emitted when accelerating rapidly (Hirschler et al. 1957). Over a complete driving cycle less than 100% of the input Pb is emitted, although there is a general increase in emission rate with mileage accumulation (Hirschler et al. 1957; Ter Haar et al. 1972).

Lead is emitted from the exhaust in two main size groupings: smaller particles of <1 µm and larger particles of 5-50 µm (Habibi 1973; Ganley and Springer 1974). The smallest particles represent primary Pb emissions, which initially are approximately 0.015 µm in diameter but are subject to rapid growth in ambient air by coagulation due to Brownian diffusion. Few particles exist in the 0.5 to 5 µm size range (Ter Haar et al. 1972), and only a small contribution is made to the emissions by particles greater than 300 µm in diameter (Habibi 1973). The ratio of small to large particles in exhaust emissions is dependent on driving mode and speed. During rapid acceleration the larger particles predominate due to resuspension from within the exhaust (Ter Haar et al. 1972), while under cruise conditions smaller particles dominate the size spectrum (Ganley and Springer 1974). This obviously affects the deposition of exhausted Pb. The larger particles are subject to rapid gravitational settling, and so are deposited close to source (Habibi 1973). The smaller particles remain airborne for longer and dominate away from the road environment (Daines et al. 1970).

Leakage of engine oil will deposit Pb on the road along with other metals derived from the wear of plating, bearings and bushes and other moving parts within the engine. Motor oil also contains heavy metals, in particular Zn compounds, which are present as stabilising additives. A number of workers have shown that a considerable build up of heavy metals can take place in motor oil during use (Table 2.4). Furthermore, Grossling (1976) estimates that 5% of engine oil leaks to the road surface which although a minor source compared with others, such as exhaust emissions, may cause highly localised metal pollution.

Zinc compounds are used as filler materials in motor tyres, and Cd is present as a result of its natural association with Zn. Estimations of the emission rates of tyre rubber wear products vary considerably and Malmqvist (1983) estimates a tyre produces 30 mg of wear products per km. In the United States, Dannis (1974) determined the average wear rate per tyre to be 90 mg km^{-1}, with a lower value under cruise conditions (5-20 mg km^{-1}) and an elevated level while cornering (>500 mg km^{-1}). Christensen and Guinn (1979) have related the concentration of Zn in urban runoff to the Zn content of tyres, and have calculated an average deposition on road surfaces of 0.003 g Zn $vehicle^{-1}$ km^{-1}. In the United Kingdom the D.O.E. (1980) estimate the concentration of Cd in tyres to be very low (5-6 µg g^{-1}). They estimate that tyres lose up to 20% of their weight during their useful lifetime, and thus produce an emission of 1 tonne per year of Cd across the United Kingdom. The wear products from tyres vary in size from 0.01 µm to large pieces of debris, with the larger particles dominating the total

Table 2.4. Metal content of new and used materials ($\mu g\ g^{-1}$).

Material	Cd*1	Cu	Pb	Zn
Lubrication grease	-	nd	nd	164
Motor oil	0.2-0.26	3	9	1060
Used oil	-	36	13600	3570 *2
Transmission fluid	-	nd	8	244
Brake linings	-	30600	1050	124
Rubber	20-90	247	1110	3570
Asphaltic pavement	-	51	116	164
Concrete	-	99	102	417
Salt	-	2	2	1

- not determined   nd not detected

Source Shaheen (1975), except *1 Lagerwerf and Specht (1970)
*2 Wilber and Hunter (1980)

mass. Measurements near a highway have shown that tyre debris mostly settles within 5 m of the pavement edge, and that airborne particulates represent only a minor fraction of the total tyre wear (Cadle and Williams 1978; Pierson and Brachaczek 1974). Thus Cd is emitted by vehicles mainly as large particles of tyre dust whose pollution contribution away from the road is slight (Harrison and Williams 1979). Another metal produced by wear of vehicle components is Cu (Table 2.4). In addition to engine wear, considerable amounts of Cu are produced by the erosion of brake linings, to which Cu is added to increase mechanical strength and assist heat dissipation. The emission of particulates from brake linings varies with the speed at which the vehicle is travelling (Jacko and DuChame 1973). Malmqvist (1983) estimates that for a car travelling at 64 km hr^{-1} and braking to a stop 1.2 times per km, 1.5 mg km^{-1} of sedimentary particulates would be produced.

The use of road salt to maintain ice free roads is a widely accepted practice. It has been suggested that heavy metal impurities in deicing salt may be a source of metal pollution (Hedley and Lockley 1975). Laxen and Harrison (1977) however estimate that this is unlikely to represent a source of more than 5% of the total highway Pb. Gosz (1977) suggests that road salting mobilises natural soil and organics which provide transport sites for heavy metals during runoff events.

Street surface construction materials are a possible source of metal contaminants. Included in this category are asphalt and portland cement, and their various abrasion products. In addition there are typically small amounts of road marking paints, crack fillers and expansion joint compounds (Table 2.4). Turner (1973) found very little Pb derived from yellow road markings. Elemental analysis of yellow road paint by Scanning Electron Microscopy (SEM) with X-ray fluorescence analysis (XRF) has shown the presence of several other metals, notably Cr, Cu, Ti and Zn (Table 2.5). Unless the paint is in poor condition only a small contribution will be made to adjacent sediments. Although large quantities of road marking paints are used, only a small proportion is in a form available for uptake by humans (Royal Commission on Environmental Pollution 1983). Sartor and Boyd (1972) identified three factors which affect the generation rate of materials from road surfaces: the age and condition of the surface; local climate; and leakages and spills of fuels and oils, which hasten the degradation of asphaltic surfaces. Pope et al. (1979) also identified the road surface as a possible source of heavy metals and reported Cu concentrations in the asphaltic fraction of crude oil in the range 1-10 $\mu g\ g^{-1}$. It was noted that metals may be extracted from the surface as oil soluble components during dry periods when considerable build up of oil on road surfaces is experienced.

Table 2.5. SEM/XRF analysis of yellow road markings.

Metal	Al	Ca	Cr	Cu	Pb	Si	Ti	Zn	
% content	0.99	40.96	2.19	2.96	7.03	32.6	5.21	1.40	for Z>12

Source Warren (1983)

2.2. Heavy Metals in the Atmosphere.

Possibly the most important pathway by which heavy metals reach the road surface is via the atmosphere. The contribution of each of the various sources to the atmospheric burden of metals depends on the quantity and physical characteristics of the aerosols containing the metals, the location and height of the emitter, the topography of adjacent areas and the prevailing meteorological conditions. Additionally, levels in ambient air are also influenced by land use characteristics of an area, and the wind entrainment of contaminated dusts. These factors lead to widespread temporal and spatial variations in atmospheric metal concentrations, and consequently in deposition rates from the atmosphere.

2.2.1. Distribution of heavy metals in the atmosphere.

A large volume of data is available concerning the concentrations of atmospheric trace metals. The results of a number of surveys of airborne concentrations at rural, roadside and urban sites are given in Table 2.6. It can be seen from this table that the atmosphere in urban areas is normally contaminated with heavy metals compared to that in rural areas.

In general the average suspended heavy metal concentration in a given area is related to the population density. In a survey of nine cities in the United States during 1968-71 mean Pb levels were found to increase from 0.17 $\mu g\ m^{-3}$ in Los Alamos, a city with a population of 11,300, to >3.0 $\mu g\ m^{-3}$ in Los Angeles which has a population of 2.8 million (Saltzman et al. 1985). This reflects the increasing intensity of metal emissions from automobile and industrial sources. Towns with a concentration of metal industries may be expected to have higher than average atmospheric metal concentrations (Kretzschmar et al. 1977). Highspots in suspended metals are associated with metal smelters, incinerators and other major point sources (Muskett et al. 1979; Turner 1979; Barrett et al. 1981, 1983). Levels of heavy metals have been shown to increase towards the centre of large cities, and at those sampling areas where traffic is an important source (Kretzschmar et al. 1977; Duggan and Burton 1983). The extent of this spatial pattern varies for different metals. In an area with no major industrial inputs Harrison and Williams (1982) observed substantial enrichment in Pb and Zn concentrations on going from a rural to an urban area. No corresponding increase in Cd levels was found (Table 2.6) and it was concluded that motor vehicles were not a significant source of Cd in the urban atmosphere.

2.2.2. Metal concentrations close to highways.

The effect of vehicle derived metal emissions on the ambient levels in the roadside environment is not clear other than for Pb. The ambient concentrations of Pb vary considerably from site to site (Table 2.6). In general the levels in various land use districts follow the sequence, central business>heavy industrial>residential >rural (Creason

Table 2.6. Heavy metal concentrations in atmospheric particulates ($\mu g\ m^{-3}$; except Cd $ng\ m^{-3}$).

Location	Cd	Cu	Pb	Zn	Reference
Chicago					
industrial	3	-	1.02	-	
urban residential	4	-	2.03	-	
suburban	2	-	1.39	-	
suburban commercial	2	-	2.04	-	Creason et al. (1971)
Champaign-Urbana					
town centre	-	-	1.43	-	
University	-	-	0.75	-	
residential	-	-	0.29	-	
suburban commercial	-	-	0.25	-	
rural	-	-	0.17	-	Solomon et al. (1977a)
M4 motorway	-	-	8.9	-	
M40 motorway	-	-	3.3	-	
M40 on embankment	-	-	6.4	-	
M40 in cutting	-	-	10.3	-	Little & Wiffen (1978)
London (heavy traffic)	-	-	1.4 (0.6-5.5)	-	Hickman & Lunn (1981)
Lancaster					
town centre	1.17	-	3.77	0.14	
rural	1.28	-	0.13	0.06	Harrison & Williams (1982)
London Heathrow					
(tunnel portal)	-	-	3.8 (0.1-24.1)	-	Colwill et al. (1983)
Kent	<1	0.04	0.2	0.05	
Carshalton	<1	0.03	0.3	0.15	
Kew	<1	0.02	0.5	0.08	
Hampstead	<1	0.01	0.55	0.08	
Greenwich	<1	0.05	1.1	0.5	
Stratford	<1	0.07	0.9	0.5	
The Strand	<1	0.03	0.9	0.2	Duggan & Burton (1983)

et al. 1971; Solomon et al. 1977a). Within each land use area certain transient traffic and weather conditions tend to be characterised by very high Pb levels. This is illustrated by tunnels (Hickman 1976), areas close to slow moving traffic (Lawther et al. 1973) and in the vicinity of motorways (Bevan et al. 1974; Little and Wiffen 1978). The Pb emissions are related not only to traffic density at a particular location, but also to the operating mode of the vehicles and the level of Pb in petrol (see Section 2.1.4).

The particulate Pb concentrations decrease with distance either side of a road according to an exponential function, with higher concentrations to the leeward side (Cholak et al. 1968; Daines et al. 1970; Bevan et al. 1974; Reiter et al. 1977; Little and Wiffen 1978). In most cases the decrease in concentration was found to be 50% for distances between 10 and 50 m from the road, depending on traffic and dispersion conditions. Therefore the most significant effect of traffic on the atmospheric Pb concentrations is limited to a narrow band bordering the road. The size of Pb bearing particles also decreases with distance away from the roadside. Daines et al. (1970) noted that 50% of the particles larger than 6.5 μm had dropped out by 600 m. Shuck (1970) in an examination of recorded data noted that 90% of the particles were less than 3.4 μm, and would therefore show little tendency for deposition. Little and Wiffen (1978) similarly noted that for motorways the fall off in concentration was primarily due to atmospheric dispersion of sub-micron particles, rather than deposition.

There are fewer studies of Pb in air levels in street canyons as opposed to open roadways. Lawther et al. (1973) observed that higher concentrations existed in narrow streets where traffic volumes were only a fraction of those on busy streets and motorways, but where dispersion was very poor. Reiter et al. (1977) assumed that the factors controlling diffusion under such circumstances were wind speed, wind direction and canyon geometry. It was found that when wind crossed the canyon at a substantial angle, a vortex flow pattern was generated. This leads to the accumulation of Pb on the leeward side of buildings. Lead was deposited within the canyon, and rarely diffused through to the lower atmosphere. Hamilton and Dunsby (1984) used published Pb in air values to develop a model for predicting Pb in air concentrations in street canyons given the canyon geometry, vehicle speed and flow, and the background Pb in air value.

Following the reduction in the permitted maximum concentration of Pb in petrol from 0.4 to 0.15 g l^{-1} in December 1985, the Pb in air levels in London fell by between 34 and 55% (Jensen and Laxen 1987). The greatest reductions were recorded at roadside sites (Table 2.7).

Table 2.7. Mean Pb in air levels following the phase-down of Pb in petrol.

Site type	n	Pb in air concentration (µg m^{-3}) before	after	reduction (%)
Roadside (tunnel)	6	15.0	7.55	49.8
Roadside	17	1.63	0.795	51.3
Roadside (playground)	12	1.45	0.737	49.3
Roadside	17	1.43	0.646	54.7
Urban background	14	0.426	0.251	41.2
Central background	7	0.313	0.177	43.5
Rural background	12	0.231	0.152	34.1

Source Jensen and Laxen (1987)

The information available in the literature for roadside levels is less extensive for other heavy metals compared to Pb. Increased Pb and Cu levels in the outlet air from a tunnel have been reported (Larsen 1966). It was calculated that the relative contribution of road vehicles to ambient air concentrations was 95% for Pb but only 8% for Cu. Creason et al. (1971) could find no obvious pattern in airborne suspended particulate and dustfall distributions for Cd and Zn with distance from the roadside, which would indicate that the roadway was a source of these metals. Wakely (1973) has shown increased Cd in air levels in areas of congested traffic.

2.2.3. Temporal and climatic variations in atmospheric heavy metal levels.

Diurnal, day to day and seasonal variations in atmospheric metal concentrations have been observed in both urban and rural locations. Diurnal changes are determined primarily by variations in source emission factors. The correlation of Pb with traffic density is evident as concentration maxima occur during the morning and evening rush hours (Cholak et al. 1968; Bevan et al. 1974; Hickman and Lunn 1981). Furthermore, the average Pb concentration is highest during the day, and a reduction in the average concentration during the weekend has been observed (Lawther et al. 1973; Hickman and Lunn 1981).

Day to day variations in heavy metal levels are strongly influenced by meteorological factors such as windspeed (Hickman 1976), wind direction and duration (Daines et al. 1970; Harrison and Williams 1982). In areas where air pollution is derived from many point sources the metal levels are generally insensitive to changes in wind direction. The prevailing winds may however, strongly influence metal concentrations downwind of an urban complex or major industrial source (Harrison et al. 1971; Neustadler et al. 1976). Periods when metal in air levels are unusually high are also often associated with the development of stagnant anti-cyclones. Demunyck et al. (1976) noted that the concentrations of nearly all determined components increased by at least a factor of eight under these climatic conditions. Afterwards levels dropped to the original values as dilution conditions returned to normal. McDonald and Duncan (1979) found that periods of fog and calm tended to increase metal levels, while rain cleared the atmosphere.

A pronounced seasonal variation in airborne metal levels has been observed at many locations. Studies in the United Kingdom commonly show higher concentrations in winter than summer. This has been attributed to extra emissions associated with increased car usage, domestic heating and power consumption, in addition to the greater number of persistent low atmospheric inversions (Peirson et al. 1973; Cawse 1974; Salmon et al. 1978; McInnes 1979; Harrison and Williams 1982; Duggan 1984).

2.2.4. Physical characteristics of metal bearing aersols.

The size and shape of metal bearing particulates vary extensively and reflect both the source features and the history of the aerosol. Considerable attention has been given to observation of particle size and shape because they determine the atmospheric behaviour of the particles.

Electron micrographs of exhaust particulates show that the following two principle types of metal bearing particle exist:

a) round, Pb bearing particles in the size range 0.01 to 0.1 µm, some single and some multiple, which appear to be characteristic of primary exhaust particles;

b) large particles greater than 1 µm which consist of aggregated grains with diverse morphology (Lawther et al. 1973; Little and Wiffen 1978; Chamberlain et al. 1979).

The physical characterisation of airborne Cd, Cu and Zn bearing particles, and Pb emissions from industrial sources is largely confined to particle size distributions. The size distributions of airborne particulates are almost always multi-modal (Willeke and Whitby 1975). This is widely interpreted as indicating different sources for atmospheric particles. Larger particles are usually attributed to natural processes such as windblown dusts and sea sprays, in addition to mechanically produced particles. The finer particles are normally ascribed to anthropogenic sources.

The particle size of an aerosol is often expressed in terms of mass median diameter (MMD), which is that diameter below which 50% of the total mass of an element is found. A summary of MMD's is given in Table 2.8. It can be seen that Pb particles tend to be of a smaller size than those of other metals, which reflects the different sources of these metals.

The MMD's for metal bearing aerosols show considerable temporal and spatial variations, which are due to such factors as specific emissions from high temperature processes in the metal industry, or the lack of control of emissions (Heindryckx 1976; Paciga and Jervis 1976).

Table 2.8. Mass median diameters for metal bearing aerosols (µm).

	Cd	Cu	Pb	Zn
median	1.53	1.27	0.4	1.38
range	0.5-6.0	0.5-30.0	0.12-0.7	0.6-12.4

Source Nriagu (1978, 1979b+c and 1980)

2.2.5. Deposition of trace metals from the atmosphere.

The transfer of particulates and their associated trace elements from the atmosphere to the surface occurs by dry deposition and by rainfall. Because of the difficulties in sampling only the wet or the dry fraction much of the published data is for bulk deposition (Table 2.9). As with airborne concentrations, the highest deposition is associated with local emission sources (Turner et al. 1980; Barrett et al. 1981, 1983; Jefferies and Synder 1981). Turner et al. (1980) found that Pb deposition was confined to within 500 m of a leadworks, whereas

Table 2.9. Deposition rates of heavy metals from the atmosphere (mg m^{-2}30 day^{-1}).

Location	Cd	Cu	Pb	Zn	Reference
Swansea/Neath (bulk)	-	2.88	3.29	7.73	
(dry)	-	0.35-7.73	1.08-4.03	1.39-3.86	Pattenden (1974)
Chicago (bulk)	0.07	-	19.26	9.22	Creason et al. (1971)
London (bulk)	0.24	-	3.94	-	Harrison et al. (1975)
United Kingdom					
rural (total)	0.16-0.49	0.63-4.03	1.32-3.45	2.96-13.15	
(dry)	0.08-0.58	0.08-1.32	0.99-1.81	0.24-6.25	Cawse (1974)
M4 motorway (bulk)					
central res.	-	-	426.6	-	
kerbside	-	-	384.0	-	
0.5m	-	-	128.1	-	Little & Wiffen (1978)
Ontario (bulk)	-	0.17	0.84	1.29	
smelter (bulk)	-	16.64	-	4.88	Jefferies & Synder (1981)
Kent (bulk)	<0.05	0.49	1.48	7.89	
Carshalton (bulk)	<0.05	0.15	2.47	6.9	
Kew (bulk)	<0.05	0.15	1.97	5.92	
Hampstead (bulk)	<0.05	0.69	4.9	9.86	
Greenwich (bulk)	0.09	1.97	14.79	19.73	
Stratford (bulk)	0.10	1.97	4.9	29.59	
The Strand (bulk)	0.05	0.79	6.9	9.86	Duggan & Burton (1983)

for roadways, deposition occurred predominantly within 25 m of the road edge. This difference was attributed to source height. Significant correlations exist between deposition and wind direction and speed (Little and Martin 1972; De Koning 1974). Regional differences in atmospheric deposition of metals stem primarily from differences in population density, the level of industrial activity and wind direction. Deposition rates also depend on the surrounding land use, as shown by increased deposition in cities compared to rural areas. However a powerful point source may mask the effects of local land use arrangements.

2.2.5.1. Dry deposition of trace metals.

The trace metal content of dustfall varies from background soil values to mg g^{-1} levels close to point sources. The values of metal deposition rate as dustfall at several sites are shown in Table 2.9. The rate of deposition is related in a very general way to the atmospheric trace metal burden at a given location. An empirical parameter that is widely used in models dealing with atmospheric deposition is the dry deposition velocity V_d defined as:

$$V_d=D_d/C_a$$

where D_d is the rate of dry deposition (g m^{-2} s^{-1}), and C_a is the concentration in the atmosphere (g m^{-3}).

The deposition velocity is a function of particle shape and surface characteristics, and the atmospheric conditions but most importantly particle size. Because of the particle size dependence the deposition of a species may be controlled by only a small size range. If a very few large particles are present then the mass deposition of those particles may be greater than that of the bulk of the remaining particles.

Apart from particle size, a number of other variables influence the deposition velocity. These have been reviewed by McMahon and Denison (1979). In summary, V_d is approximately a linear function of windspeed and friction, and therefore varies with height above the surface. This variation is most significant very close to the surface, with V_d becoming nearly constant at elevations greater than 1 m. The deposition of particles beneath trees and close to hedges varies significantly, with values ranging from 2 to 16 times that measured in adjacent open terrain. The deposition velocities for particles may vary by 3 orders of magnitude (Sehmel 1980a), which reflects the many factors influencing gravitational settling, diffusion, impaction on surface obstacles and the retention of deposits.

2.2.5.2. Wet deposition of trace metals.

The mechanisms of wet removal of heavy metals from the atmosphere are not clearly understood, in particular the relative contributions of wash-out and rain-out. In heavily polluted areas wash-out (below cloud scavenging) is believed to be the dominant process, whereas in remote regions rain-out predominates (Müller and Bielke 1975). As with dry deposition an empirical parameter is used in wet deposition models, this is the wet deposition velocity:

$$V_w = D_w / C_r$$

where D_w is the wet deposition rate (g m^{-2} s^{-1}), and C_r is the concentration in rain (g m^{-3}).

As with dry deposition the metal content of precipitation varies considerably between sampling sites. The values of wet deposition at several sites can be inferred from the data in Table 2.9. Ombrogenic levels of metals show spatial variations that are related to changes in source contributions. Lazrus et al. (1970) and Galloway et al. (1982) found that rainfall deposition of heavy metals in the United States may be correlated with the intensity of urbanisation and industrialisation. It was also noted the Pb levels in rainwater showed good correlation with gasoline consumption in the area in which the samples were taken. However Randall et al. (1978) found that rainfall pollutants tend to wash out in relatively uniform amounts throughout metropolitan areas regardless of land use, location and distance from city centre, even though the source of metals may be area specific.

A 2 to 3 fold increase in metal concencentrations have been observed in convective storm showers compared with slow drizzle, with the exception of Cu which showed no difference (Struempler 1976). Storm showers also tend to be characterised by wide fluctuations in metal concentrations. In a steady prolonged precipitation event the metal content was found to rapidly decrease to a relatively constant value (Struempler 1976; Müller and Bielke 1975; Nynyen et al. 1979). Randall et al. (1978) noted that aerial deposition was independent of the magnitude or intensity of precipitation. It would appear that pollutants are washed out in the first few minutes of rainfall. It was also noted that the length of the antecedent dry period was an important factor influencing pollutant loads from rainfall.

2.2.6. Metal Deposition near roadways.

Lead emitted from vehicle exhausts is subject to rapid dispersion by turbulence and depletion by deposition. On motorways Little and Wiffen (1977) and Huntzicker et al. (1975) calculated that only 10% of the emitted Pb was deposited within 30 m of the road. However, on the basis of long term approximations of emissions and accumulations in roadside soils and vegetation Ward et al. (1975) and Little and Wiffen (1978) estimate a greater proportion is deposited (40%). The reasons for this discrepancy may be related to deposition during rainfall, or resuspension of Pb from the road especially when it is wet. Attempts to measure pollutant loss through vehicle generated spray have proved difficult due to factors such as traffic speed and direction, and rainfall intensity and duration (Jones and Tinker 1984).

The Pb deposition rate shows a rapid decrease with distance from the road. This is shown in soil and vegetation Pb concentrations which fall to background levels within 30 m of the road (Motto et al. 1970; Daines et al. 1970; Vandenbeele and Wood 1972; Rolfe and Jennett 1975). Because the particle size profile tends towards smaller particles with distance from the road a significant proportion of particles remain airborne for long periods. Huntzicker et al. (1975) estimate that 32% of the emitted Pb in the Los Angeles basin is transported out of the area and over long distances. Similarly Katen (1974) estimated as much as 45% remains airborne within 10 km of the source. Johnston and Harrison (1984) have investigated the deposition rates of Cd, Cu and Pb in the vicinity of a motorway and observed that a major fraction of metal deposition occurred within 15 m of the carriage-way.

The response of Pb deposition to decreased use of Pb in petrol has been investigated in the United States by Eisenreich et al. (1986). Annual Pb fluxes in precipitation declined from 20.0 to 3.7 mg m^{-2} yr^{-1} at an urban site during the period 1979 to 1983, following the removal of Pb in petrol.

2.3. Heavy Metal Levels in Urban Street Surface Sediments.

Urban dusts have long been recognised as a potential contributor of Pb and other heavy metals to stormwater pollution, and to the body burden of children. Numerous studies have been made of Pb levels in street surface sediments but other heavy metals have not been so extensively researched. Reported metal levels show considerable spatial and temporal variations which reflect the influence of factors such as local traffic and weather conditions. Heavy metal levels can be described by two parameters, the metal concentration ($\mu g\ g^{-1}$) in road dust and the metal loadings ($mg\ m^{-2}$) on the road surface. Much of the reported data is for concentrations only. A selection of findings from heavy metal surveys of urban street dust are given in Table 2.10.

2.3.1. Historical perspective.

The majority of the data given in Table 2.10 is for Pb, which reflects concern over the toxic effects of this metal arising from its use in petrol as an anti-knock agent. Dustfall with elevated Pb concentrations pre-dates the introduction of Pb in petrol. Dunn and Bloxam (1933) analysed dusts for Pb, Cu and Zn, and found appreciable amounts of these metals, particularly Zn (Newcastle upon Tyne) and Pb (Leeds). The authors cite work by Manley who noted that higher concentrations of heavy metals were to be found near the city centre, with lower concentrations towards the outskirts of Leeds. Burning of coal and industrial processing of metals and metal compounds were identified as the sources of this pollution. Kaye and Reznikoff (1947) showed that the average increase in the Pb concentration of street dirt between 1924, when Pb in petrol was introduced, and 1934 was 50%.

2.3.2. Spatial variations in heavy metal levels.

Typical heavy metal concentration values of about 1000 $\mu g\ g^{-1}$ for Pb and Zn, 50-100 $\mu g\ g^{-1}$ for Cu and <10 $\mu g\ g^{-1}$ for Cd have been reported for road sediments in residential urban areas away from major roads and industrial sources, both in the United Kingdom and United States (Table 2.10). These values may be elevated 2-4 times in the immediate vicinity of major urban arterial roads, but not necessarily in the vicinity of open or elevated motorways in proportion to traffic density. The importance of emission and dispersion conditions is shown by the difference in metal levels (particularly for Pb) between these road types.

Table 2.10. Heavy metal levels in urban street sediments.

	Metal concentrations ($\mu g\ g^{-1}$)				
Location	Cd	Cu	Pb	Zn	Reference
Leeds	–	1700	4123	–	
		(100–7200)	(40–15000)		
Newcastle	–	426	245	3173	
		(300–700)	(17–909)	(1970–4700)	Dunn & Bloxam (1933)
London (central)	–	–	2200	–	
Hatfield (A1)	–	–	1700	–	Turner (1973)
8 cities U.S.A.–					
residential	3.1	91	1600	380	
	(0–8.8)	(33–190)	(230–5700)	(110–810)	
industrial	4.1	120	1600	360	
	(0–11.0)	(32–280)	(65–10000)	(140–880)	
commercial	5.1	170	3600	520	
	(0–25.0)	(25–810)	(0–10000)	(190–1100)	Pitt & Amy (1973)
Manchester	–	–	970	–	Day et al. (1975)
			(90–10200)		
Birmingham	–	–	1663	–	Archer & Barratt (1976)
			(160–50000)		
Champaign-Urbana	6–8	–	240–6640	–	Solomon & Hartford (1976)
Glasgow	–	–	960	–	Farmer & Lyon (1977)
			(150–2300)		
London					
Lambeth	–	–	1840	–	
Islington	–	–	1330	–	
Wimbledon	–	–	1040	–	
Edgeware	–	–	1040	–	
Harold Wood	–	–	920	–	
rural	–	–	35	–	Duggan & Williams (1977)
Lancaster					
car parks	7.0	206	6630	1600	
	(1.0–14.6)	(104–375)	(2200–15000)	(1010–3720)	
urban	4.6	143	1880	534	
	(1.3–10.1)	(57–312)	(920–3560)	(200–940)	
rural	2.1	79	550	297	
	(1.0–2.9)	(53–150)	(150–870)	(160–710)	Harrison (1979)

Table 2.10 Continued

London					
motorway	6.3	386	2296	1212	
trunkroad	5.3	280	1826	695	
residential	6.0	91	978	2133	
rural	1.3	43	111	119	Ellis and Revitt (1982)
Lancaster					
motorway	3.3	312	1570	496	
major road	2.8	199	2540	458	
car park	3.7	71	939	440	
urban road	3.7	75	1090	260	Harrison et al. (1981)
Greenwich					
playgrounds	–	–	510	–	
			(220–1180)		
roads	–	–	2142	–	
			(1910–2400)		Millar & Cooney (1982)
Glasgow					
urban	2.0	–	630	530	
	(1.6–2.5)		(510–678)	(453–633)	
rural	0.1	–	52	96	Hampton & McKirdy (1983)
London	5.2–7.9	191–204	2008–4053	1171–1176	
New York	4.6–11.4	171–540	2213–2952	984–2638	
Halifax					
(Canada)	1.4–0.6	54–119	674–1919	315–620	
Christchurch	0.8–1.1	48–258	887–10700	365–850	
Kingston					
(Jamacia)	0.8	59–72	817–909	533–996	Fergusson & Ryan (1984)
U.K.– roads	1.7	75	707	367	
	(1–28)	(7–3030)	(45–8860)	(46–22880)	
playgrounds	1.8	44	269	402	
	(1–68)	(3–1554)	(11–4240)	(11–5424)	Thornton et al. (1985)

Metal loadings (mg m^{-2})

8 cities U.S.A.–					
residential	0.14	4.30	83.98	20.75	
industrial	0.30	18.28	158.08	34.58	
commercial	0.17	1.88	49.40	5.46	Pitt & Amy (1973)
Champaign–					
Urbana	0.007–0.02	–	1.59	–	
			(0.72–15.20)		Solomon & Hartford (1976

Where automobiles are the major source, only a small proportion of the published data shows Pb levels in street dust in excess of 5000 $\mu g\ g^{-1}$. However, extremely high values have been reported at certain locations such as road tunnels (E.P.A. 1973), and enclosed car parks and garage forecourts (Harrison 1976, 1979; Fergusson and Simmonds 1983). In the latter situations Pb appeared to be derived from the deposition of highly enriched particles dislodged from exhausts rather than the spillage of organic Pb (Harrison 1976).

The variability in heavy metal content is considerable both within and between different locations as evidenced by the wide range and standard deviations of reported values (Table 2.10). These variations may be partly due to the large number of input and output factors affecting the heavy metal levels in the street environment. However, some of the variability between samples results from differences in the sampling and analytical techniques employed (see Chapter 3).

In the United States, Pitt and Amy (1973) conducted a nationwide study of heavy metal levels in urban street sediments. No clear trends in metal concentrations between the 8 cities studied were observed, but it was noted that the cities with high sediment loadings also had high metal loadings. In the United Kingdom only one nationwide study of metal concentration in settled dust has been undertaken. This showed that the mean concentrations of metals in London were higher than the national average (Culbard et al. 1983; Thornton et al. 1985).

Spatial variations of heavy metals on a city wide scale have been extensively studied in the United Kingdom, United States and New Zealand. In Manchester, Pb concentrations were found to be similar throughout the city irrespective of sampling site (Day et al. 1975). In Birmingham and Lancaster marked differences between sites was observed (Archer and Barratt 1976; Harrison 1979). A sharp decline in metal concentrations on going from urban to rural areas has been shown by several studies (Day et al. 1975; Pollitt 1976; Duggan and Williams 1977; Hampton and McKirdy 1983). Most urban samples are at least 1-2 orders of magnitude greater than those in rural areas, with the exception of areas where mining activities have taken place (Barltrop et al. 1974).

The influence of land use on heavy metal levels in street dust has been investigated by Sartor and Boyd (1972). No obvious pattern could be observed for concentration variations, but loading intensities were found to be heaviest in industrial areas and lightest in commercial areas. Pitt and Amy (1973) showed that industrial and commercial areas consistently had higher concentrations compared to residential areas (Table 2.10). More substantial trends were shown for metal loadings. The highest loadings were associated with industrial land use areas for all metals. Loadings were clearly influenced by the amount of road surface particulates found in a given area. Similar studies in the United Kingdom have not been made. Archer and Barratt (1976) investigated variations in Pb concentrations between a residential area, a major arterial road and an industrial area and a similar pattern to that observed in American studies emerged. It should be noted that many areas are in the vicinity of a network of roads, and in this situation there may be no significant spatial variations in metal concentrations (Little and Heard 1978).

Lead concentrations in street dust have been related to traffic density by a number of workers. Archer and Barratt (1976), Day (1977) and Harrison (1979) have observed that Pb concentrations were reduced with decreasing traffic density. Lau and Wong (1982) showed that Pb in street dust could be correlated with annual average traffic density. Fergusson and Simmonds (1983) noted that Pb and Cu concentrations were greater on a main road than on a side road. Zinc showed the reverse trend due to the use of galvanised roofs in residential areas.

A number of studies have been performed which illustrate the effects of traffic flow on heavy metal levels. Day (1977) studied variations in Pb concentrations in samples taken at traffic lights, round-abouts, bus stations, junctions and parked vehicles along a primary route out of Christchurch, New Zealand. Areas where traffic flows were restricted, and where traffic density increased were found to have increased concentrations of Pb in street sediments. Harrison et al. (1981) have shown similar trends for Pb and other metals in samples taken around Lancaster. The primary vehicular source of metals such as Cd, Cu and Zn is wear of moving parts, and so it might be expected that their emission would increase at sites such as round-abouts and junctions where cars undergo acceleration and deceleration. Dannis (1974) observed that tyre wear is much greater when cornering than during cruise conditions, consequently Zn emissions are also increased. Fergusson et al. (1980) observed that Pb concentrations at intersections were higher (3020 $\mu g\ g^{-1}$) than along the roadway (2400 $\mu g\ g^{-1}$). At traffic lights, concentrations of Pb increased by 2.0-2.8 times, whereas crossroads and round-abouts showed less spatial variation. Parked cars have been shown to have a marked effect on the loadings of metal pollutants (Sartor and Boyd 1972).

In the vicinity of industrial sources, particularly leadworks, heavy metal concentrations in dust may be elevated by up to and above 2 orders of magnitude compared to those of the urban background. These increases will depend on the works size, and the proximity to site boundaries. In an investigation of seven United Kingdom leadworks, Pb in dust levels of up to 7% (70,000 µg g^{-1}) were found in the gutters surrounding many of the works (Turner et al. 1980). Fugitive emissions on vehicles leaving the works appeared to be the main route for transporting Pb out of the site. The levels of Pb, even along routes out of the works, decreased rapidly and reached the urban background levels within 500 m. These findings are not dissimilar to those of previous studies (D.O.E. 1974; Archer and Barratt 1976; Pollitt 1976; Elwood et al. 1977; Hampton and McKirdy 1983) where the bulk of the contamination was found to be contained within 1500 m of the source. Jensen and Laxen (1985) noted Pb levels in excess of 5000 µg g^{-1} around print-works in Fleet Street, London. This compared with a range of Pb concentrations of 1360-3380 µg g^{-1} for other busy roads in London. Tin levels were also high suggesting Pb alloy used in printing as the source. Highest concentration levels were near the doors of print-works indicating movement on shoes and clothing as the major pathway out of the works. The pollution extended to 150-200 m from the works.

There is a general lack of information on spatial variations likely to occur over a limited area. Duggan and Williams (1977) and Solomon and Hartford (1976) have shown that where the sampling area was dominated by one road, Pb concentrations and loadings fall off rapidly with distance from the gutter. The bulk of the solids, and consequently the metal loadings, lie in the gutter within a few centimetres of the kerb (Sartor and Boyd 1972; Ellis 1979; Ellis and Revitt 1982). The kerb appears to act as a barrier to transportation of the solids off the street surface. Finer particles are dispersed by wind and rain and will tend to collect in sheltered areas. Shaheen (1975) observed that the curb height was an important factor influencing the retention of sediments. Vehicle induced resuspension is a major mechanism for the lateral dispersion of road surface sediments which has not been fully investigated. Sehmel (1980b) showed that the fraction of dust resuspended was proportional to vehicle speed but independent of windspeed. Resuspension was also reduced after the particles had been on the road surface for several days.

Solomon and Hartford (1976) extended their study to the immediate environs of a house, where an increase in Pb concentrations was associated with the weathering of paints. There has been considerable concern over the possible pollution caused by deteriorating paintwork. Raised Pb levels have also been noted where reparation of surfaces has been carried out (see Section 2.1.3). Millar and Cooney (1982) have also found elevated Pb concentrations in a school playground which derived from deteriorating paint.

Although other heavy metals have found applications in the paint industry little work has been carried out on their levels in dust eroded from painted surfaces. Levels of Cd have been reported for dusts surrounding houses (Solomon and Hartford 1976), and for playground dusts (Rundle and Duggan 1980). The levels were found to be similar to those in other urban areas.

It is assumed in all of the studies mentioned that representative samples of road sediment have been collected. The results of several small scale surveys have shown the difficulties in obtaining such samples. In a study conducted by the Greater London Council, 30 samples were taken from a school playground which had no leadworks or major roadways nearby. Sampling was on one day, over an area of 3500 m^2 using a 10 m^2 grid. The Pb concentrations ranged from 250 to 2200 $\mu g\ g^{-1}$ with an average of 700 $\mu g\ g^{-1}$ (Duggan 1981). It is evident that taking a limited number of samples could give misleading results.

2.3.3. Temporal variations in heavy metal levels.

Temporal variations in heavy metal levels have not been studied as extensively as spatial variations. Metal concentrations in street sediments can vary considerably over a period of a few weeks (Duggan 1984). Factors influencing temporal variations include elapsed time since the streets were last cleaned either intentionally or by rainfall, and the season of the year. Turner (1973) found a lack of variability in the Pb concentrations of samples taken over several weeks, when moderate amounts of rainfall were recorded. This was attributed to the insolubility of the Pb compounds present in road dusts (carbonates and oxides). Very heavy rainfall, snow and street cleaning operations may be expected to remove recently deposited dusts, which are less compacted than aged dusts. Heavy rainfall falling a few days prior to sampling has been associated with low concentrations of Pb in street dusts (Fergusson et al. 1980; Tsang 1982). Fergusson and Simmonds (1983) observed a fall in Cd, Pb and Zn concentrations after heavy rainfall (>70 mm in 5 days), but no change in Cu concentrations. The accumulation rate of materials deposited on street surfaces prior to wash-off is not linearly related to time. Accumulation rates fall off after several days due to the removal of deposited material by the passage of vehicles (Sartor and Boyd 1972; Shaheen 1975; Pitt 1979). Shaheen (1975) derived an expression for this process:

$$L = K_1[1-\exp (K_2/T)]$$

where L is the roadway pollutant loading lb/mile, T is the total traffic in axles, K_1 is the per axle deposition rate and K_2 is a function of the removal rate.

Seasonal variations in heavy metal levels have been investigated by Shaheen (1975) and it was found that Pb and Zn loadings were higher in warmer seasons but levels of other metals remained uniform regardless of season. This trend was attributed to increased tyre wear in warmer weather. Duggan (1984) observed no long term or seasonal trends in average Pb concentrations which showed no significant difference between each of the two years studied.

2.3.4. Heavy metal concentrations as a function of particle size.

The affinity of heavy metals for small particle sizes is well documented. Sartor and Boyd (1972), Rameau (1972), Pitt and Amy (1973), Biggins and Harrison (1980) and Ellis and Revitt (1982) have all demonstrated the relationship of increasing metal concentration with decreasing particle size. The greater mass of sediment in the larger size fractions means that in many cases the greater mass of metal is associated with larger grain sizes in the dust (Rameau 1972; Biggins and Harrison 1980; Ellis and Revitt 1982). The metal concentrations in each size fraction have been found to remain relatively constant within a specific test area and time period, but the percentage composition of the different sizes can vary significantly (Pitt 1979). Beckwith et al. (1985) investigated the relationship between metal levels and particle size distribution along a transect across a residential road. The results showed a gradual increase in metal sediment concentration towards the centre of the road, and a higher affinity of heavy metals for smaller particle sizes. Sediment distribution curves show that for many metals the median grain size is in the region of 250 µm (Ellis and Revitt 1982). Particles >250 µm represent those most efficiently removed by street sweeping procedures (Ellis 1979).

Pitt (1979) collected samples from five test areas, which represented different surface types, and size fractionated them into eight particle size ranges. For all the metals investigated except Cu, and at all test sites, higher metal concentrations were found with decreasing particle size. The particle size distribution for a range of different test areas showed average median particle sizes ranging from 150 to 400 µm with asphalt streets in good condition having the smallest median particle sizes. Asphalt/chipping surfaced streets showed the largest median particle sizes. Street surfaces made with chippings had significantly different pollutant strengths associated with different particle sizes. These were generally lower by a factor of two than the concentrations in other areas. This is possibly due to the larger quantities of street wear products diluting the pollutants originating from other areas. Sartor and Boyd (1972) noted that asphalt surfaces had 80% greater pollutant loadings than concrete.

2.3.5. Control measures for heavy metals in street sediments.

Control measures, such as conventional street cleaning practices, are most effective in removing large particle sizes but have been shown to be unable to efficiently remove enough of those pollutants associated with the less abundant smaller particle sizes. Sartor and Boyd (1972) observed that sweeping removed 70% of the sediment particles >2000 µm but only 15% of particles <43 µm. Ellis (1979) and Pitt (1979) have investigated the sediment removal efficiencies of conventional road cleaning procedures. Considerable amounts of fine sediments, together with associated metal pollutants remain on the street surface and in roadside gutters after sweeping. However, Malmqvist (1978) estimates that sweeping removes 30-65% of the metals and 57% of the sediment available for runoff. Sweeping moves much of the material out of the gutter and redistributes it onto areas which were previously cleaner (Sartor and Boyd 1972; Ellis 1979). The efficiency of road sweeping is improved with the greater number of 'multiple runs' over the same sample area, with secondary runs alone removing 50% of the remaining residue (Sartor and Boyd 1972). Sweeping efficiency is also governed by the method employed with vacuum sweeping being more effective than manual techniques and mechanical sweeping the least effective (Ellis 1979). Pitt (1979) showed that sweeping efficiency also depends on the intrinsic characteristics of the swept particle sizes and their spatial distribution, the morphology of the highway surface, the initial loading and the interval between sweeping. Street sweeping is not always practical, such as in situations where cars are regularly parked and where there is traffic congestion.

2.4. Physico-Chemical Forms of Heavy Metals in Urban Street Dusts.

It is now widely recognised that the main factor influencing the toxic effect of a pollutant is not the total concentration, but the specific compounds of that element present. Hence in recent years attention has been focused on the problems of identifying the physico-chemical forms or speciation of trace metals in the environment. Such information is very valuable as metal speciation not only affects the metal bioavailability and toxicity, but also the chemical and physical behaviour and hence the mobilisation and transport of metals in the environment. The chemical speciation of heavy metals in street dusts has involved two major types of experimental technique; X-ray powder diffraction (XRD), and chemical extraction schemes.

2.4.1. X-ray powder diffraction analysis of street dusts and soils.

The speciation of Pb in street dusts has been investigated using XRD by several research groups. The Pb compounds may be enriched by magnetic and density separations. Olsen and Skogerboe (1975) separated magnetic material by means of an electro-magnet, and then removed a fraction of density >3.32 g ml^{-1} from the non-magnetic sediment by suspension in a di-iodomethane/carbon tetrachloride mixture. The dense, non-magnetic fraction was then analysed by XRD. Compounds were identified by d spacing and intensity matching with both standard diffraction files, and with standard compounds run on the same instrument. The principal compound identified in soils was $PbSO_4$, while elemental Pb was identified in one sample taken from a car park. Biggins and Harrison (1980) modified the technique to improve the quantity of the non-magnetic fraction obtained, and used it on a greater number of street dust samples. Elemental Pb was found in samples taken from a multi-storey car park, a petrol station and a city centre street. This was probably derived from the cold starting of parked cars. The presence of $2PbCO_3.Pb(OH)_2$, Pb_3O_4 and $PbO.PbSO_4$ was thought to be due to contamination of dusts by paints. As in the previous study the predominant crystalline phase was $PbSO_4$ which is formed by water leaching of $PbSO_4.(NH_4)_2SO_4$ deposited from the atmosphere. This compound is the major Pb compound found in similar studies of street air (Harrison and Laxen 1980). In many street and urban dust samples no Pb compounds were identifiable by XRD, and at most the identified compounds accounted for only a few percent of the total Pb. In the British environment rainwater leaching rapidly converts the Pb to non-crystalline forms not amenable to XRD analysis, thus rendering XRD of limited use for speciation of metals in this type of sample.

2.4.2. Available metals in street sediments.

The available fraction of metals in street sediments have been investigated by several workers (Duggan and Williams 1977; Day et al. 1979; Harrison 1979; Millar and Cooney 1982; Gibson and Farmer 1984). These workers have used 0.07N HCl to extract the metals. This represents the metal content of a sediment which is soluble in HCl at the concentration existing in the stomach, and hence represents metals which are available to the bloodstream. The technique is outlined in the Pencil and Graphic Instruments (Safety) Regulations 1974. Substantial quantities of metals were found to be available for uptake (Table 2.11). Gibson and Farmer (1984) observed a wide range of extractability which varied between metals for individual samples. However a fairly uniform mean percent of the total overall concentration was observed.

Table 2.11. Percentage fraction of metals in street dusts extracted by 0.07N HCl.

	Cd	Cu	Pb	Zn
Duggan and Williams (1977)	-	-	59	-
Harrison (1979)	61	53	77	73
Gibson and Farmer (1984)	47	28	41	44

2.4.3. Organic lead in street dusts.

Reported levels of organic (tetra-ethyl and tetra-methyl) Pb have been found to represent only a small proportion of the total Pb found in street sediments. Harrison (1976) extracted the tetra-alkyl Pb compounds from a number of street dusts. Extraction was performed using cold ammoniacal methanol. After addition of iodine to the sample the Pb content was determined using atomic absorption spectrophotometry. Concentrations ranging from 0.4 to 7.4 µg g^{-1} were found, which represents less than 1% of the total Pb found in street dust. Higher levels may be expected in enclosed car parks and petrol station forecourts. Although overall total Pb levels are high in such samples this appears to be due mainly to particles dislodged from exhausts and not spillage from petrol tanks (Harrison 1979).

2.4.4. Partitioning of heavy metals in street sediments.

A third approach to chemical speciation of metals has been to use sequential extraction schemes to distinguish forms of metal association in street sediments. Soil is the major contributor to urban street dust providing 60% of the total sediment loadings for samples collected in London. An additional 21% was found to be derived from tyre wear and 15% from cement with vehicle exhaust emissions and salt each contributing 0.5 and 1% respectively, the rest of the sediment being organic material (Hopke et al. 1980; Fergusson and Ryan 1984). The crystalline compounds of Pb progressively dissolve in rainwater and are redeposited in the forms typical of soils (Harrison and Laxen 1980). These forms include:

a) metals dissolved in the interstitial waters;

b) metals loosely adsorbed either as metal ions or as hydroxy-carbonato species, metals held by electrostatic attraction to negatively charged ion exchange sites on mineral colloids (clays), organic particles and hydrous oxides. This phase is in equilibrium with the interstitial waters and metals can be readily adsorbed or desorbed as a consequence of changes in physico-chemical parameters or concentration gradient;

c) metals adsorbed to oxides, hydroxides and hydrous oxides of Fe and Mn and possibly Al, which exist as nodules, concretions, cement between particles or as surface coatings;

d) metals bound to organic matter either absorbed in living organisms and detritus or as coatings on mineral particles. The complexation properties of natural organic matter (notably humic and fulvic acids) are well recognised as is the phenomenon of bioaccumulation in living organisms;

e) metals incorporated into the crystalline lattice structure of mineral particles.

These locations represent a range in the degree by which metals may be considered to be bioavailable or environmentally mobile. The first four phases represent metals which are biologically and geochemically available and the final residual phase represents metals which are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

Speciation techniques which differentiate between these fractions have been developed for soils (Le Riche and Weir 1963; McLaren and Crawford 1973; Garcia-Miragaya et al. 1981; Gibson and Farmer 1986) and for aquatic sediments (Gibbs 1973; Engler et al. 1977; Tessier et al. 1979; Salomons and Forstner 1980). These techniques have also been found to be suitable for use with street dusts (Harrison and Laxen 1980; Harrison and Wilson 1982). A summary of the methods used for extraction of metals from the major chemical fractions in sediments and soils is given in Table 2.12. Although there is some overlap between the schemes because a wide range of techniques have been used, comparisons of results obtained by different workers is difficult.

The schemes outlined above do not define accurately the various metal species present. The trace metal distributions in any extraction scheme is operationally defined by the method of extraction rather than by some fundamental property of the metal complex (Rendell et al. 1980; Rapin et al. 1986). The schemes do however provide useful information about the origin, mode of occurrence, biological and physico-chemical availability, mobilisation and transport of trace metals.

2.4.5. Application of selective extraction schemes to street sediments.

Harrison et al. (1981) and Fergusson and Ryan (1984) have applied the selective extraction scheme devised by Tessier et al. (1979) to the speciation of Cd, Cu, Pb and Zn in street dusts and roadside soils. Gibson and Farmer (1984) used a similar procedure but separated metals associated with the easily and moderately reducible fractions. The results of these studies show a predominant association of Pb and Zn with the carbonate and Fe-Mn oxide phases of the sediment. The behaviour of Cd was similar but with a significant exchangeable component. Copper was found to associate primarily with the organic fraction. Fergusson and Ryan (1984) could find no differences in the

Table 2.12. A summary of methods employed for the extraction of metals associated with various chemical fractions in soils and sediments.

Major extractable phase	Extractant	Reference
Exchangeable cations	CH_3COONH_4 (pH 7)	Jackson (1958)
	CH_3COONa (1M, pH 8.2)	Chapman (1965)
	$MgCl_2$ (1M, pH 7)	Gibbs (1973)
	$BaCl_2$-triethanolamine (pH 8.)	Jackson (1958)
Carbonate phase	CH_3COONa and/or CH_3COOH (pH 5)	Gupta & Chen (1975)
	CO_2-treatment of suspension	Patchineelam (1975)
Reducible fraction	Acidified $NH_2OH.HCl$ (+ 0.01M HNO_3)	Chao (1972)
	$C_2O_4(NH_4)$	McKeague & Day (1966)
	$NH_2OH.HCl/CH_3COOH$	Chester & Hughes (1967)
	dithionite-citrate	Anderson & Jenne (1970)
	(in order of Fe release)	
Organic fraction (incl. sulphides)	H_2O_2-CH_3COONa	Engler et al. (1977)
	H_2O_2-HNO_3	Gupta & Chen (1975)
	$NaOH$-H_2SO_4	Volkov & Fomina (1974)
Residual phase	alkaline fusion	Gibbs (1973)
	HF-$HClO_4$	McLaren & Crawford (1973)

metal distribution patterns between samples taken from a range of cities. A common feature of the metal distribution patterns was the decreasing significance of the residual fraction with increasing total metal concentrations. The most noticeable difference between street sediments and roadside soils was the greater importance of the combined exchangeable and carbonate fractions in street dirt (Harrison et al. 1981; Gibson and Farmer 1984). This has been attributed to the greater abundance of calcite in street sediments relative to soil (Harrison et al. 1981). The mobility and availability of the metals in street dirt can be considered to decrease in order of the extraction phases. Only Cd is observed to have a significant exchangeable fraction which is readily available. Lead and Zn can be considered to be moderately available, because of their predominant association with the carbonate and Fe-Mn oxide phases. Although the largest portion of Cu is in the organic phase, which is considered less environmentally mobile than preceding fractions, some organically bound Cu may in fact be highly mobile (McLaren and Crawford 1973; Purves 1977). The results suggest that the mobility and potential bioavailability of the four metals declines in the following order Cd>Pb, Zn>Cu.

2.4.6. Remobilisation of metals.

Changes in the environmental conditions may result in a mobilisation of metals from road sediments or movement between the various phases. Such changes include:

a) lowering of the pH, which leads to dissolution of carbonate and hydroxide minerals, and as a result of H^+ ion competition to increased desorption of metal cations (Gambrell et al. 1981; Forstner 1982; Reuther et al. 1983);

b) changes in redox condition, such that oxygen deficiency leads to an initial dissolution of Mn oxides followed by that of Fe oxides and any co-precipitate with the metal oxide coatings will become remobilised (Gambrell et al. 1981);

c) elevated salinity, which would occur during road salting, results in desorption of metals resulting from competition for surface binding sites by Ca^+, Mg^+ and Na^+ ions (Ramamoorthy and Rust 1978);

d) increasing concentrations of complexing agents which will strip metals from their association with weaker complexing agents (Reuter and Perdue 1977; Ramamoorthy and Rust 1978).

2.5. Heavy Metals in Stormwater Runoff.

Urban stormwater runoff may be highly contaminated with heavy metals; although the concentrations of metals in stormwater runoff may be less than that found in raw sewage entering a municpal treatment works, mass loadings of metals in urban runoff may be considerably greater at times of peak stormflows. There is considerable variation in the heavy metal levels found in stormwater runoff. The degree of industrialisation, traffic type and volume and road surface condition within an urban catchment affect the heavy metal contributions to stormwater. Variations in concentrations and loadings of one or two orders of magnitude are common place (Ellis 1979). However maximum and mean concentrations are spasmodic and irregular in level and duration, and furthermore seem to bear little relationship to catchment characteristics or antecedent conditions (Ellis 1982). The potential pollution impact of stormwater is therefore difficult to assess.

2.5.1. Stormwater washoff.

The major removal mechanism for solids and their associated heavy metals from the road surface is stormwater washoff. This process is not entirely complete, and is therefore also an important transport mechanism for the movement of heavy metals across road surfaces. Runoff leaving the road surface is comprised of three fractions:

a) soluble and particulate associated metals derived directly from rainfall and carried across the catchment surface;

b) metals solubilised by rainfall as it passes over the catchment surface;

c) sediment associated metals transported by the surface flow.

These categories are not distinct as the hydrological system is dynamic, and metals are continually being exchanged between the soluble and solid phases of stormwater.

2.5.2. The contribution of rainfall to runoff.

A comparison between metal concentrations in rainfall and stormwater runoff is shown in Table 2.13. An assessment of the contribution of rainfall to metal levels in runoff is difficult to make because few studies have reported both, and where this is the case different sampling and analytical techniques have often been employed. Wilber and Hunter (1980) and Owe et al. (1982) found that precipitation provided only a small percentage of those metals leaving an urban area

Table 2.13. A comparison of total metal concentrations in rainfall and stormwater runoff ($\mu g\ l^{-1}$).

	Cd	Cu	Pb	Zn	Reference
Rainfall	-	0.007-0.03	0.03-0.06	0.04-0.12	
Stormwater	-	0.03-0.31	0.06-0.4	0.17-0.57	Malmqvist & Svensson (1977)
Rainfall	-	0.015	0.1	0.15	
Stormwater	-	0.14	0.14	0.16	Roberts et al. (1977)
Rainfall	-	0.007	0.067	0.06	
Stormwater	-	0.05	0.34	0.25	Dauber et al. (1978)
Rainfall	0.001	0.012	0.11	0.08	
Stormwater	0.001	0.01	0.11	0.13	Geottle (1978)
Rainfall	-	0.0064	0.045	0.044	
Stormwater	-	0.176	0.87	0.47	Wilber & Hunter (1980)
Rainfall	0.001-0.004	0.005-0.095	0.058-0.186	0.047-0.183	
Stormwater	0.02-0.28	0.12-1.38	0.073-0.297	0.089-4.74	Owe et al. (1982)

in runoff. Randall et al. (1978, 1979 and 1982) determined that wash-out of heavy metals during storm events was the dominant source of metals in runoff. Pope et al. (1978) examined the aerial transport of metals close to highways during precipitation events, and found that concentrations in rainwater close to the road were comparable to road surface water at the begining of a storm. Undoubtedly vehicle generated spray and splash contributed to such rainwater concentration levels. The authors suggest that washing of the road surface is less important than the direct input of precipitation.

2.5.3. Leaching of road sediment by rainfall.

As rainfall passes over road sediment a fraction of the metals present in the sediment dissolve as free or complexed species. Metals may also precipitate out of solution and adsorb on to the sediment. Hem and Durum (1973) determined Pb solubility from thermodynamic data for pure Pb compounds. Solubility falls with increasing pH, levelling off at about pH 8 (Table 2.14). Solomon et al. (1977b) examined the solubility of Pb in road dust and observed solubilities ranging from 0.5 to 5.0 mg Pb l^{-1}. The difference between experimently determined values and thermodynamic predictions, were thought to be due in part to clays present in the road dust acting as buffering agents to the pH which becomes alkaline after dust addition (Solomon et al. 1977b).

Table 2.14. Predicted solubilities for a range of Pb compounds compared with that determined for road dust.

	pH	Pb solubility mg l^{-1}	
Predicted	4	500-1000	
	5.5	0.5-10.0	
	8	<0.001	Hem & Durum (1973)
Determined for road dust	initially 4	0.5-5.0	Solomon et al. (1977b)

Ellis and Revitt (1980, 1982) have examined the solubility in rainwater of a number of metals in road sediments over 1-30 day time periods. The solubility curves varied according to the metal. Cadmium was found to desorb most readily from sediments with peak leachate levels reached within 10 days. Lead leachate levels showed little dependence on time. The extraction efficiency of rainwater for the four metals studied here was found to be Cd>Zn, Cu>Pb, with Pb some 1000 times less extractable than Cd. The highest overall leachate levels were found for Zn. The metal leachate patterns generally showed no obvious depenence on particle size or pH. In contrast to Solomon et al. (1977b) the pH was found to remain relatively constant throughout the time period of the experiment.

2.5.4. The movement of road sediment by rainfall.

The splashing of rain droplets and the hydrodynamic drag forces created across the road surface cause the movement of road sediment particles. Hydraulic models have been used to describe this transportation process. The equation developed by Yallin (1963) has been demonstrated to be applicable to particle movement by shallow flow in street gutters (Sutherland and McCuen 1978). In the model it is assumed that sediment is lifted from the street surface when lift forces of flow exceed a critical value. Once a particle is lifted the drag force of flow moves it downstream until the weight of the particle forces it to settle out. Foster and Mayer (1972) noted that the Yallin equation is sensitive to local flow parameters, and therefore requires a hydrological model to predict the hydraulic radius of the gutter flow during a given rainfall event. The rate of transport as calculated by the model is a function of a number of interdependent factors. These include the hydrological characteristics of the catchment such as the percentage of impervious area, the length and slope of gutter, the initial total solids loadings in the gutter and the rainfall-time relationship (Pratt and Adams 1982). These factors provide primary input into the modified Yallin model. Sutherland and McCuen (1978) determined the effect of rainfall intensity and volume on sediment removal for various sediment particle sizes. Rainfall intensity was found not to be a significant factor. The percentage of sediment removed in each size fraction was related to rainfall volume by the equation:

$$TS_j = k_j(TS_i)$$

where TS_j is the percentage removal of solids in a size range due to rainfall volume j, TS_i is the percentage removal of solids in a size range due to 1/2 inch of rainfall, and k_j is a factor relating TS_j to TS_i

taken from tables.

In addition to particle size, the nature of the road surface will influence the entrainment and cross surface transportation to the gully pots and drains. Where the road surface is cracked and in poor condition a greater effective depth of rainfall is required to cause overland flow, and enable the road surface to be effectively washed. The microtopography of the road catchment is also an important factor influencing the response time to runoff after the initial rainfall input (Harrop 1983; Ellis et al. 1986). Although Sutherland and McCuen (1978) found rainfall volume to be the most significant rainfall characteristic many other workers have demonstrated that rainfall intensity and duration influence washoff of sediment from road surfaces (Waller 1972; Sartor and Boyd 1972; Pope 1980). Harrop and Ellis (1984) noted that solids removal correlated well with recorded rainfall volume, and this was particularly true for sediments finer than 2 mm. Rainfall intensity and sediment removal were observed to show similar temporal patterns and both showed a summer maximum. In addition the duration of precipitation events was found to be particularly important in determining sediment removal rates.

The influence of antecedent dry period on sediment removal is a subject of much discussion. American work suggests that this is an important factor in evaluating water quality from road surfaces (Sartor and Boyd 1972). More recent work shows a weak relationship between solids removal and antecedent dry period (Mance and Harman 1978; Whipple et al. 1978; Bedient et al. 1980; Harrop and Ellis 1984; Ellis et al. 1986). Waller (1972) suggests that the influence of street cleaning, and car and wind deflation effects lead to poor correlation of solids removal with antecedent dry period.

2.5.5. Roadside gully pots.

Roadside gully pots are known to be active contributors to and important regulators of pollution loads to stormwater runoff. Levels of metals which have been measured in gully pot liquors are shown in Table 2.15. Mance and Harman (1978) observed an increase in total heavy metal concentrations in gully liquors after flushing by heavy rainfall. It was suggested that this was due to bacterial mobilisation of sediments. Metal levels were also found to vary with the incidence of rainfall, where concentrations were initially high rainfall caused a decrease.

Table 2.15. Metal concentrations in gully pot liquors (mg l^{-1}).

Cd	Cu	Pb	Zn		Reference
-	-	-	0.09	total	Fletcher et al. (1978)
-	0.02	0.17	0.11	total	Mance & Harman (1978)
0.058	0.012	0.058	0.65	total	
-	0.05	0.032	0.10	soluble	Pratt & Adams (1984)

The principal purpose of the roadside gully pot is to act as a settling chamber for particulates and organic debris transported from the road surface. However gully pots have been found to be ineffective in removing all but the larger particles. Mance and Harman (1978) found that the effects of the gully reservoir on mass flow of particulates through the system were highly variable. Pratt and Adams (1984) demonstrated that for sediments of less than 1 mm diameter the mass of sediment removed was greatly exceeded by that washed through. In a comparison of heavy metal levels on adjacent road surfaces with those entering gully pots an enhancement of metal levels was found in the latter (Harrop et al. 1983). This was attributed to the preferential removal of the more polluted fine particles from the road surface by stormwater runoff. Beckwith et al. (1984) investigated the relative enhancement of metal levels with respect to particle size for sediment entering the urban drainage system. A concentration enhancement was found for all particle sizes in gully pot basal sediment. The residence times of metals within the gully pot vary significantly with Cd, Cu and Zn remaining, on average, within the gully pot for the duration of one storm event whereas Pb, because of its higher solid association, is considerably more persistent (Morrison 1985).

2.5.6. Characteristics of stormwater quality.

Metal concentrations in stormwater are highly variable, being dependent on the level and type of activity in a catchment and on the characteristics of individual storm events. Typical concentrations and loadings are not found. In general, suspended solid concentrations follow the stormwater hydrograph. The largest concentration increase is usually associated with the initial flow, with the response becoming less pronounced with each subsequent increase in flow. Heavy metals which are particulate associated follow a similar but less consistent pattern to suspended solids. Peak concentrations are dependent on the length of antecedent dry period, storm intensity and local land use activity (Ellis 1979). Soluble metals show an increase in concentration that is followed by a rapid and sustained decrease (Mance 1981). Multiple peaks in pollutographs are not uncommon and Ellis (1976) suggests that these are related to the late or retarded discharge of paths, drives and roofs.

After a prolonged dry period, material deposited in the channels and pipes as the previous precipitation event ended, can be readily washed out. This is often referred to as the first flush. The first flush is significantly poorer in quality than any subsequent flow. Wilber and Hunter (1980), Ellis et al. (1982) and Mance and Harman (1978) found that metal concentrations peaked within the first 20-40 minutes of a storm, although Mance and Harman (1978) noted that this was not a consistent feature of all pollutographs.

2.5.7. The partitioning of metals in stormwater.

Stormwater solids contain predominantly fine particles enriched in heavy metals (Revitt et al. 1982; Morrison et al. 1984a). Consequently the total metal concentrations in suspended solids are generally higher than corresponding street sediments (Table 2.16). Harrison and Wilson (1983) suggest that this may be due to the hydrodynamic sorting of the finer particles. Under low flow conditions only fine particles, which have a high affinity for heavy metals (see Section 2.3.4), are taken up. Morrison et al. (1984b) observed that metal concentrations were even higher than those found in the fine fraction of road sediments and therefore other factors such as adsorption play a role. Metals are solubilised by acid rain and carried into the drainage system where buffering takes place, following which re-adsorption onto fine suspended sediment can occur. Heavily salted road sediment would assist the initial desorption process particularly for metals which form strong chloro-complexes.

The dissolved phase contains between 5 and 50% of the total heavy metal loading, with Cd being particularly soluble (see Section 2.5.3). Morrison et al. (1984a) observed that Cd, Cu and Zn were predominantly found in the dissolved phase, while Pb is strongly associated with the suspended soilds phase. Similar results were reported for Cd, Cu and Pb by Harrison and Wilson (1983). The controlling parameters for the partitioning of heavy metals between the

Table 2.16. Partitioning of heavy metals in stormwater runoff.

	Cd	Cu	Pb	Zn	Reference
Suspended solids (µg g^{-1})	-	-	5800	-	Sylvester & De Walle (1972)
Suspended solids (µg g^{-1})	up to 670	160-1660	1200-8500	700-8000	Revitt et al. (1982)
Suspended solids (µg l^{-1})	0.01-20.5	14.1-288	84.8-1260	-	
Dissolved (µg l^{-1})	0.23-19.8	6.4-68.1	5.9-84.7	-	Harrison & Wilson (1983)
Suspended solids (µg g^{-1})	11.5-60.3	414-482	1911-2464	414-552	
Dissolved (µg l^{-1})	3.4-9.1	47.2-53.8	17-17.8	163-227	Morrison et al. (1984a)

dissolved and suspended solids phases include pH, suspended solids concentration, dissolved organic carbon concentration and ionic strength (Morrison et al. 1984b). Chemical fractionation of suspended solids has shown that about 10% of Cu and 20% of Pb and Zn is in a readily available form (Wilber and Hunter 1979).

2.5.8. Inpipe deposition.

There is very little data on inpipe deposition of sediments and metals in storm sewers. Gameson and Davidson (1963) have provided data for combined sewers. According to Mance (1981) approximately 15 g m^{-1} $day^{-1}$of sediment was deposited in a separate sewer during dry weather. Harrop et al. (1983) and Beckwith et al. (1984) have observed enhanced metal levels in sediments deposited in gully pots and sewer pipes.

2.6. Health Effects of Heavy Metals in Road Sediments.

Metals are an integral part of the environment and of living organisms. Some metals play essential roles in living organisms and exert a beneficial biological influence when present at certain concentrations through mechanisms which are poorly understood. A number of metals have no positive biological role and their only known effects are harmful. Toxic effects may be experienced with any metal should exposure exceed a critical level. To cause an acute toxic effect following a single dose of a metal, relatively large amounts are necessary even for the most toxic metals. Of particular concern is the chronic toxicity which may result after long term exposure to low metal concentrations. Both beneficial and toxic effects of metals can be influenced by other elements in the environment, and by biological factors. In addition toxicity can often be lessened by biological adaptation.

2.6.1. The toxic effects of heavy metals on non-human targets.

The susceptibility of an organism to a particular metal depends on a number of factors including the type of organism, the life stage, time of exposure and environmental parameters such as water hardness, concentration of organic ligands, temperature, pH and dissolved oxygen levels. Some of these factors influence the amount of metal in a bioavailable form (hardness and pH), and others affect the capacity of the organism to resist the effects of a metal (dissolved oxygen, temperature and hardness).

Table 2.17. Toxic levels of heavy metals in the aquatic environment.

	Metal concentration (mg l^{-1})			
	Cd	Cu	Pb	Zn
Plants	0.02-1.0	<0.1	0.1-5.0	-
Invertebrates (LC_{50})	0.003-0.5	0.006-225.5	0.002-670.0	0.5-5.0
Fish (LC_{50})	0.09 - 105.0	0.017-1.0	0.5-1.0	0.5-5.0

Source Moore and Ramamoorthy (1984)

Cadmium is not known to be biologically essential or beneficial to plant or animal metabolisms, but the metal is widely recognised as being a highly toxic substance. Maximum toxicity to aquatic organisms is associated with poorly buffered water at low pH. Micro-organisms show a highly variable response to Cd (Table 2.17). The presence of other heavy metals can result in a synergistic effect on Cd toxicity. The lethal threshold of Cd is reduced by 40% when mixed with Cu and Zn.

Copper is a common pollutant in natural waters and is of concern because it is toxic to many aquatic organisms at low concentrations (Table 2.17). Copper is more toxic to fish than any other metal except Hg (Moore and Ramamoorthy 1984). Free Cu ions appear to be the most toxic species, however this is complicated by the many complexation reactions the metal may undergo (Hart 1982).

Lead is toxic to aquatic organisms at low concentrations. Algae have a relatively high threshold for Pb, and the effects of Pb seem more pronounced in higher forms of organism. Although Daphnia remain unaffected by concentrations of 30 µg l^{-1}, rainbow trout suffer sub-lethal effects at 6 to 12 µg l^{-1}. Generally in fish acute lethal effects occur only at high concentrations and rainbow trout, for example, will suffer long term effects at 100 µg l^{-1}. The hardness of the water has been found to be an important influencing factor in metal toxicity (Davies et al. 1976).

Lethal poisoning of birds (in particular swans) by spent Pb shot and fishing tackle has been extensively reported (Piotrowski and Coleman 1980). Generally, studies of Pb exposure and effects on animals have been confined to small mammals and domestic animals surrounding smelters (Roberts et al. 1978). For domestic animals chronic effects have been found at Pb levels of 80-300 µg g^{-1}in pastures (Piotrowski and Coleman 1980).

✓ Zinc is an essential element in animal and plant nutrition that is required for more than seventy metallo-enzyme systems. Zinc toxicity to plants is highly variable and many species are able to adapt to high levels of the metal. Acute toxicity to aquatic organisms is low (Table 2.17). Adverse effects are noticeable at concentrations lower than 50 µg l^{-1} in soft waters. In some cases algae and invertebrates appear to be more sensitive to Zn than do fish.

There are in force several European Community directives which govern the management of water quality. Five directives have been adopted in the United Kingdom dealing with water for human consumption, surface waters intended for abstraction, bathing waters, waters supporting freshwater fish and saline waters supporting shellfish. These guidelines have been reviewed by Gardiner and Mance (1984). The water quality standards for the protection of freshwater organisms are outlined in Table 2.18. These standards are defined as 95 percentile values, based on monthly sampling except where water quality is significantly better than the standards. Highly toxic heavy metal discharges in stormwater runoff may exceed the guidelines described below (see Section 2.5).

Table 2.18. E.E.C. water quality standards for the protection of freshwater organisms (µg l^{-1}).

	Salmonid fish	Coarse fish	Other organisms
Cd (total)	5	5	5
Cu (<0.45 µm)	1-28^{*1}	1-28^{*1}	1-28
	5-112^{*2}	5-112^{*2}	
Pb (<0.45 µm)	4-20	50-250	5-60
Zn (<0.45 µm)	10-125^{*1}	75-500^{*1}	100
	10-500^{*2}	300-2000^{*2}	

*1 Applies to water not specifically designated by the appropriate directive.

*2 Applies to waters specifically designated by the appropriate directive.

Source Mance and Gardiner (1984)

2.6.2. The toxic effects of heavy metals on humans.

Cadmium and Pb are not thought to be essential to human body functions, whereas Cu and Zn are widely recognised as essential elements in human metabolism. The major non-occupational human intake of Cd is via food and tobacco. Excessive intake causes nausea, vomiting, diarrhoea, abdominal pains, myalgia and weakness. Reported cases of death following Cd poisoning in Japan led to increased concern regarding levels of this metal in the environment. Cadmium retention in the lungs is dependent on particle size. A retention level of 25% has been estimated and of this deposited material, 60% is taken up in the bloodstream (Lauwerys 1978). The uptake of Cd in the gastro-intestinal tract is about 2% in animals and between 3% and 8% in humans (Friberg et al. 1979). The liver and kidneys have the highest concentrations in the body as these organs play a dominant role in the long term accumulation of Cd (Friberg et al. 1974). Excretion of Cd has been shown to be very low (Piscator 1979).

Although Cu toxicity to humans is low, ingestion of large quantities (mg doses) can cause vomiting and diarrhoea (Hart 1982). The metal is not retained by the body and therefore does not accumulate to toxic proportions (Hart 1982).

Lead is an accumulative poison to humans and has received widespread attention. Children appear to be the most sensitive human group, because of their greater ability to absorb ingested Pb, and their more rapid growth. Childhood plumbism is a particular problem in some populations. The main source of Pb in such cases is the home environment where Pb based paints have been used. The tendency of some small children to take various non-food objects into their mouths is of particular concern. This habit (pica) may persist over several years. Pre-school children (2-3 years) with normal mouthing habits are also a vulnerable group since at this age the child is moving about and tends to spend most of its waking hours crawling on the ground (Ter Haar 1979). Old paintwork in the home is the single most common cause of severe childhood Pb poisoning in the United Kingdom accounting for one third of known cases (D.H.S.S. 1980). Although Pb paintwork has been identified as being a major source, dust brought into the house and paint residues from previous owners are additional sources (Vostal et al. 1974). For slightly older children, play areas outside the home such as gardens, paths and pavements are the most important areas, followed by pedestrian pavements, recreation grounds and nursery schools.

Lead is a health hazard to all age groups, including adults, if taken in large enough doses. Normally adults who are not occupationally exposed are unlikely to be exposed to environmental Pb levels to a degree which is of concern. But the inhalation of dust laden air arising from rubbing down Pb paintwork or ingestion of flakes, directly or via food can cause problems in adults (Manton 1985).

Lead induces a number of effects of which the most widely known refer to derangement of haem synthesis. Anaemia, to which children are most susceptible, may develop. Additional injury is thought to take the form of slight but irreversible damage to brain development in growing children. Such impairment may develop at moderate levels of exposure and is reflected in increased irritability, impaired concept formation and reduced learning ability (Landsdown et al. 1974). This is very difficult to quantify, and its existence is disputed. There is also some evidence to link Pb in blood with high blood pressure (Pocock et al. 1985; Schwartz 1985).

Some authors have questioned the causal relationship of these effects at low Pb exposure levels as it is difficult to distinguish between the effect of environmental Pb and an impoverished social environment (W.H.O. 1977; Peterson 1979).

For most members of the community, food is the main source of Pb intake (D.H.S.S. 1980). In adults the uptake from the gastro-intestinal tract is between 13% and 18%, whilst in children it is probably higher (Chamberlain et al. 1978; D.H.S.S. 1980). Lung retention of airborne Pb depends on the particle size and respiratory volume. On average, retention is about 30% of the amount originally present in the air (W.H.O. 1977). Of the amount deposited in the lungs only a part is taken up, the rest being transferred back to the larynx by mucocillary transport. Within the body Pb is distributed amongst all the tissues and body fluids. Blood and soft tissues represent a rapid exchange compartment which relatively quickly becomes equilibrated with uptake. The skeleton constitutes the slow exchange compartment and so plays a significant role in accumulation. Elimination of ingested Pb is primarily by the faeces and of the Pb taken up in the bloodstream 76% is excreted in the urine and 16% in the faeces (W.H.O. 1977).

Any increase in long term exposure to Pb is reflected in Pb blood levels. At low exposure an increase of 1 $\mu g\ m^{-3}$ is reflected by a 1 $\mu g\ dl^{-1}$ increase in blood Pb level (Snee 1982). The shape of the relationship between blood and airborne Pb concentrations is usually assumed to be curved (Chamberlain 1983). Snee (1982) and Angle et al. (1974) both recommend a linear model which takes account of sources other than the atmosphere. The average blood Pb levels for non-occupationally exposed groups is 5-10 µg dl^{-1} for children and 10-20 µg dl^{-1} for adults (Quinn and Delves 1985).

The ingestion of dust via dirty hands has been suggested by a number of workers as being a significant source of Pb intake particularly for young children (Angle et al. 1974; Roberts et al. 1974; Barltrop et al. 1975; Duggan and Williams 1977; Roels et al. 1978; Brunekreef et al. 1983; Royal Commission on Environmental Pollution 1983). Duggan (1980, 1983) has reviewed the evidence for this particular pathway and concludes that a quantitative relationship between the Pb in dust concentration and the blood Pb value exists. Using theoretical calculations, Duggan (1980) determined that an increment of 1000 µg g^{-1} in the dust concentration will lead to an increase in blood Pb of 5 µg dl^{-1} for children. Furthermore this increase is in addition to any increase due to airborne Pb. Not all workers agree with the view that ingestion via dirty hands is an important pathway for Pb into the body. Ter Haar (1979) attributes the peak in blood Pb value found in 2-3 year old children as being due to gnawing of paint. Gallacher et al. (1983) found that in areas exposed to a variety of traffic conditions housedust was of negligible importance in contributing to blood Pb levels. Roels et al. (1978) have suggested that low level resuspension of street or surface dust may also be a pathway for ingestion in young children.

Zinc can be toxic to humans at high levels, however such exposure is unlikely to be encountered. Zinc does impart an undesirable taste to foods and water which are contaminated by the metal. Like Cu, Zn does not appear to accumulate in tissues (Hart 1982).

2.6.3. Reference levels for heavy metals.

Airborne Pb levels are monitored in relation to the European Community Directive 82/844/EEC. (EEC. 1982). This requires that the Pb in air level does not exceed 2.0 µg m^{-3} expressed as an annual mean. Very few reference or guidance values exist for heavy metals in street sediments. Those that do, refer only to Pb. The former Greater London Council set a guideline value of 500 µg g^{-1} for total Pb in surface dusts which is used in conjunction with a Pb in air guideline value of 1 µg m^{-3} (Schwar 1983). Lead levels exceeding these guidelines require further investigation. In making an assessment the guidelines can be considered to be met if the level by which one of the values is exceeded is matched by a corresponding decrease in the other. The former Greater London Council also set an 'interim action level' for surface dust of 5000 µg g^{-1} which if exceeded in areas where the Council had particular responsibility would have lead to appropriate remedial action being taken. No guideline values exist for metals other than Pb in surface dusts. However, the Department of the Environment sets a 'trigger concentration' of 3 µg g^{-1} for Cd in soils. Above this concentration a site may be regarded as contaminated (DOE. 1983a). A similar 'trigger concentration' of 500 µg g^{-1} is also set for Pb.

Blood Pb levels are governed by a number of guidelines. The European Community Directive 77/312/EEC (EEC 1977), requires that if the reference levels given below are exceeded the Commission must be told and measures taken to trace and reduce the source of the exposure.

Maximum of 20 µg dl^{-1} for 50% of a group
Maximum of 30 µg dl^{-1} for 90% of a group
Maximum of 35 µg dl^{-1} for 98% of a group

However the guideline does not define the population which constitutes a group. The DOE/WO. circular 22/82-31/82 advises that when one person is confirmed to have a blood Pb level greater than 25 µg dl^{-1} the environment must be investigated for sources, and steps taken to reduce the exposure (DOE. 1982).

CHAPTER 3. SAMPLING AND ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF HEAVY METALS IN STREET SEDIMENTS.

3.1. Introduction.

Although a large number of authorities and organisations are involved in the measurement of heavy metals in street sediment, either for research or monitoring purposes, there are no widely recognised procedures or standard methods available to workers in this field. A knowledge of the sampling and analytical procedures which have been employed is required if comparisons are to be made with reference levels, as well as between the results of different workers. The purpose of this Chapter is to outline the procedures used during the course of this study. The methods described have been based on procedures given in the literature but modified to achieve the objectives of this project (see Chapter 1), and to suit the facilities available in the Urban Pollution Research Centre, Middlesex Polytechnic.

3.2. Sampling Techniques.

A number of different techniques have previously been employed to collect samples of street sediment and these are summarised in Table 3.1. The most widely used method in the United Kingdom is sweeping the dust into a suitable container which is normally a plastic dustpan or scoop. The major drawback of this technique is the loss of fine particles due to resuspension during the sweeping action. It is also difficult to remove sediment from indentations on coarse road surfaces. Vacuum techniques have been widely used in the United States for collecting street sediments. Some workers have used specially modified wet and dry type vacuum cleaners or have adapted air sampling pumps. Although fine particles are not lost through resuspension when using vacuum techniques, a proportion of the fine particles collected is inevitably lost during the sediment transfer to sample containers, and during the subsequent cleaning of the equipment. Sample collection is slower because the sampler must be carefully cleaned after each collection and these methods are also more expensive and require additional equipment such as power generators.

Other techniques which have been used for surface dust collection include: wiping the surface with a paper tissue; scooping up a sample with a plastic spatula; and pressing self adhesive labels onto

Table 3.1. Methods used to collect street surface sediments.

Method of sample collection	Reference
Sweeping into a container	Turner (1973), Archer & Barratt (1976), Farmer & Lyon (1977), Fergusson & Simmonds (1983) Harrison (1979), Ellis & Revitt (1982), Harrison et al. (1981), Kiezer et al.(1982), Millar & Cooney (1982), Tinsley et al. (1983), Schwar (1983), Thornton et al. (1985)
Vacuum techniques	Sartor & Boyd (1972), Pitt & Amy (1973), Shaheen (1975) Solomon & Hartford (1976), Pitt (1979) Hopke et al. (1980), Linton et al. (1980) Dong et al. (1984)
Self adhesive labels	Lepow et al. (1974)
Smearing with damp tissue	Vostal et al. (1974)

the surface. Such techniques provide very small samples and so may not be representative. Only concentrations and not loadings can be determined using these methods. In a number of surveys the sampling method used is not reported.

When collecting street sediments it should be noted that heavy metal levels can show considerable spatial and temporal variations. Because of these possible variations surface dust samples need to be collected from as large an area as possible, and on a number of occasions during a given sampling period. The choice of location and area to be sampled must be dictated by local circumstances and by the aims of the investigation. Thus for local authority surveys of roadside dust, pavement sweeping may be sufficient, but for surveys researching stormwater sources the actual road surface and in particular the gutters must also be included. Schwar (1983) recommends that an area of at least 1 m^2 should be sampled, but if only a small amount of sediment is present a larger area may need to be used.

3.3. An Assessment of the Efficiency of Sediment Collection Techniques.

In order to maximise the accuracy and completeness of the information obtained in this investigation, an assessment of the collection efficiency of the two most widely used methods of sediment sampling was carried out; sweeping with a plastic dustpan and brush or using a wet and dry vacuum cleaner.

3.3.1. Details of the sampling techniques.

A single large sample of road sediment was collected for use in the testing of the different sampling techniques. The sediment was sieved into several size fractions and an 'artificial' street sediment of known particle size composition produced (Table 3.2). Because the collection efficiencies for the finer particle sizes (<63 µm) were of particular interest, the proportion of these in the test sediment was increased compared to that in the actual sediment collected. The test sediment was spread over a 10 m^2 area of rough concrete located inside a garage. The use of an enclosed surface avoided resuspension of the dust by gusts of wind. The sample area had previously been cleaned by several brushing operations and by use of the vacuum cleaner. The applied sediment was collected using the dustpan and brush. After the surface had been cleaned again, the experiment was repeated but sample collection was made using a vacuum cleaner. Three replicate collections were made for each technique. The experiment was then repeated for sediment which had been dampened by an application of approximately 500 ml of water over the 10 m^2 area using a hand held spray. When using the dustpan and brush, care was taken during sweeping both to ensure that as much of the sediment as possible was collected, and to reduce resuspension of the fine particles. The sediment after collection was gently brushed into a plastic bag using a soft paint brush.

Table 3.2. The collection efficiency of vacuum techniques and dustpan and brush for different sediment particle sizes.

		Collection efficiency (%)			
		Vacuum cleaner		Dustpan and brush	
Particle size range (μm)	Initial sediment weight (g)	Dry sediment	Dampened sediment	Dry sediment	Dampened sediment
>1000	100.0	91.8	97.8	93.1	96.8
500–1000	100.0	93.9	88.8	96.1	103.4
250–500	100.0	101.5	104.5	103.2	107.1
125–250	100.0	102.2	95.1	99.9	89.1
63–125	50.0	83.3	77.2	90.4	85.2
38–63	40.0	91.4	77.8	68.2	49.8
<38	30.0	107.7	68.4	63.0	51.2

The vacuum cleaner used was a Shelton J-Vac wet and dry type in which the motor is mounted on top of a tank, into which dust is drawn. An automotive type paper air filter prevents dust from passing to the motor. Large particles of debris and water fall to the bottom of the tank and do not impede the airflow. The filter had been modified by covering it with a 5 μm size nylon mesh. This provides a known particle size cut off, and also facilitates emptying the cleaner between samples. A phenolic epoxy coating reduced the possibility of sample contamination by the metal tank. Additionally any exposed metal parts were covered by masking tape. During sampling the leading edge of the vacuum head was slightly elevated to permit an adequate airflow and to collect large particles.

After sample collection was completed the dust inside the tank was allowed to settle for a few minutes, then brushed into a plastic bag. The filter and tank were carefully brushed and the collected dust transferred to the plastic bag. The collected sediments were size fractionated using stainless steel sieves. Damp sediments were dried overnight before sieving.

3.3.2. Relative efficiencies of different collection techniques.

The results of the experiment are shown in Table 3.2. It can be seen that using the vacuum cleaner to sample the dry sediment is the most effective collection method with an overall removal efficiency of 96%. Pitt (1979) reports that using similar equipment, dry vacuum sampling is capable of removing more than 99% of the particles from the street surface along with more than 80% of the major pollutants including heavy metals. The three other sampling methods give very similar overall sediment recoveries of approximately 92%. All four sampling techniques have similar efficiencies for individual particle size groupings coarser than 63 µm. However when sampling dry sediment the vacuum technique shows a considerably higher collection efficiency for the lower size ranges. The other three techniques show a marked decline in sediment recovery for the small particle sizes (<63 µm), particularly the dustpan and brush when collecting dampened sediment. This is due in part to the inability of the dustpan and brush to remove fine particulates from indentations in the surface, and also to soiling of the equipment when collecting damp sediments.

Sample collection usually took place after two days of dry weather. Despite this precaution, the sediment was occasionally damp below the surface. This caused problems when using the vacuum cleaner as sediment became lodged in the vacuum pipe and on the filter causing intermixing of samples. To avoid this, if the sediment was found to be damp, sample collection was performed using the dustpan and brush although it was realised that this collection method was the most inefficient tested.

In this study, all road surface areas sampled were based on a 5 m length of curb. A large area of road or pavement was therefore sampled in areas where sediment loadings are low in order to obtain representative samples. The gutter width was taken as 0.33 m and the resulting smaller area which was sampled balanced the considerably higher sediment loadings.

3.4. Sample Pretreatment.

After collection, sediments were dried overnight at 40 °C before sieving through stainless steel sieves. This process removes large material from the sediment such as twigs, stones and metal objects, and serves to homogenise the sample. There is considerable variation amongst workers in the choice of sieve aperture size used in sample pretreatment. The importance of the correct selection of sieve aperture size is demonstrated by the data given in Figure 3.1. This shows the variation in Pb concentrations for sediments of particle size smaller than a given mesh aperture, calculated from data cited by Rameau (1972). The graph shows that if all the sediment had been digested then the Pb concentration would have been 588 µg g^{-1}, whereas if the <500 µm and <250 µm fractions were analysed the effect would have been to increase the Pb concentration to 650 µg g^{-1} and 950 µg g^{-1}, respectively. In order that determined metal values were a true reflection of actual metal levels in the total sediment, and also to avoid errors caused by a small number of particles of anomalous composition a sieve aperture size of 500 µm was chosen in this work for sample pretreatment.

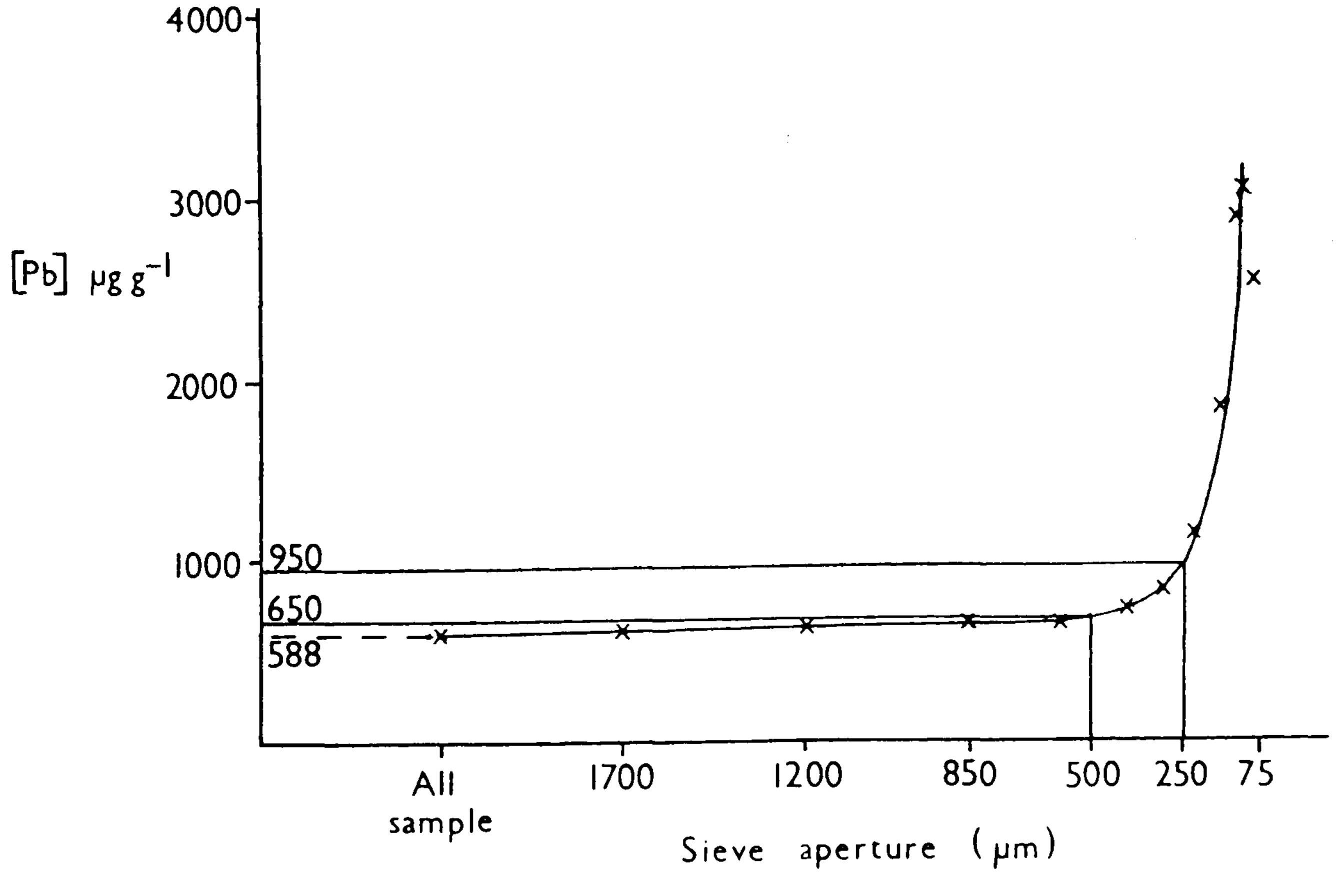


Figure 3.1. The effect of sieve aperture size choice on Pb in road dust concentration.

3.5. A Review of Metal Extraction Techniques.

Many different analytical techniques have been used for determining heavy metals in environmental materials such as street dust. The most common technique employed is digestion by strong acid(s) followed by atomic absorption spectrophotometric analysis. Strong oxidising acids are used as they not only dissolve all precipitates and adsorbed metals but also destroy organic materials, freeing metals and removing possible analytical interferences. Alternatively dry ashing may be utilised to destroy organic matter prior to solubilisation of the metals by acid. There is, however, a risk of volatilisation losses and contamination when using this technique. The chemical nature and concentration of the acids used by different workers varies considerably. Nitric acid is commonly used, and after digestion the sample is evaporated to dryness to cause more complete decomposition of the organics present in the sample.

It has been shown that acid digestion procedures can lead to incomplete extraction of metals from soils when compared to direct determination of undigested samples by flameless atomic absorption spectrophotometry (Jackson and Newman 1983). However direct introduction of slurries into a graphite furnace leads to slower throughput of sample analyses than flame atomic absorption, and is also subject to matrix interferences. In an alternative approach suspensions of powdered solids have been aspirated directly into the flame of atomic absorption spectrophotometers, but this method suffers from poor reproducibility (Štupor and Ajlec 1982).

Acid extractions may yield incomplete recoveries of metals unless repeated evaporations are employed. This is time consuming and may lead to high blanks, therefore more rigorous digestion conditions must be used. Complete dissolution of samples is possible but requires digestion by acid mixtures including HF in P.T.F.E. lined bombs or beakers (Harrison and Laxen 1977; Price and Whiteside 1977; Farmer and Gibson 1981). This technique is unsuitable for large surveys as it requires expensive equipment, is time consuming and may be dangerous. For polluted sediments several extraction methods which are less hazardous and can be used under less severe conditions have been reported. Mixtures such as HNO_3 and $HClO_4$ (Ritter et al. 1978; Markunas et al. 1979; M.A.F.F. 1981; Veneman et al. 1982; Agemain and Chau 1976), HNO_3 and HCl (Harrison and Laxen 1977; Ritter et al. 1977; Schwar 1983) and HNO_3 and H_2O_2 (Krishnamurty et al. 1979) have been reported to give results which are comparable to HF attack. A number of workers have found the extraction mixtures mentioned above to be equally effective for the determination of metal levels in sediments. However a wide range of sediment types have not been tested (Ahl and Lundevahl 1980; Eastwood and Jackson 1983). Davis and Charlton-Smith (1982) have reported that HNO_3 and $HClO_4$ mixtures give slightly higher results than other acid mixtures, but more importantly give better precision.

Several workers have reported using much weaker extracting agents to provide comparative values of extractable or available metals, such values are particularly relevant to investigations into the health effects of metals (Harrison 1979; Sinex et al. 1980; Tinsley et al. 1983). Extractants such as CH_3COONH_4, CH_3COOH, dilute HNO_3 and dilute HCl have the advantage of being rapid and relatively cheap. However where gross contamination is to be investigated it is more appropriate to determine total metal contents.

When selecting an analytical technique a number of requirements must be fulfilled. The method must be sensitive for all the metals being studied, and it must be able to deal with the complex matrix in which the metals are found. The technique should also be free from interferences and comparable to previous work in the field. Good precision is required especially as there is a lack of a standard reference material available for validation purposes.

3.6. An Assessment of the Importance of Digestion Conditions on the Extraction of Heavy Metals From Road Sediments.

Variations in heavy metal levels as a result of the chosen analytical technique have been investigated by Jones and MacDonald (1983). It was found that the mean Pb level determined in soils was depressed by sample grinding and also by using an increased ashing temperature. Higher Pb levels were produced when sample digestion was carried out under refluxing conditions in comparison to simple boiling of the samples in acid. Samples 'refluxed' in a beaker with a watch glass placed over the mouth showed consistent losses of Pb which the authors could not explain.

In order to investigate variations caused by the use of different digestion conditions, and to maximise the extraction of heavy metals from road sediments a number of experiments were carried out to determine the influence of sample grinding, digestion under simple refluxing conditions, acid mixture composition and cold overnight pre-digestion. For this purpose a single sample of street dust was collected, sieved to less than 500 μm and mixed thoroughly.

3.6.1. Determination of the effect of grinding the sample.

In order to determine the effect of sample grinding prior to digestion two sediment batches, each comprised of twelve subsamples were digested. One batch was dried at 105 °C before the replicates were weighed. The second batch was ground using a rotating arm and mesh laboratory mill before drying. Digestion was carried out using a 9:1 mixture of HNO_3 and $HClO_4$ as outlined in Section 3.7. Metal analysis was performed by atomic absorption spectrometry.

The results shown in Table 3.3 indicate that the ground samples gave reduced Pb and Cd values compared to the unground samples, although the trends remain within the standard deviations about each mean.

Table 3.3. The effect of grinding the sample before digestion.

	Mean metal concentration ($\mu g\ g^{-1}$)	
	Cd	Pb
Samples ground	2.5±1.0	1155.4±159.3
Unground samples	3.5±0.5	1375.2± 83.5

Similar results were obtained by Jones and MacDonald (1983). These authors suggested that grinding breaks down the particles and so exposes a larger surface area to the action of the extracting acids. However, increasing the surface area of the sediment would expose more of the metal content and so increase the metal recovery. The lower metal levels found in the ground samples in this experiment may be explained by the loss of very fine sediment during the grinding process. The results for Cu and Zn are excluded from Table 3.3 because part of the grinding mill was found to be made from brass.

3.6.2. Determination of the effect of cold overnight digestion on metal recovery.

Two batches, each comprised of twelve subsamples of road dust were digested using the technique outlined in Section 3.7. In the first batch the acids were evaporated away immediately. The second batch was covered and left overnight before the acids were boiled away.

The results shown in Table 3.4 indicate that cold overnight pre-digestion slightly increased the extraction efficiency of all the metals analysed. The increased time allows the extractants to break down the more strongly bound metals in the sediment, such as those bound to organic materials.

Table 3.4. The effect of delayed and immediate sample digestion on metal extractions.

	Mean metal concentration ($\mu g\ g^{-1}$)			
	Cd	Cu	Pb	Zn
Samples digested immediately	3.3±2.7	79.5± 9.0	1258.3±70.0	438.0±19.7
Samples left overnight	3.5±0.5	90.7±16.6	1375.2±83.5	495.0±39.5

3.6.3. Determination of the effect of increasing the proportion of perchloric acid used in the digestion.

To investigate the effect of increasing the proportion of $HClO_4$ in the extraction reagent, four batches of six subsamples were treated with the following HNO_3 and $HClO_4$ mixture ratios: 10:0; 9:1; 8:2 and 7:3.

The results of this experiment are given in Table 3.5. It can be seen from this table that increasing the proportion of $HClO_4$ in the digestion mixture slightly increases the levels of Cd, Pb and Zn extracted from road dust. For Cu, increasing the $HClO_4$ content has no definite effect. The results from all the treatments generally fall within one standard deviation. Increasing the $HClO_4$ content of the acid mixture results in improved precision for all metals except Pb, which after an initial drop in precision shows no change. The results of this experiment are in general agreement with those of Davis and Charlton-Smith (1982), who reported slightly higher results and greater precision when using $HClO_4$ mixtures. For safety reasons it was decided to use only a 9:1 mixture of HNO_3 and $HClO_4$.

Table 3.5. The effect of increasing the proportion of perchloric acid in the digestion.

Acid ratio	Mean metal concentration (μg g^{-1})			
	Cd	Cu	Pb	Zn
HNO_3 only	3.1±1.0	92.3±27.7	1356.0±19.4	471.7±18.6
9:1	3.1±0.2	80.5± 8.6	1352.5±38.8	476.6±12.8
8:2	3.4±0.4	89.0±18.4	1360.9±37.0	473.5± 6.2
7:3	3.6±1.2	78.8± 7.5	1364.3±37.0	476.5±16.4

3.6.4. Determination of the effect of refluxing during the digestion procedure.

To determine the influence of refluxing on the extraction efficiency of the digestion procedure, three batches of six subsamples of road sediment were digested using the procedure outlined in Section 3.7. One batch was evaporated to dryness in an open beaker. The second set was boiled under simple reflux conditions in beakers covered with a watch glass for 1 hour. After an hour the watch glass was removed and the acids evaporated to dryness. The final batch was 'refluxed' in beakers covered with watch glasses until the sediment was dry.

The results of this experiment are given in Table 3.6, and show that refluxing the acid mixture results in higher Cu, Pb and Zn values but lower Cd results. Precision for all metals was reduced by refluxing the samples, and this may be due to loss of the sediment because of bumping. This effect was particularly noticeable when sediments were 'refluxed' to dryness. It was decided that the improvement in metal extraction was not sufficient to outweigh the loss in precision, and subsequently all samples were boiled to dryness without refluxing.

Table 3.6. The effect of refluxing on the extraction procedure.

	Mean metal concentration (μg g^{-1})			
	Cd	Cu	Pb	Zn
Boiled to dryness	4.2±1.4	95.8± 4.4	1418.6±28.8	486.6±12.0
Refluxed for 1 hour	3.9±1.6	98.8±13.5	1421.0±63.4	487.7±15.5
Refluxed to dryness	3.2±1.1	101.4±31.4	1475.6±84.5	422.5±15.3

3.7. The Extraction Technique Adopted In This Study.

As a result of the series of experiments outlined in Section 3.6, a method for extracting heavy metals from road sediments was established and this is outlined below.

a) Road sediment (1.0 to 2.0 g) was weighed out into a 100 ml beaker which had previously been soaked in 10% HNO_3 for 24 hours and then washed in de-ionised water. All glassware used in the procedure had been similarly treated. The sediment had been oven dried at 40 ^oC, then sieved to <500 µm so that the sediment was representative of the bulk sample. The sieved sediment was oven dried at 105^oC for 24 hours to achieve a constant moisture content.

b) 20 ml of concentrated HNO_3 and $HClO_4$ mixture in the ratio 9:1 was added to the beaker.

c) The samples were allowed to stand at room temperature overnight. Digestion was completed by gentle warming on a heating mantle or sandbath to ensure that losses due to splashing were avoided. Heating was continued until a minimum of liquid remained.

d) The soluble metals in the residue were taken up in 25 ml of 1M HNO_3 by warming on a hotplate.

e) The sample was filtered through a Whatman No. 42 filter paper into a 100 ml volumetric flask. All of the sediment was washed onto the filter paper using 1M HNO_3, and the sample volume made up to 100 ml.

f) Prior to analysis by atomic absorption spectrometry the sample was stored in a polypropylene container at 4^oC. The container had been pre-washed with 10% HNO_3.

The digestion procedure outlined above was applied to the determination of heavy metals in a range of environmental samples collected during this research project. These included atmospheric particulates, dissolved and suspended metals in rainfall and stormwater. Only slight modifications were made to the technique to take account of the lower metal levels in these samples. These include using 10 ml of conentrated acid mixture in stage (b), using 10 ml of 1M HNO_3 at stage (d) and pouring directly into a 25 ml volumetric at stage (e).

3.8. Analytical Techniques For Heavy Metal Determinations In Road Sediments.

3.8.1. Atomic absorption spectrometry.

Atomic absorption spectrometry is a sensitive analytical method which is widely used for the determination of metals in solution from trace quantities upwards. The technique can be applied to analyse over sixty elements provided they are in a homogeneous solution. Atomic absorption spectrometry has good specificity, sample preparation is relatively simple and handling errors are minimal. Furthermore analyses can be performed rapidly. Interelement effects are not very pronounced and can be readily minimised. Detection limits of less than 0.1 mg l^{-1} are obtainable for most of the commonly determined elements. Modifications to the technique such as flameless atomic absorption spectrometry have resulted in even lower detection limits of 0.001 to 0.005 mg l^{-1}. However, this adaptation is more time consuming and suffers from more matrix interference effects than conventional flame atomic absorption.

The instrument used in this study was a Pye Unicam SP2900 fitted with deuterium background correction. Typical flame performance figures for the elements under study are given in Table 3.7. Alterations to the instrumental settings were kept to a minimum and so a stoichiometric flame, a slit width of 0.4 nm and a burner height of 10 mm were used for all metals.

Table 3.7. Flame performance figures for the SP2900 atomic absorption spectrometer (Pye Unicam 1980).

Element	Wavelength nm	Flame	Sensitivity mg l^{-1}	Detection limit mg l^{-1}	Lamp current mA
Cd	228.8	Air/C_2H_2	0.01	0.002	6
Cu	324.8	,,	0.029	0.003	4
Pb	217.0	,,	0.08	0.01	4
Zn	213.9	,,	0.01	0.001	7

As with all spectroscopic methods of quantitative analysis, the relationship which describes the absorption of radiation by ground state atoms in atomic absorption spectrometry is the Beer-Lambert equation.

This equation assumes that the resonance line is resolved from all other emission lines, and that the resonance emission line width from hollow cathode lamps is much greater than the corresponding absorption line of the atomic vapour. This latter assumption is not strictly true, and although a linear concentration-absorption relationship is usually followed for absorbances of less than 0.3-0.4, above these values calibration becomes increasingly non-linear. This effect is most pronounced for elements such as Cd and Zn because of self absorption.

All modern atomic absorption instruments have electronic facilities for converting the absorption obtained for three or more standards into a linear calibration, and thereby giving a direct read-out of sample concentration. In most cases this is carried out by linear regression analysis using least squares curve fitting. However this may be of little use when dealing with an absorption calibration that is initially a straight line becoming progressively more curved at higher concentrations (Tyson 1984). Effects such as ionisation and flame reaction kinetics may cause the curve to be more complex in shape with points of inflection and even regions of negative slope (Thompson 1979). Furthermore, outliers could be present due to errors in the preparation of calibration standards. For these reasons the results from computing facilities must be treated with caution. It is not good practice to work with absorption values greater than 0.8. Visual inspection of the calibration curve was used to ensure a linear concentration-absorption response.

3.8.2. Anodic stripping voltammetry.

Anodic stripping voltammetry is an electrochemical technique for determining metals at $\mu g\ l^{-1}$ to $ng\ l^{-1}$ concentrations which is of comparable sensitivity to graphite furnace atomic absorption spectrometry. The technique involves two steps; first the metals are plated from solution onto a mercury cathode by means of a predetermined controlled potential for an accurately timed period. In the second step the electrode is made the anode and the metals are stripped sequentially by applying a potential sweep (often pulsed). The metals are stripped at characteristic potentials, and the currents which flow are proportional to the concentration of the element in the sample solution. Anodic stripping is only applicable to a small range of metals including Cd, Cu, Pb and Zn. The technique can be used for the separate determination of complexed or bound metals. The sample throughput using anodic stripping voltammetry is small, but all four of the elements under study can be analysed simultaneously, although Zn is usually analysed separately to avoid the formation of intermetallic compounds.

The instrument used in this study was a Princeton Applied Research model 384, the instrumental parameters for which are given in Table 3.8. Before each measurement the sample solution was de-aerated by bubbling through nitrogen to remove dissolved oxygen, as the reduction of this interferes with the polarographic determination of other elements. De-aeration also removes some dissolved CO_2 from the sample and hence the pH is raised. It is necessary to add a buffer to the sample in order to maintain the pH in the original range. The buffer also acts as a supporting electrolyte to maintain a constant ionic strength during the plating/stripping processes. Calibration was always carried out by the standard additions method when using this technique.

Table 3.8. Instrumental settings for the determination of Cd, Cu, Pb and Zn by anodic stripping voltammetry.

Electrode	H.M.D.E. (medium)
Initial potential	Cd, Cu, Pb -0.9 V, Zn -1.2 V
Final potential	Cd, Cu, Pb 0.0 V, Zn -0.9 V
Purge	240 s
Drop time	0.5 s
Scan increment	2 mV
Deposition time	180 s
Equilibrate	30 s
Pulse height	0.05 V

Supporting electrolyte 2M CH_3COONa buffer to pH 7

3.9. Calibration by Standard Additions.

The method of standard additions is often used in order to compensate for matrix interferences. Harrison and Laxen (1977) found that slight inaccuracy is incurred in metal determinations if these are not accounted for. In the standard additions method the concentration of an unknown is determined by making new solutions from the original one by adding successive known amounts of that substance. Extrapolation of a plot of absorbance or current against concentration added curve gives the analyte concentration from the intercept on the concentration axis. The limitations of the technique are:

a) It is necessary to work in the linear portion of the calibration graph;

b) The method will not correct for non-specific background absorption when using the atomic absorption spectrometer.

For the method to be successful the interferences must effect the slope of the calibration to the same percentage depression. This may not always be the case (Tyson 1984).

3.9.1. The effect of using standard additions in the atomic absorption spectrometric analysis of heavy metals.

In order to determine the effect on the analytical values of using the standard addition technique replicate subsamples of a road sediment were digested using the procedure outlined in Section 3.7. Determination of the metal levels in the sample by atomic absorption spectrometry was made using both calibration curve and the standard addition techniques.

The results of this experiment indicate that determination of metal concentrations using a calibration curve leads to a suppression in the results obtained, when compared to the standard addition technique (Table 3.9). However the standard additions method involved making up a considerable number of complex solutions which, is time consuming when dealing with large numbers of samples. Furthermore, the precision of the technique was lower compared with the calibration curve procedure. It was therefore decided that the standard calibration curve technique should be used in the determination of heavy metals by flame atomic absorption spectrometry.

Table 3.9. A comparison of calibration by standard additions and calibration curve.

	Metal concentrations ($\mu g\ g^{-1}$)			
	Cd	Cu	Pb	Zn
Standard additions	4.2±1.4	95.5±17.7	1421.0±43.5	490.8±16.8
Calibration curve	3.9±0.9	92.8± 4.4	1406.6±28.8	486.6±12.0

3.10. Lead Analysis in Road Sediments Using X-ray Fluorescence.

Metal determinations by extraction with strong acids followed by atomic absorption spectrometry may take up to two days to complete. Glassware has to be carefully cleaned to prevent contamination, and standard solutions prepared. An alternative method of metal determination is X-ray fluorescence, for which it is seldom necessary to carry out more than a simple sample preparation. In the case of street dust, grinding to a fine powder is normally sufficient. The technique is also non-destructive which makes possible repetitive measurements, or subsequently other forms of analysis on the same sample.

An Oxford Instruments Lab X 250, X-ray fluorescence analyser was available for this study. Samples were irradiated with X-rays to produce secondary X-rays which are characteristic of the individual elements present, and which possess intensities proportional to their concentration in the sample. In the Lab X 250 instrument, a pair of filters isolate the signal appropriate to the element under study. One filter transmits the background radiation plus the radiation of interest while the other transmits the background radiation only. The difference between counts is proportional to the concentration of the chosen element. Unfortunately in the instrument used, only filters which allowed the detection of Pb were available. Nevertheless a comparison of the method with Pb determinations by acid extraction and atomic absorption spectrometry was undertaken.

Twenty three samples of ground street dust were used as standards. The street dusts had previously been analysed for Pb by the Greater London Council Analytical Services Branch, using HNO_3-HCl extraction followed by atomic absorption determination (Schwar 1983). The calibration curve of X-ray fluorescence signal plotted against metal concentration derived by this procedure was used to determine the Pb content of fourteen samples of road dust collected from the A41 Hendon Way and M1 motorway. The samples had been size fractionated and the larger fractions (>106 µm) had been ground in a ring mill. In addition to the collected sediments a sample of road sediment, which had undergone nearly 200 replicate determinations for Pb by acid extraction and atomic absorption, was analysed using the Lab X 250 instrument.

Figure 3.2 shows the calibration curve for the Lab X 250. Using this curve the Pb concentrations in the A41 and M1 sediments shown in Table 3.10 were determined, along with that for the reference sample.

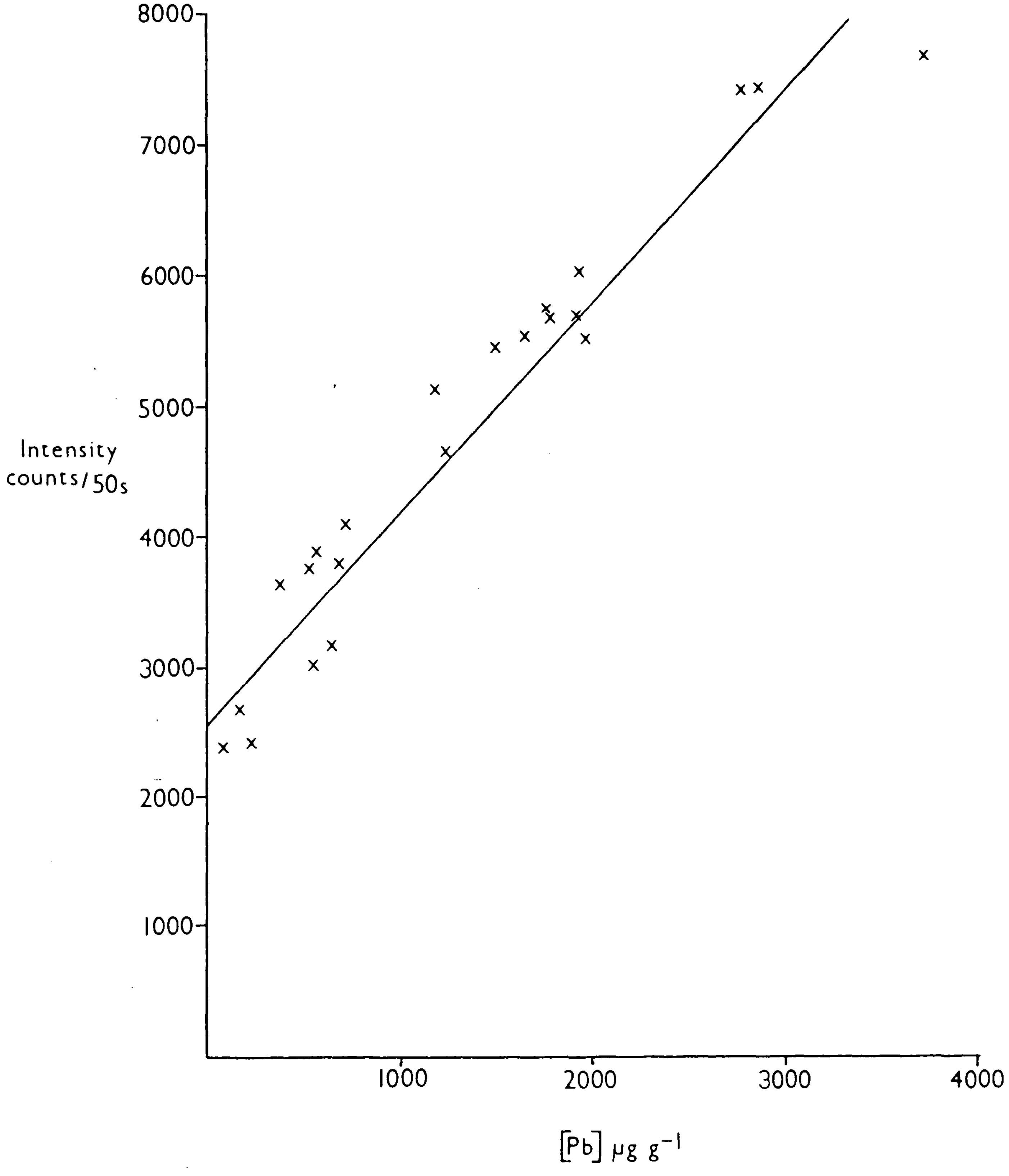


Figure 3.2. The Lab X 250 calibration curve for Pb.

The values obtained for the reference sample show reasonable agreement between the two analytical techniques. However it can be seen from Table 3.10 that determination of Pb content by X-ray fluorescence consistently obtained results lower than those obtained by atomic absorption spectrometry. Similar observations have been made by Turner et al. (1980), particularly where Pb concentrations are high.

The measurement of Pb in street sediment using the Lab X 250 X-ray fluorescence analyser was found to be a much quicker and simpler method, when compared with the acid extraction and atomic absorption spectrometry method. The time consuming preparation of glassware and detailed extraction procedure were replaced by grinding the sample, and cleaning the sample cells after use by wiping with a damp cloth. However, for the purposes of this study the Lab X 250 available was considered inappropriate as it did not allow the determination of Cd, Cu and Zn.

Table 3.10. Lead concentrations in street dust determined by XRF.

Sample	Intensity Pb counts	[Pb] by XRF $\mu g\ g^{-1}$	[Pb] by AAS $\mu g\ g^{-1}$	XRF-AAS $\mu g\ g^{-1}$
M1				
>1000	4165	974	1055	-81
500-1000	5203	1608	2469	-861
250-500	5893	2029	2957	-928
125-250	5475	1774	3496	-1722
63-125	7851	3226	5274	-2048
38-63	8491	3617	4836	-1219
<38	9173	4034	4409	-374
A41				
>1000	3670	671	366	305
500-1000	5169	1587	3833	-2246
250-500	5637	1873	1924	-51
125-250	5316	1677	3084	-1407
63-125	7130	2785	3901	-1116
38-63	7604	3075	3449	-374
<38	8203	3441	3624	-183
Reference sample	5407	1732	1668	64

3.11. Analytical Techniques Employed During This Investigation.

During the course of this study heavy metal levels were determined in a number of different types of environmental sample in addition to road surface dusts. Besides total metal determinations by acid extraction a sequential extraction procedure was also applied to street sediments (Chapter 5). This necessitated instruments capable of determining metals both at parts per million and parts per billion levels. For the routine determination of total metal concentrations in road dusts flame atomic absorption was used. During the sequential extraction experiments where flame atomic absorption could not be used electrothermal atomisation was preferred. In the determination of total metal levels in atmospheric and stormwater samples, described in Chapter 7, anodic stripping voltammetry was used.

CHAPTER 4. SPATIAL AND TEMPORAL VARIATIONS IN HEAVY METAL LEVELS IN URBAN ROAD DUST.

4.1. Introduction.

Urban street sediments have been recognised as an important source of toxic metals which is readily available to young children and which also provides a significant contribution to metal loadings in stormwater. Consequently a large number of surveys of concentrations and loadings have been carried out. A review of the published data reveals considerable variability in reported metal levels (see Section 2.3.2). This may be due partly to the complex relationships between the various input and output factors governing metal levels at a specific sampling site (see Figure 2.1), and partly to differences in sampling site characteristics such as surface type and composition (see Section 2.3.2). Further differences are caused by the wide range of techniques employed for sample collection and heavy metal analysis (see Chapter 3).

Spatial variations in heavy metal levels in street dusts have been studied on a variety of scales, ranging from countrywide surveys through city wide and district surveys to small scale investigations of metal levels over a few metres of roadway. Metal levels have been found to vary with traffic density, distance from the road surface, the degree of dispersion and driving conditions (see Section 2.3.2).

Temporal variations in heavy metal levels have not been as fully investigated as spatial variations. The work that has been carried out has shown substantial short term fluctuations in concentrations, but no apparent seasonal or long term trends (see Section 2.3.3).

From the previously reported investigations a number of general points emerge. Much of the data is for Pb, with very little information on small scale variations of other heavy metals, reflecting the concern over the pollution consequences of leaded petrol. Additionally the majority of the data refers to metal concentrations. Metal loadings on street surfaces are a particularly important parameter in mass balance studies, and also when considering the roadway as a source of metals to stormwater runoff. Implicit in all of the surveys is the assumption that representative samples have been taken. Surveys which have been made over a limited area have shown considerable variations in Pb levels even over distances as short as a few metres (Solomon and Hartford 1976;

Duggan 1984). The heterogeneous nature of roadside dust increases the problem, as even within a specific location any sample collected is likely to contain individual particles from different sources which are of widely varying chemical compositions. Further difficulties are caused by the previously noted wide short term fluctuations in metal levels. Guidelines on monitoring environmental Pb levels are available (Schwar 1983; I.E.H.O. 1984), but these only give limited advice on the sampling of settled dusts. This includes the need to sample as large an area as possible, and to take replicate samples temporally and spatially. There is therefore a need to investigate two aspects related to the variations in concentrations and loadings of a range of heavy metals in addition to Pb. These are, the variations in metal levels within a limited area at a particular location and the need to extend the investigation to monitor long term or seasonal changes in heavy metal levels at individual sampling locations.

The objective of this work was to investigate variations in the heavy metal concentrations and loadings across a number of urban road surfaces. In particular to assess the relationships between heavy metal incidence and surface type and condition, traffic loadings and hydrometeorological conditions. The information obtained in the survey can be applied to the development of representative sampling strategies for urban street dust.

4.2. Experimental: Sampling and Analysis.

4.2.1. Details of the sampling strategy.

Sample collection was carried out at approximately bimonthly intervals staring in August 1982. The samples were taken along a transect across the three roadway sites identified in Figure 4.1. The sites were chosen in consultation with the Air Pollution Section of the former Greater London Council Scientific Branch and included:

i) a busy trunk road (site A);
ii) an estate perimeter road (site B);
iii) a residential side street (site C).

All three sites are located in the Hendon area of North West London. The land use within this area is primarily residential, with very little industry. Highways account for a significant proportion of the area, including 0.16 ha contributed by the Hendon Urban Motorway (M1). The characteristics of the sampling sites are given in Table 4.1.

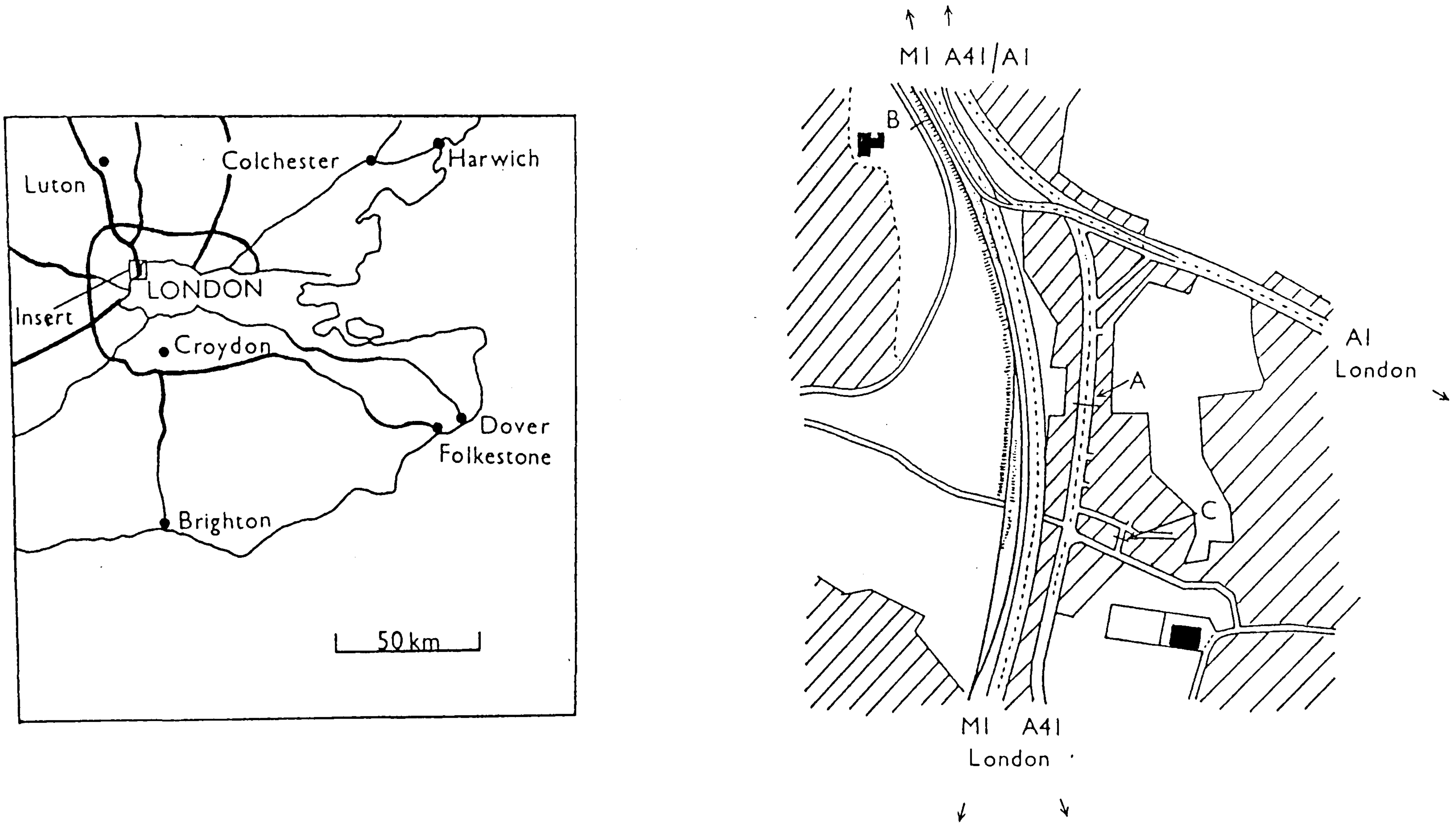


Figure 4.1. The location of sampling sites.

In order to obtain sufficient quantities of road sediment, particularly from the traffic lanes and pavements, a large surface area had to be sampled and these areas are given in Table 4.2. All sample areas were based on a 5 m length of road. Samples were collected by the vacuum technique where possible, but additionally by dustpan and brush if the sediment was damp or present in large quantities. Vacuum techniques allow a greater proportion of the fine sediment to be collected, this is particularly important when sampling from the road surface and pavements (see Section 3.2). Care was taken to reduce the disturbance of fine particulates, which are readily lost by resuspension. Also as much of the sediment in a given area was removed as possible in order to enable an accurate assessment of metal loadings.

Table 4.1. Sampling site characteristics.

	Site	Traffic density	Surface type
A	trunk road, dual carriage-way A41, Watford Way, Hendon, NW London	1100-1200 hour^{-1} southbound 1400-1500 hour^{-1} northbound 40-50 mph; cars goods and commercial vehicles.	smooth asphalt
B	perimeter road, Grahams Park estate, Colindale NW London	100-200 hour^{-1}; 30-40 mph cars and light commercial vehicles.	asphalt -stone
C	residential side street, Sunnyhill Hendon, NW London	<50 hour^{-1}; 25-30 mph; cars and vans.	coarse asphalt -stone

4.2.2. Additional information relating to the sampling scheme.

Additional data required for this investigation was obtained from external sources. Wind direction and speed data was provided by the Meteorological Office from the weather station at R.A.F. Northolt. Rainfall data was supplied by the Greater London Council Scientific Branch from their monitoring station at Mill Hill. The London Borough of Barnet Highways Department provided the dates on which road sweeping took place.

Table 4.2. Areas sampled at each site (m^2).

Site A

southbound (eastern side)	
1. pavement	14.4
2. kerbside	11.0
3. inside gutter	1.7
4a. inside lane	12.5
4b. centre lane	12.5
4c. outside lane	12.5
5. outside gutter	1.7
northbound (western side)	
1. pavement	13.7
2. kerbside	8.0
3, 4, 5 as for southbound	

Site B

eastern and western sides	
3. gutter	1.7
4. road surface	12.5

Site C

eastern side	
1. pavement	7.7
2. kerbside	4.4
3. gutter	1.7
4. road surface	12.5
western side	
1, 3, 4 as for eastern side	
2. kerbside	3.5

4.2.3. Analytical methodology.

The collected sediment was dried, weighed and sieved to <500 µm. Metal concentrations were determined by atomic absorption spectrometry as described in Chapter 3. Where possible, six subsamples were analysed. However, the amount of sediment collected did not always permit this level of replication for the road surface samples.

4.3. Discussion of the Results.

4.3.1. Overall average heavy metal levels.

The monthly and overall average concentrations and loadings for Cd, Cu, Pb and Zn at each of the sampling sites are given in Tables 4.3 and 4.4. The two carriage-ways at site A have been treated separately for comparison. Concentration values were derived by calculating the total metal mass for each transect, and dividing this value by the total mass of sediment collected from that transect. Loadings were similarly calculated by dividing the total metal mass in a transect by the total area sampled (Table 4.2).

The concentration values shown in Table 4.3 are consistent with values obtained from earlier work carried out in the same area of North

Table 4.3. Monthly and overall average concentrations ($\mu g\ g^{-1}$).

Site	Metal	August 1982	October 1982	December 1982	March 1983	June 1983	September 1983	Overall average
Site A northbound	Cd	3.3	3.4	2.5	2.8	3.8	5.1	3.5
	Cu	212.3	221.1	118.4	192.0	400.0	243.6	235.7
	Pb	2944.1	2908.2	1740.8	2226.1	3733.7	4987.1	3142.0
	Zn	548.6	532.0	457.8	519.6	654.8	698.3	572.5
Site A southbound	Cd	4.3	3.3	2.3	1.3	4.9	5.2	3.5
	Cu	394.1	282.0	93.6	161.2	319.5	324.1	272.4
	Pb	3205.8	2052.7	912.2	1615.7	2665.5	3238.9	2835.3
	Zn	718.2	549.9	294.7	484.7	717.6	846.8	614.1
Site B	Cd	3.0	3.0	2.5	4.3	3.2	4.1	3.2
	Cu	227.3	140.0	99.9	189.7	290.9	201.0	183.4
	Pb	3324.4	1820.7	1621.4	2208.4	3268.2	4133.0	2558.1
	Zn	508.3	483.4	455.6	628.3	561.3	625.5	540.3
Site C	Cd	2.1	2.0	2.2	2.6	2.6	3.2	2.3
	Cu	89.7	68.3	63.2	91.5	115.8	134.0	94.0
	Pb	1072.4	904.1	802.1	1302.2	1450.5	1882.3	1198.9
	Zn	435.8	413.8	410.1	426.1	568.2	521.3	462.2

Table 4.4. Monthly and overall average loadings (mg m^{-2}).

Site	Metal	August 1982	October 1982	December 1982	March 1983	June 1983	September 1983	Overall average
Site A northbound	Cd	0.34	0.08	0.09	0.10	0.20	0.21	0.18
	Cu	24.2	4.8	4.4	6.5	21.1	10.2	12.0
	Pb	335.9	63.5	65.3	75.2	197.4	208.8	159.5
	Zn	62.6	11.6	17.2	17.6	34.6	29.2	29.1
Site A southbound	Cd	0.74	0.19	0.24	0.17	0.34	0.52	0.37
	Cu	76.9	16.2	9.6	21.6	22.0	32.4	29.1
	Pb	552.2	117.9	93.3	216.2	183.7	323.3	254.4
	Zn	123.7	31.6	30.2	64.9	49.4	84.6	65.6
Site B	Cd	0.12	0.05	0.13	0.13	0.06	0.04	0.09
	Cu	9.4	2.3	5.2	5.6	5.8	1.9	5.1
	Pb	137.3	30.3	83.7	65.3	65.2	38.1	70.8
	Zn	21.0	8.0	24.0	18.6	13.2	5.8	15.0
Site C	Cd	0.23	0.07	0.06	0.09	0.15	0.08	0.12
	Cu	9.7	2.4	1.6	3.3	6.7	3.6	4.7
	Pb	115.5	32.0	20.2	47.5	83.8	49.8	59.7
	Zn	47.0	14.7	10.3	15.6	32.8	13.8	23.0

West London, and with metal analyses of road sediment from other similar road types in urban/residential areas (see Section 2.3, Table 2.10). Ellis and Revitt (1982) have reported metal concentrations in sediments collected from areas close to sample sites A and C of this investigation (Table 4.5). The sieve size used in the earlier study was 250 µm, compared to 500 µm used in this investigation and the concentrations are therefore slightly higher than those found here. The main differences occur for Cd where the results of this survey (Table 4.3) are lower at both sites than those obtained in the earlier study. The overall average Pb concentration obtained for site A is greatly in excess of that observed by Ellis and Revitt (1982). There is however a substantial variation in the monthly results, with the December 1982 and March 1983 results for Pb being similar to those observed by Ellis and Revitt (1982). Conversely the Zn concentration obtained in the earlier study is considerably greater than any found at site C, where the monthly Zn concentration remains reasonably constant throughout the sampling period.

Table 4.5. Heavy metal concentrations in dust for the Hendon area of NW London (µg g^{-1}).

	Size category (µm)	Cd	Cu	Pb	Zn
Watford Way (A41)	<250	5.3	280	1826	695
Sunnyside Gardens (residential road)	<250	6.0	91	978	2133

Source Ellis and Revitt (1982)

Very little published data on metal loadings in street sediments is available for comparison with the present study. Solomon and Hartford (1976) reported Pb loadings of 21.3 mg m^{-2} and 190.0 mg m^{-2} for a residential site and a major roadway in Champaign-Urbana, Illinois. These values are comparable with those reported in Table 4.4 for site A, the major trunk road. Solomon and Hartford (1976) also reported Cd loadings of between 0.007 and 0.02 mg m^{-2} for residential areas which are lower than those observed in this investigation at site C. The Cd loadings at site A compare well with the value of 0.134 mg m^{-2} found by Solomon and Hartford (1976) at the side of a major roadway.

The Pb concentrations reported in Table 4.3 exceed the Greater London Council's suggested maximum permissible level of 500 $\mu g\ g^{-1}$ (Schwar 1983) in all instances, although no overall average value exceeds the Council's 'interim action level' of 5000 $\mu g\ g^{-1}$. These guideline values are the only widely recognised guidelines for heavy metal concentrations in surface dust. There are no similar guidelines with which to assess the levels of Cd, Cu and Zn. The Department of the Environment (1983a) suggest a 'trigger concentration' for Pb and Cd in soils above which a site may be regarded as contaminated (Table 4.6). The guideline value for Pb in gardens and allotment corresponds with the 500 $\mu g\ g^{-1}$ limit suggested by the Greater London Council. Comparison of the observed Cd concentration results for sites A and B (Table 4.3) shows that these are in excess of the 'trigger concentration' for domestic gardens and allotments, but considerably below that for parks and playing fields.

Table 4.6. D.O.E. 'trigger concentrations' for Pb and Cd in urban soils ($\mu g\ g^{-1}$).

Cd	Domestic gardens and allotments	3
	Parks, playing fields and open space	15
Pb	Domestic gardens and allotments	500
	Parks, playing fields and open space	2000

D.O.E. (1983a)

4.3.2. Spatial variations in overall average heavy metal levels.

The results shown in Tables 4.3 and 4.4 indicate that metal concentrations and loadings generally decrease from site A, which has the highest traffic density (Table 4.1), to the residential side street (site C). The decline in concentrations is not directly proportional to traffic density. The decrease in concentration levels of all metals between sites B and C is much larger than that between sites A and B, although traffic densities at sites B and C are considerably lower than those at site A. Similar observations have been made by Ratcliffe (1981) and Ellis and Revitt (1982), who noted from collated literature data that metal levels on motorways are often lower than those found in urban areas. This may be the result of additional inputs from sources of heavy metals other than vehicles, such as industry, in urban areas. It is also a reflection of the importance of emission conditions on heavy metal levels, particularly Pb. Lead is emitted in greater quantities under conditions where vehicles are accelerating, during the stop/start urban cycle, than when travelling under cruise conditions (see Section 2.1.5). The concentration values reported in Table 4.3 show that Cu declines the most from sites A and B to site C followed by Pb, Cd and then Zn. This pattern in concentration levels is contrary to known sources of the metals which show that Pb, being primarily derived from vehicular sources, would be expected to show the greater tendency to follow changes in traffic density (see Section 2.1.2, Table 2.2).

The results shown in Table 4.4 indicate that metal loadings reflect the differences in traffic densities between the three sites more closely than concentration values. Loadings for all metals decline markedly between sites A and B. Between sites B and C, Cd and Zn loadings show an increase in level, whereas Cu and Pb loadings decline. The increase in Cd and Zn loadings may be due to the nature of the road surface at site C which is coarser (Table 4.1), and would therefore cause increased wear of tyres compared to the other road surfaces sampled. Tyre wear is the major vehicle derived source of Cd and Zn inputs to road sediments (see Section 2.1.5).

Although the metal concentrations on the two carriage-ways at site A exhibit similar overall values, the loadings on the two halves of the roadway are markedly different (Tables 4.3 and 4.4). The northbound carriage-way has 105% more Cd, 142% more Cu, 59% more Pb and 125% more Zn than the southbound carriage-way. The differences in traffic densities between the two carriage-ways are not sufficient to explain these differences (Table 4.1). The northbound carriage-way has considerably higher sediment loadings than the southbound (217% more). Because of their close proximity and similar traffic densities it is reasonable to assume that metal inputs to both areas from the general urban background are similar. It would therefore appear that metals deposited on the northbound carriage-way at site A are not removed as readily as on the opposite carriage-way.

4.3.3. Temporal changes in the monthly overall average heavy metal levels.

The average metal concentrations for each bimonthly sampling period show a distinct seasonal pattern (Table 4.3). The values gradually decrease from August to December 1982. This is followed by increasing concentrations from December 1982 to the final sampling date in September 1983. The trend is strongest for sites A and B, particularly for the metals Cu and Pb. A similar seasonal trend is found with the average monthly loadings (Table 4.4). There is a relatively large decrease in loadings after the August sample collection, which represents metal accumulations over a number of months prior to the start of the sampling programme. After the June 1983 sample collection the metal loadings at sites B and C show a decrease, whereas the loadings generally continue the rise observed in previous months at site A. Shaheen (1975) observed similar results for Pb and Zn loadings, which were higher in the warmer months while other metal loadings remained uniform. This was attributed to increased tyre wear during warmer weather. Duggan (1984) observed no long term or seasonal trends in Pb concentrations. A pronounced seasonality has been reported for airborne heavy metals with higher levels recorded in winter months than summer months. This has been associated with increased car usage, domestic heating and the occurrence of more persistent low atmospheric inversions (see Section 2.2.3.).

The individual site metal accumulations are related to a number of variables such as the effect of local source strengths, vehicle induced resuspension, the incidence and intensity of storm events and the frequency and efficiency of street cleaning practices.

The accumulation rate of pollutants deposited on street surfaces is not linearly related to time. Accumulation levels fall off after several days due to the removal of deposited material by the passage of vehicles. The resuspension of sediment from road surfaces has been investigated by Sehmel (1973). In considering pollutant accumulation over a dry period of duration t (hours), it is assumed that the initial loading is zero. Pollutant deposition may be described by:

$$dm / dt = D$$

and pollutant removal by resuspension by the expression;

$$dm / dt = -\Lambda Nm$$

combining gives;

$$dm / dt = D - \Lambda Nm$$

integrating this gives;

$$M_t = [D / \Lambda N](1 - e^{-\Lambda N t}) \text{ g m}^{-2} \qquad (1)$$

where Λ is the resuspension rate (vehicle^{-1}), D is the pollutant dry deposition rate (g m^{-2} hour^{-1}), N is the traffic flow rate (vehicles hour^{-1}).

It follows from this equation that when resuspension is negligible (when $\Lambda N t << 1$) the pollutant accumulates linearly with time due to deposition. Furthermore when resuspension is dominant (when $\Lambda N t \gg 1$) the mass M_t approaches an equilibrium value of M_o where:

$$M_o = D / \Lambda N \qquad (2)$$

The time required for M_t to reach 90% of its equilibrium value M_o can be derived from equation (1):

$$T = 2.3 / \Lambda N \qquad (3)$$

where T is the time required for resuspension to dominate.

Using a Pb in petrol level of 0.40 g l^{-1}, vehicles with an average petrol consumption of 30 mpg will consume Pb at a rate of 3.7×10^{-5} N g m^{-1} hr^{-1}. Assuming that 70% of the burned Pb is emitted and that 4% of the emitted Pb is deposited on the carriage-way (Little and Wiffen 1978), we have $D = 5.2 \times 10^{-8}$ N g Pb m^{-2} hr^{-1}.

Substituting into equation (2) gives $M_o = 5.2 \times 10^{-8} / \Lambda$ g Pb m^{-2}. Using an experimental value for M_o of 3.0 mg Pb m^{-2}, a value of 1.7×10^{-5} vehicle^{-1} is obtained for Λ. This is consistent with other vehicle induced resuspension rates quoted in the literature (Sehmel 1973; Sehmel 1980b).

At site A which is a major urban roadway and has the highest traffic density of the sites sampled, from equation (3) the time required for vehicle induced resuspension to dominate would be 54 hours. At sites B and C, which have much lower traffic densities, vehicle induced resuspension seldom becomes a dominant process.

Over a period of time surface sediment will also be removed by rainfall and street cleaning, resulting in a complex accumulation curve (Sartor and Boyd 1972; Shaheen 1975; Alley and Smith 1981). The incidence of these variables was monitored during the course of sampling and are summarised in Table 4.7. It can be seen that a number of factors might result in the seasonal trends in metal concentrations and loadings observed in Tables 4.3 and 4.4. The incidence of street sweeping was noticeably greater during the October to December 1982 sampling period. Additionally the average daily intensity of rainfall during this period was higher than at other times during sampling. Monthly concentrations and loadings show a marked decrease during this time period, and monthly loadings increase towards the end of the sampling period as the volume and intensity of rainfall declined. Although the rainfall values and the incidence of street sweeping rose during the March and June sampling periods, when metal levels were also elevated relative to previous months, the number of days of antecedent dry weather also increased.

Linear correlation analysis has been carried out on the heavy metal concentrations and loadings data given Tables 4.3 and 4.4 with the parameters listed in Table 4.7. The results of this analysis are given in Table 4.8, and it can be seen that overall average heavy metal concentrations show no relationship with the incidence of street sweeping. Metal loadings also show a poor correlation with street sweeping, with the exception of Pb and Zn at site B. A poor correlation would be expected between street sweeping and metal levels as the metal data represents an average for all sample areas at a particular sample site, whereas street sweeping would effect only the gutters. At site B no pavement or kerbside samples were collected and therefore the influence of street sweeping is more apparent at this site.

No significant correlation coefficient was obtained for the total rainfall (mm) falling between sampling visits and the overall average metal concentrations at the three sites. Metal loadings show some significant correlation coefficients notably for Cu at site B, but no consistent trends were observed. The data in Table 4.8 indicates that rainfall intensity (mm day^{-1}) is a factor influencing metal concentrations. Where rainfall intensity is high metal concentrations appear reduced, although the strength of this association is not particularly strong. However the trend is consistent with observations made by Fergusson et al. (1980), Tsang (1982) and Fergusson and Simmonds (1983) who have demonstrated that heavy rainfall prior to sampling leads to reduced metal concentrations due to the preferential removal of fine particulates into the stormwater system (see Section 2.5). Metal

Table 4.7. The hydrometeorological data and incidence of street sweeping during the sampling.

Intervals between sampling	Number of street sweepings	Rainfall total (mm)	Rainfall average intensity (mm day^{-1})	No. days of antecedent dry weather	% of days wind blowing from the south west
9-8-82 to 4-10-82	non	119.0	2.12	1	56.9
5-10-82 to 5-12-82	5	175.2	2.78	2	46.2
6-12-82 to 3-3-83	2	165.0	1.85	1	54.6
4-3-83 to 10-6-83	3	246.9	2.49	7	45.5
11-6-83 to 3-9-83	2	64.7	0.76	1	25.6

Table 4.8. Correlation matrix for heavy metal concentrations and loadings with weather parameters.

		Concentrations				Loadings			
		Street sweeping	Rainfall total	Rainfall intensity	Dry days	Street sweeping	Rainfall total	Rainfall intensity	Dry days
Site A southbound	Cd	-0.343	-0.508	-0.796	0.062	0.082	-0.004	-0.494	0.510
	Cu	-0.209	0.431	-0.050	0.808^{*}	0.117	0.552	0.034	0.902^{**}
	Pb	-0.332	-0.405	-0.745	0.172	-0.085	-0.584	-0.861^{*}	-0.101
	Zn	-0.248	-0.191	-0.647	0.363	0.274	0.288	-0.240	0.712
Site A northbound	Cd	-0.132	-0.142	-0.395	0.454	0.092	-0.380	-0.658	0.158
	Cu	-0.580	-0.198	-0.506	0.332	-0.366	-0.435	-0.887^{**}	-0.010
	Pb	-0.441	-0.318	-0.709	0.236	-0.278	-0.759	-0.962^{****}	-0.538
	Zn	-0.423	-0.296	-0.717	0.247	-0.164	-0.440	-0.878^{**}	-0.159
Site B	Cd	-0.388	-0.370	-0.783	-0.283	0.577	0.363	0.490	-0.181
	Cu	-0.111	0.421	-0.180	0.739	0.615	0.888^{**}	0.673	0.550
	Pb	-0.095	-0.252	-0.717	0.267	0.897^{**}	0.680	0.643	0.347
	Zn	-0.243	-0.209	-0.733	-0.039	0.759	0.556	0.692	0.074
Site C	Cd	0.065	-0.278	-0.760	0.068	0.039	0.681	0.145	0.895^{**}
	Cu	-0.092	-0.161	-0.694	0.303	-0.024	0.539	-0.023	0.847^{*}
	Pb	-0.154	-0.293	-0.798	0.138	-0.074	0.481	-0.110	0.784
	Zn	0.067	0.242	-0.277	0.721	-0.009	0.701	0.234	0.924^{**}

Levels of significance

****	$\rho=0.01$
***	$\rho=0.02$
**	$\rho=0.05$
*	$\rho=0.1$

loadings do not show the same overall trend as metal concentrations. Although Cu, Pb and Zn loadings on the northbound carriage-way at site A appear to be strongly influenced by rainfall intensity. This contrasts with the previously noted higher metal loadings on this carriage-way when compared with those on the southbound carriage-way (Section 4.3.2) which suggest reduced removal of these pollutants from the road and adjacent surfaces on this carriage-way. The number of dry days recorded before sampling does not seem to influence metal concentrations or loadings with the exception of metal loadings at site C which show significant correlation coefficients with the number of antecedent dry days.

It is realised that the small number of sampling visits undertaken during this investigation is a major drawback when conducting the type of correlation analysis described above. In order to obtain an increased statistical significance monthly or twice monthly sampling would have been more suitable.

4.3.4. Spatial distributions of heavy metal concentrations across the sample sites.

The spatial and temporal variations in the metal concentrations across the three sampling locations are shown in Figures 4.2 to 4.9. The trends shown in these figures are clearly related to the differences in traffic density. For the more heavily used road (site A), the Cd concentrations observed are distributed evenly over all the surfaces for the first three months of sampling (Figure 4.2). The levels for the latter half of the sampling programme are increased, and show considerably more variation in level. No consistent spatial trends were observed for Cd concentrations at this site. In general Cu, Pb and Zn concentrations at site A are also uniformly distributed across the road surfaces for the first three sampling visits, but unlike Cd also show a uniform distribution for the March 1983 sampling visit (Figures 4.3, 4.4 and 4.5). Copper shows one very high value for the road surface in the October 1982 samples. The final two sampling periods show extremely variable Cu results with several of the road surface samples exhibiting very high Cu concentrations (>500 $\mu g\ g^{-1}$). The Pb and Zn concentrations obtained in December 1982 at site A exhibit two high values for the same road surface sampling areas, the outside lane southbound and inside lane northbound (Figures 4.4 and 4.5). A preliminary examination of these samples by scanning electron microscope with energy dispersive X-ray

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

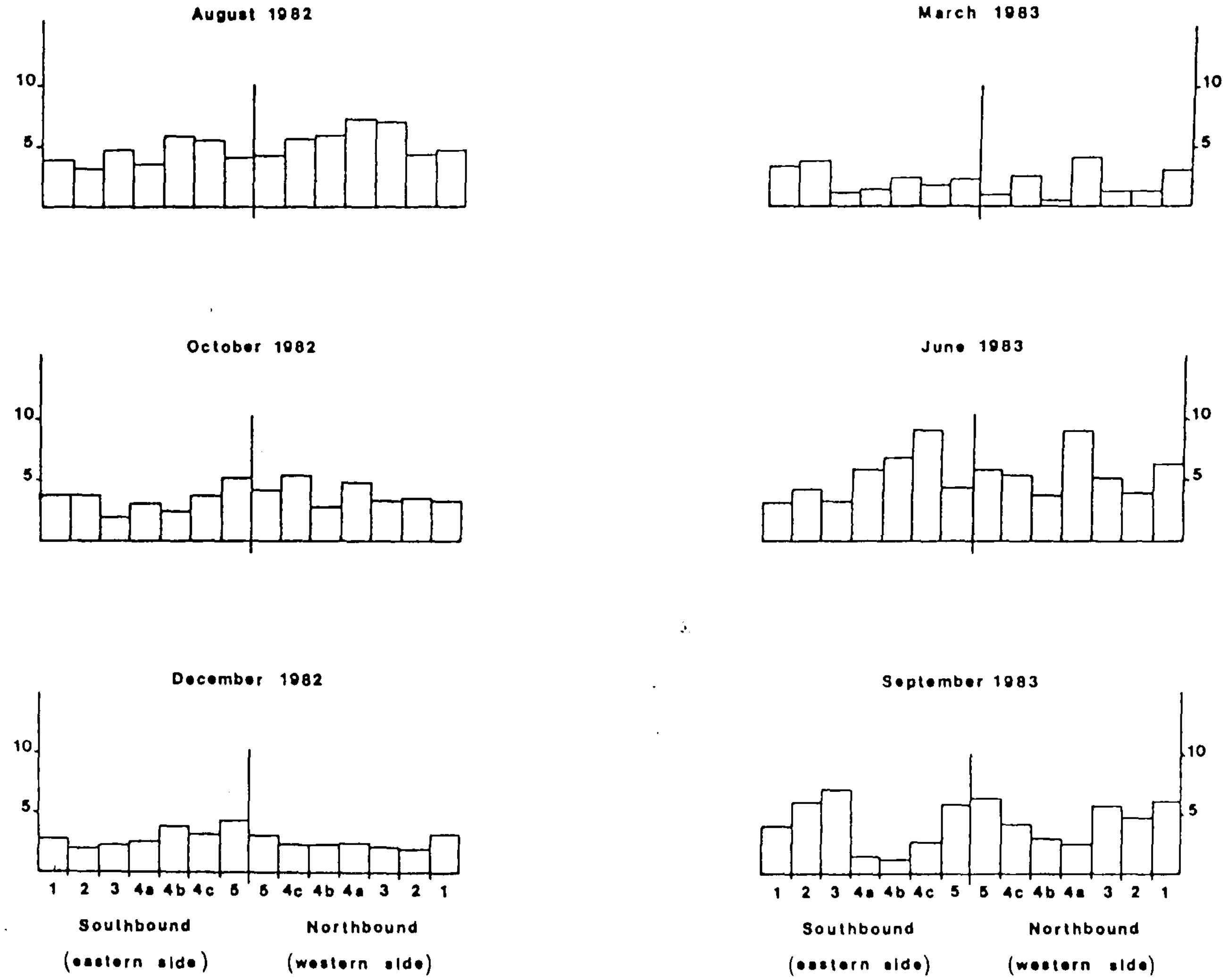


Figure 4.2. Cadmium concentration levels in street dust at site A (µg g^{-1}).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

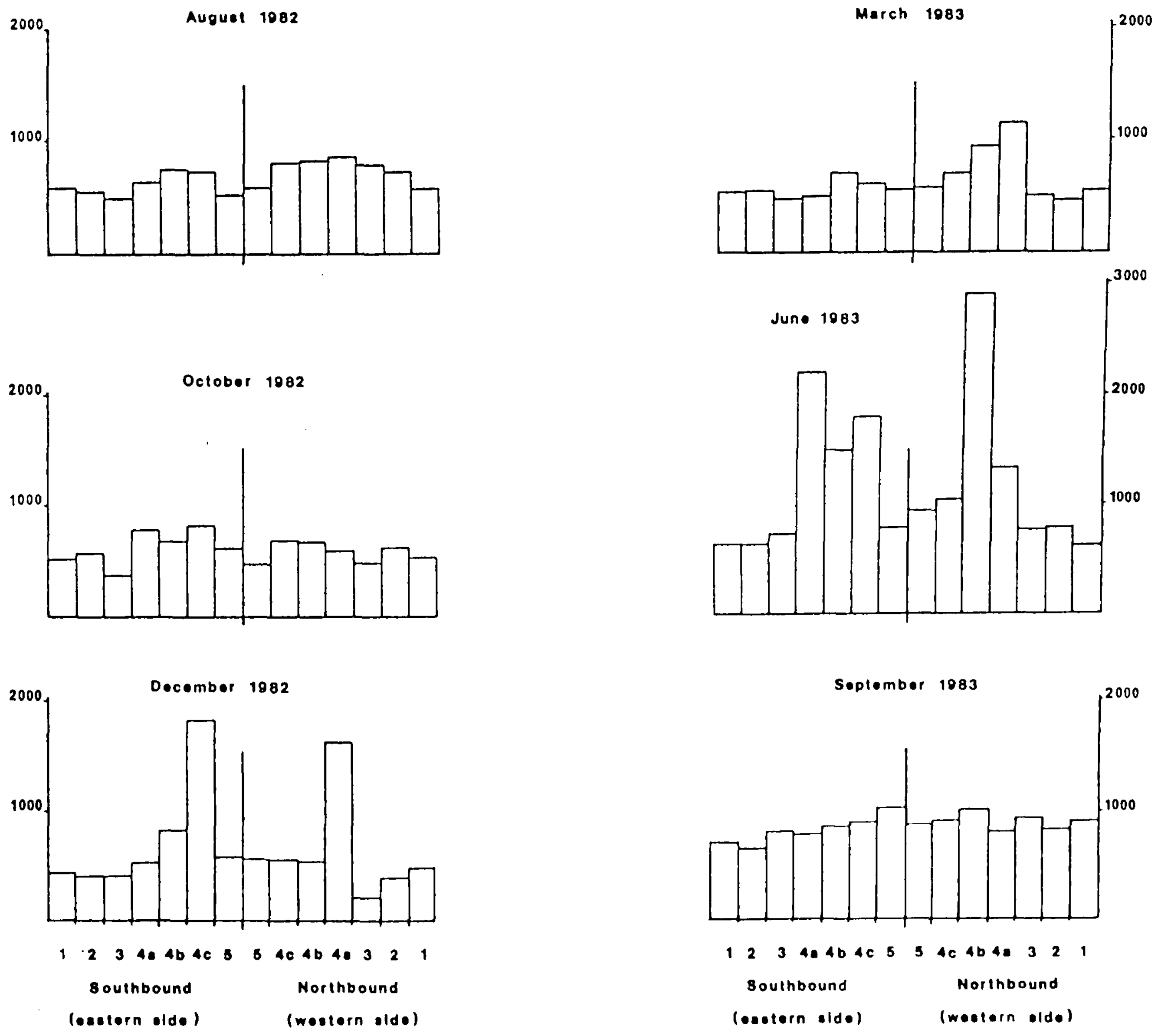


Figure 4.3. Copper concentration levels in street dust at site A ($\mu g\ g^{-1}$).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

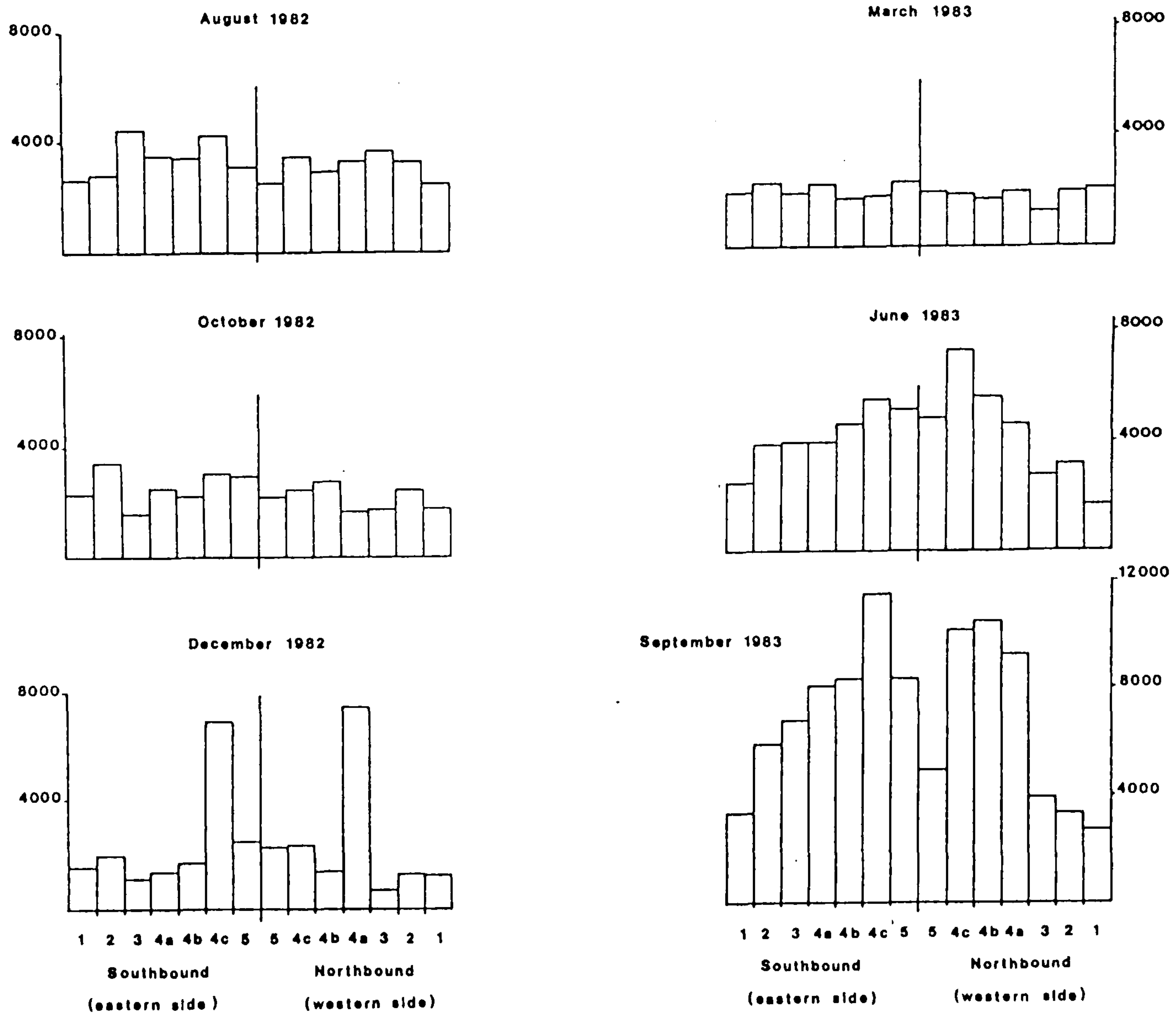


Figure 4.4. Lead concentration levels in street dust at site A ($\mu g\ g^{-1}$).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

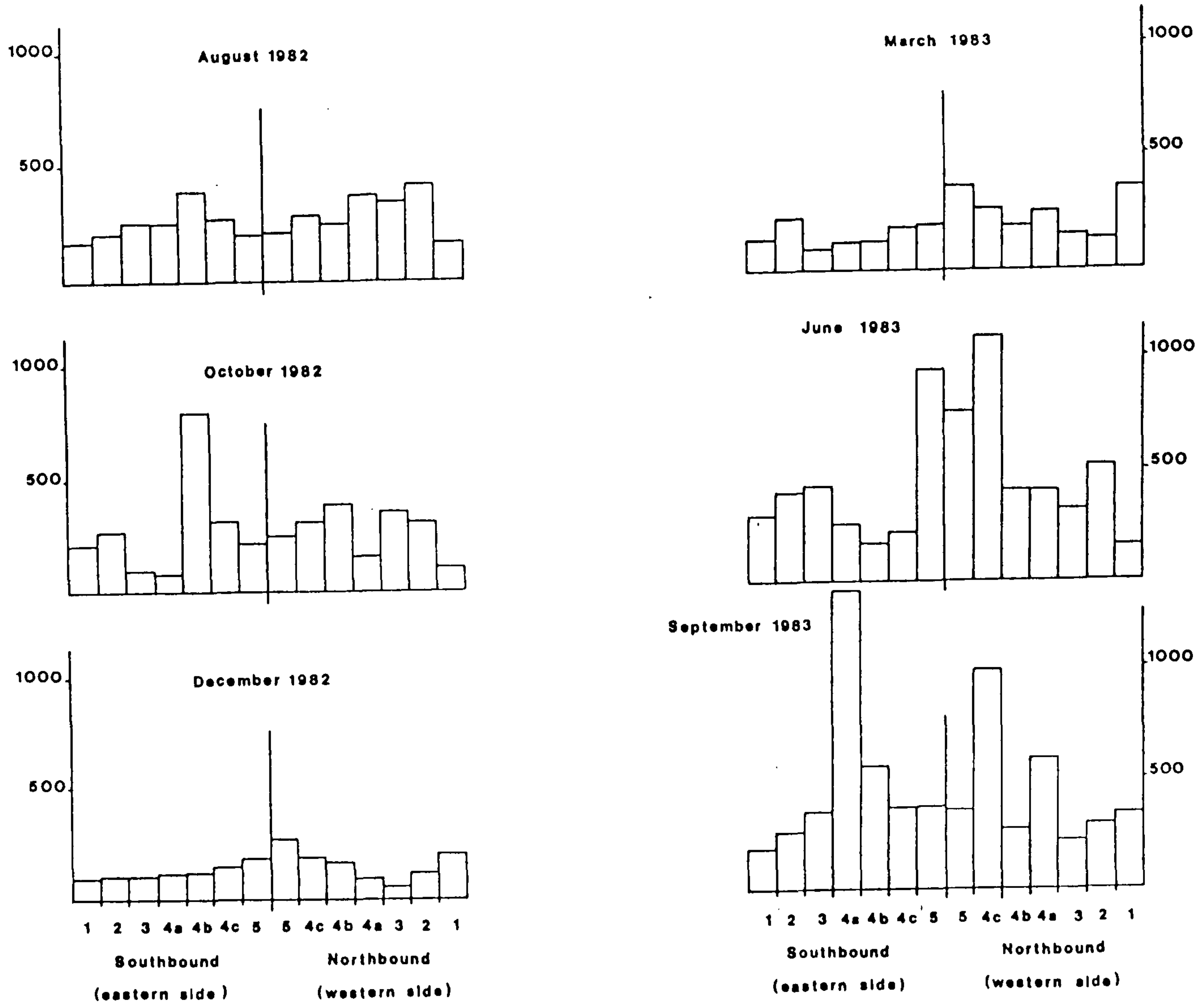


Figure 4.5. Zinc concentration levels in street dust at site A ($\mu g\ g^{-1}$).

analysis indicated the presence of a small number of highly contaminated but relatively coarse particles, which suggests a unique pollution source.

Lead concentrations show a marked enhancement in the last two sample periods, additionally the levels are highly variable and exhibit no apparent spatial trends. Most of the samples collected in September on the southbound carriage-way and all the road surface samples on the northbound carriage-way exceed the Greater London Council 'interim action level' of 5000 µg g^{-1} for Pb (Figure 4.4). Zinc concentrations are highly variable in the samples collected on the June 1983 sample visit, with particularly high levels on the road surface. It has been noted earlier that Shaheen (1975) observed higher Zn levels in summer months due to increased tyre wear. Tyre wear products tend to be deposited on or close to the road surface (Cadle and Williams 1980). The results for September 1983 show Zn more evenly distributed across the sample site with no consistent spatial trends (Figure 4.5).

At site B, which is of intermediate traffic density and speeds, only gutter and road surface samples were collected. Cadmium concentrations at this site exhibited no consistent spatial trends. In general the eastern half of the road showed the higher concentration levels. However, with the exception of the September 1983 samples this trend is only marginal (Figure 4.6). Copper and Pb concentrations at this site are usually enhanced on the road surface as compared with the gutter samples. Lead on the road surface during August, September and June exceeds the 'interim action level' as at site A (Figure 4.8). Zinc concentrations are the most uniformly distributed across the road surfaces at this site. Only the results for August and October 1982 show a slight enhancement in concentration on the road surface (Figure 4.9).

Site C has a much lower traffic density than the other two sample sites. The Cu and Pb concentrations show similar distribution patterns on both sides of the road for all sampling dates (Figures 4.7 and 4.8). This pattern consists of a progressive increase in Pb or Cu levels from the pavement to the road surface, but with very little difference between pavement and kerbside values. The Cd and Zn concentration patterns at this site differ in that they exhibit slightly higher levels in the gutter compared to the road surface samples (Figures 4.6 and 4.9). Lead concentrations rarely exceed the Greater London Council guideline value at this site.

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

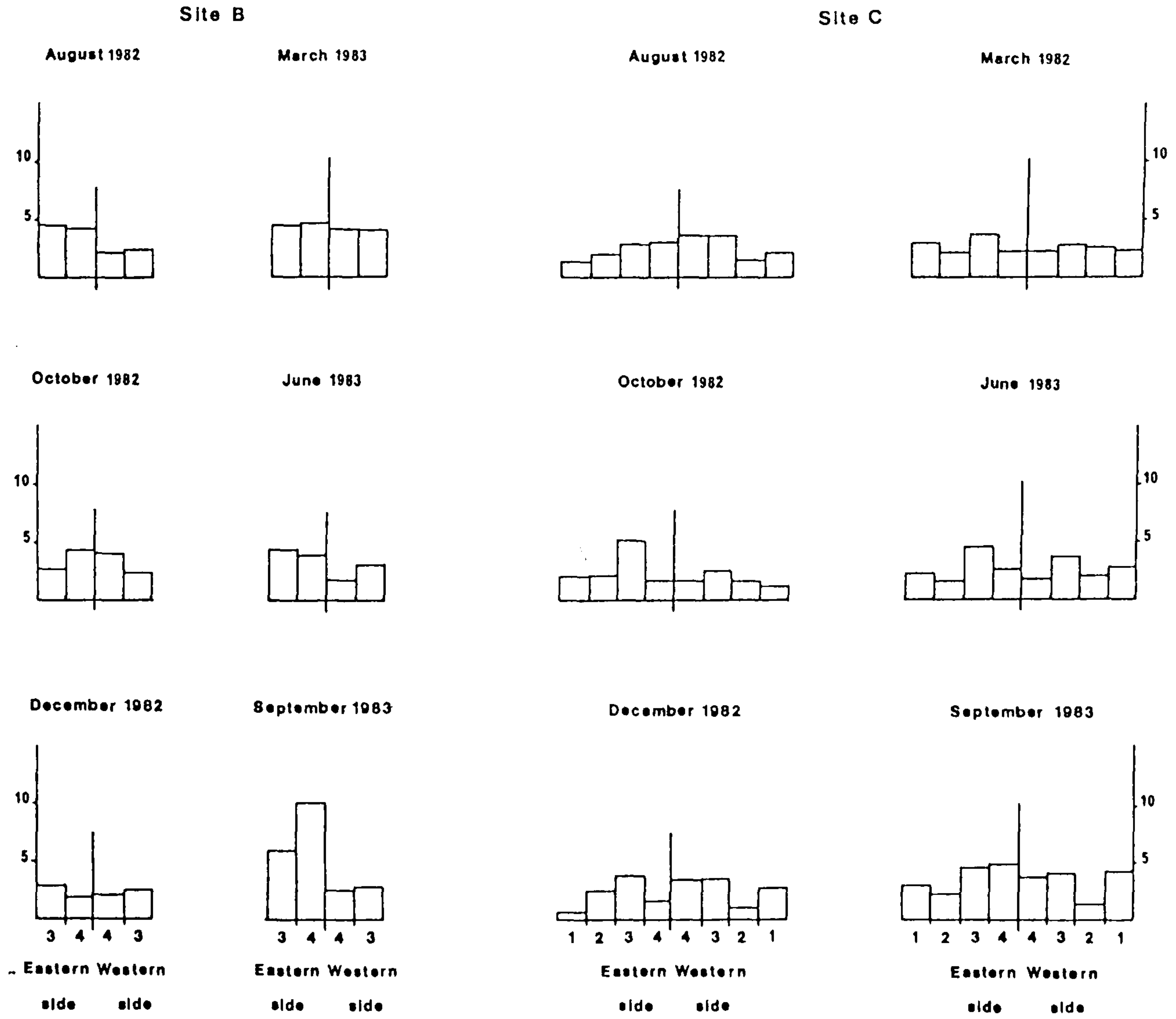


Figure 4.6. Cadmium concentration levels in street dust at sites B and C ($\mu g\ g^{-1}$).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

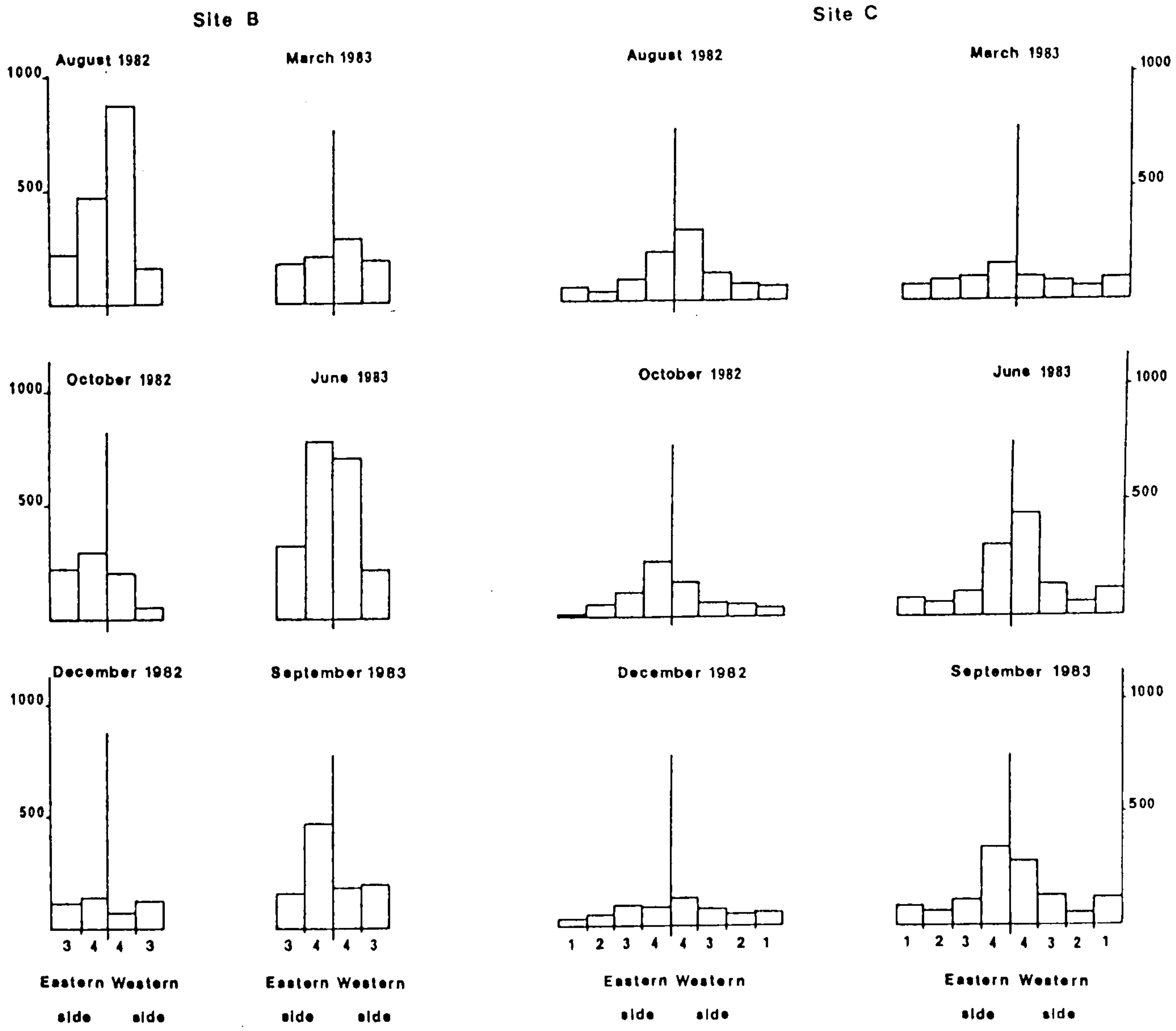


Figure 4.7. Copper concentration levels in street dust at sites B and C (µg g^{-1}).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

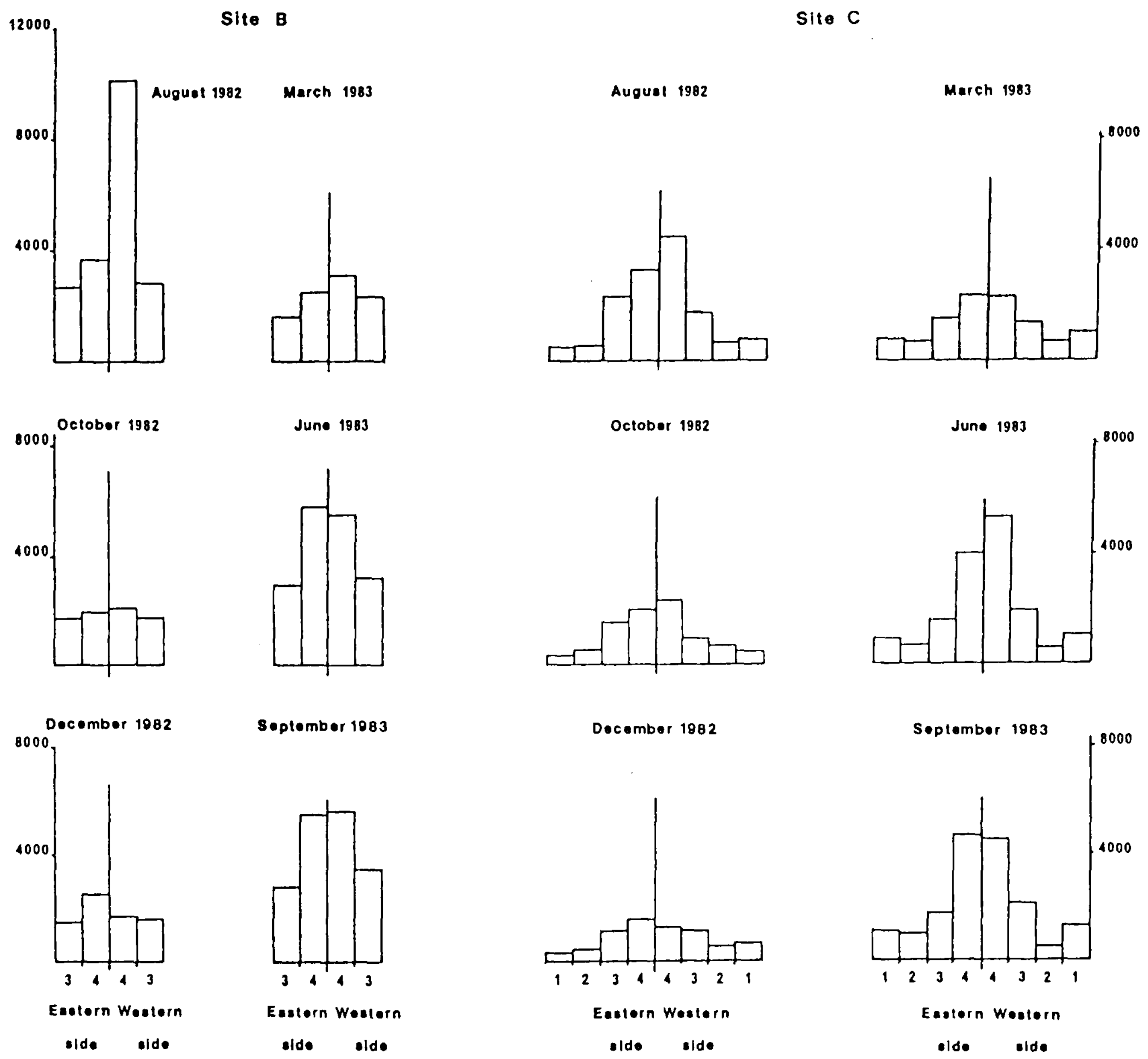


Figure 4.8. Lead concentration levels in street dust at sites B and C ($\mu g\ g^{-1}$).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

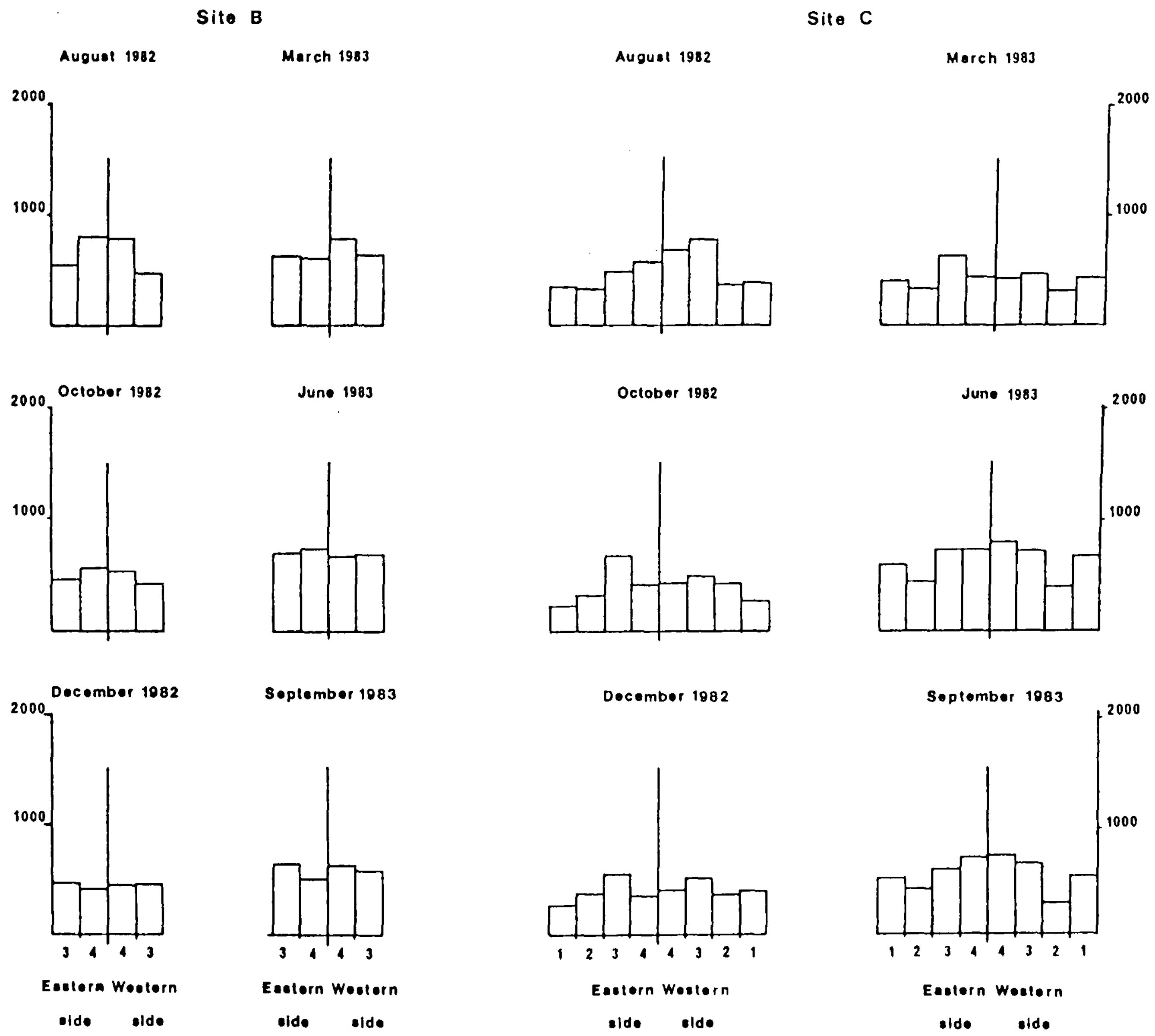


Figure 4.9. Zinc concentration levels in street dust at sites B and C ($\mu g\ g^{-1}$).

Very little published information on the spatial distributions of heavy metal concentrations across highway surfaces is available for comparison with the work reported above. Solomon and Hartford (1976) and Duggan and Williams (1977), observed a decline in Pb concentrations with distance away from the kerbside of both main and side roads and this is confirmed in the present study. The former authors reported a relatively uniform distribution of Cd concentrations in their study areas. Beckwith et al. (1985) have reported the concentrations of Cu, Pb and Zn in sediments collected along a transect across a road of similar traffic density to site C. Concentrations of these metals were generally found to increase from pavement to road gutter, and from the road gutter to road centre. The trend was most obvious for Pb and least consistent for Cu, with Zn occupying an intermediate position. The trends for Cu and Zn found at site C contrast with that of Beckwith et al. (1985) in that the positions of these metals are reversed with Cu showing enhanced concentrations on the road surface and Zn showing a more uniform distribution. The sampling site was positioned close to a junction and therefore a higher incidence of braking might be expected at this site which would lead to greater inputs of Cu.

Despite the differences in traffic densities between the three sites the metal concentration levels on the road surfaces are remarkably similar. It has been shown earlier (Section 4.3.2) that vehicle induced resuspension is an important mechanism for sediment transport at site A. The more rapid speed of vehicles at site A results in the movement of many of the more highly contaminated fine particles towards the side of the road. The combination of these particles with contaminated soil derived material in the gutter and pavement areas provides a possible explanation for the even metal concentration distributions at this site. The relatively high road surface metal concentrations at site C may be due to the coarser nature of the road surface (Table 4.1) which will not only assist the retention of finer particles but will also increase the input of metals derived from tyre wear. This explanation is consistent with the high initial road surface concentrations at site C, which represents the accumulation of small highly polluted particles over a long period.

4.3.5. Spatial distributions of heavy metal loadings across the street surfaces.

All metals studied in this investigation follow a similar pattern with respect to loading distributions across the road surfaces (Figures 4.10 to 4.17). This pattern reflects the greater weights of sediment found in the gutters and kerbside compared to the pavements and road surfaces. The metal loading distributions show significant patterns on both sides of the road at site A (Figures 4.10 to 4.13). Both road surfaces carry minimal loadings of all metals, and there is an obvious concentration of total metal and sediment weight on both inside and outside gutters with progressively lower amounts on the kerbside and the pavement. Solomon and Hartford (1976) have shown a similar sharp decrease in Pb loadings and also concentrations with increasing distance from the gutter. Apart from this work there is no other data in the literature on metal loading distributions over a confined area.

On the southbound side of site A there is a gradual increase in metal loadings from the pavement to inside gutter. Metal loadings then decline between the inside and outside gutters on this carriage-way. The southbound outside gutter shows enhanced metal loadings compared to the equivalent northbound gutter. Metal loadings on the northbound carriage-way are generally enhanced relative to the southbound carriage-way. The preference for the total metal mass to collect in the gutters on the western side cannot be explained purely in terms of wind direction since the prevailing winds are from the south west (Table 4.7). The wind passing over houses bordering the western side of the road may generate a vortex flow pattern, which would lead to the accumulation of metals and sediment along the western side of the road. Although the relatively low height of the houses compared with the width of the road suggests this is unlikely. Alternatively, the dispersive effect of fast moving traffic may create localised wind gusts and eddy currents which appear from the evidence of metal loadings to be orientated mainly towards a westerly direction.

The exaggerated movement of Pb towards the inside gutter on the northbound lane is consistent with the 20-25% higher traffic flow on this side of site A (Table 4.2). It has been noted earlier (Section 4.3.1) that the difference in traffic flow between the two carriage-ways is insufficient to explain all of the difference in metal loadings. Additional effects such as transport by runoff and spray processes during wet weather will assist the accumulation of sediment,

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

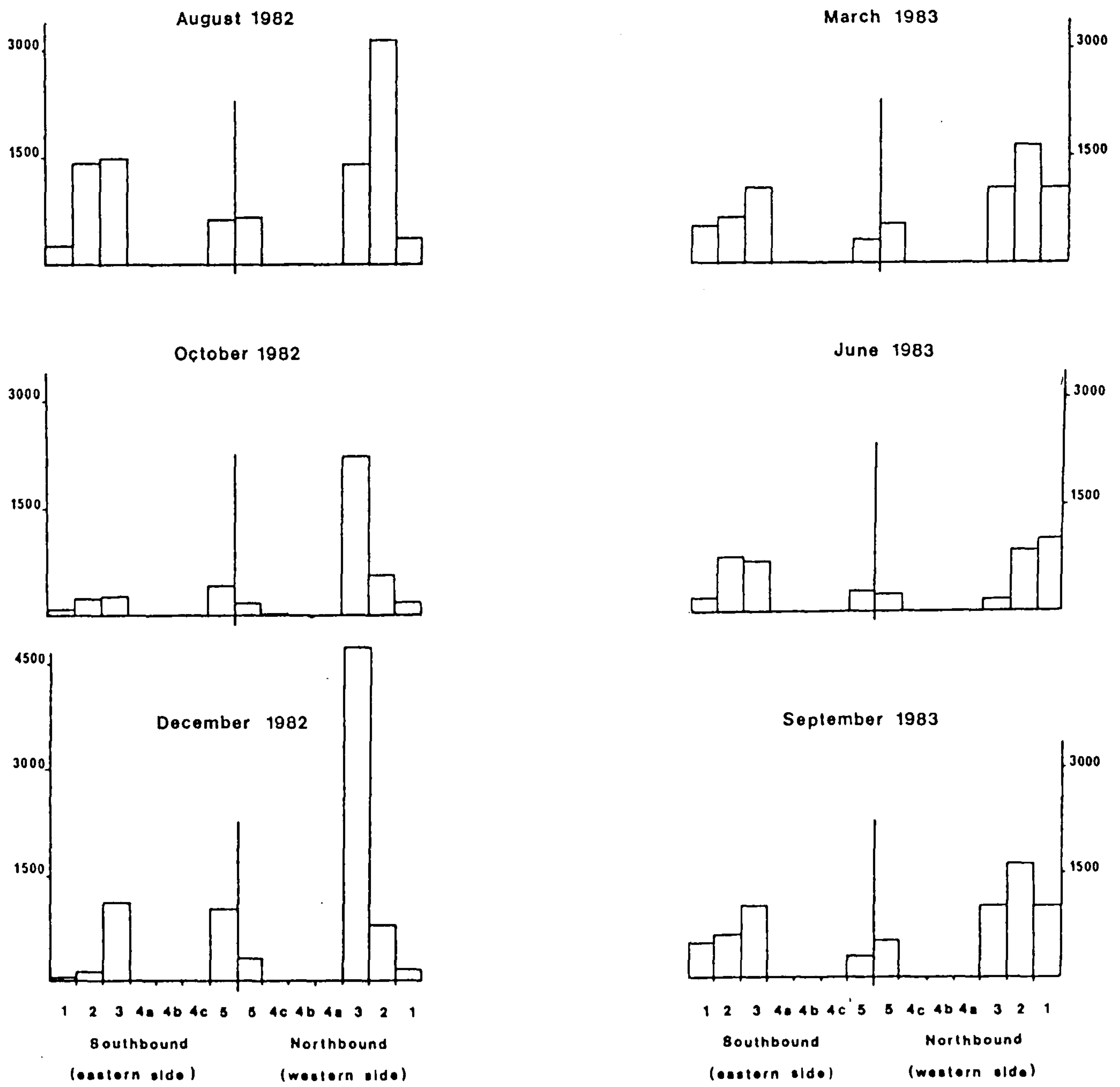


Figure 4.10. Cadmium loadings on the road surface at site A ($\mu g\ m^{-2}$).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

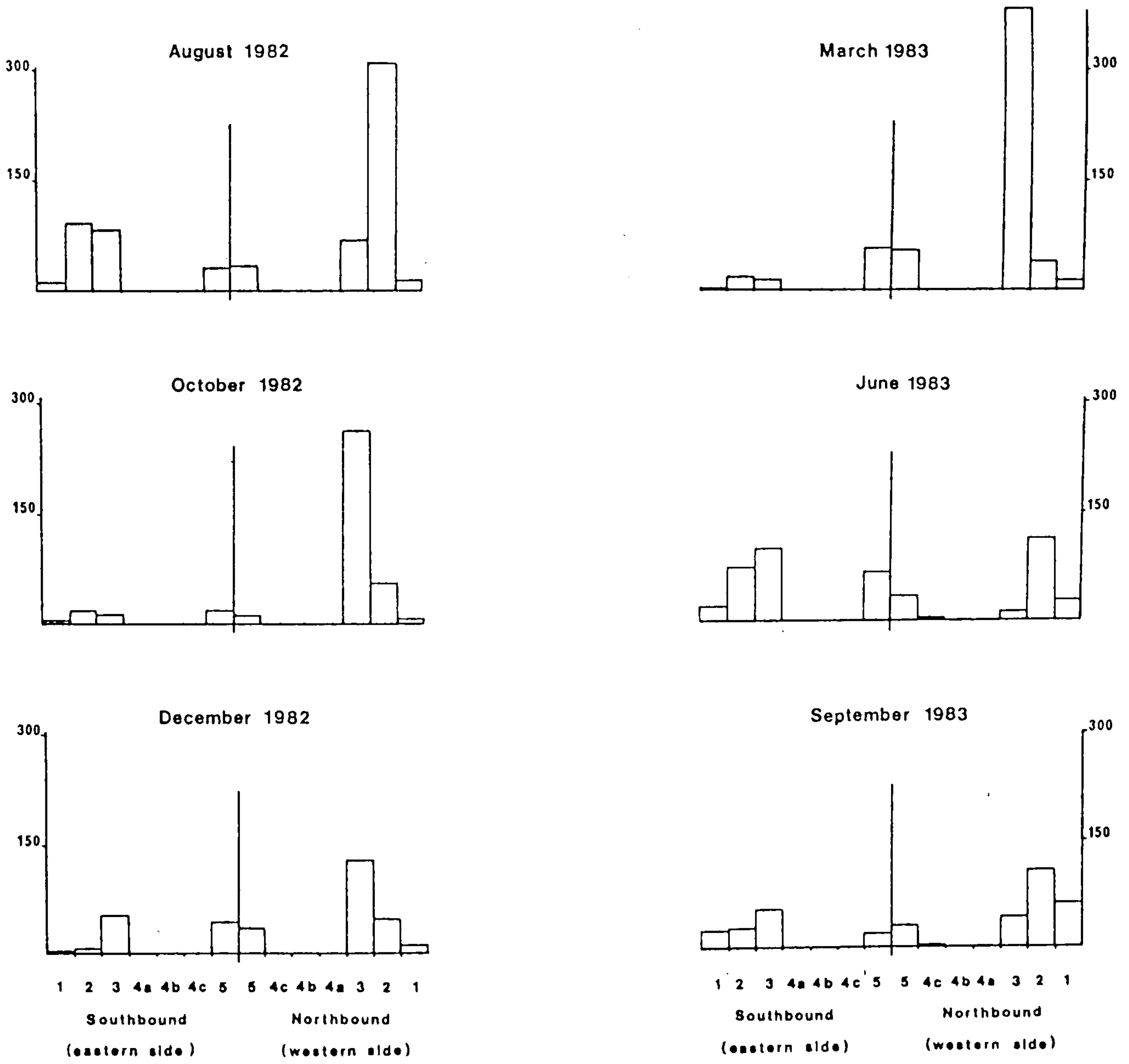


Figure 4.11. Copper loadings on the road surface at site A (mg m^{-2}).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

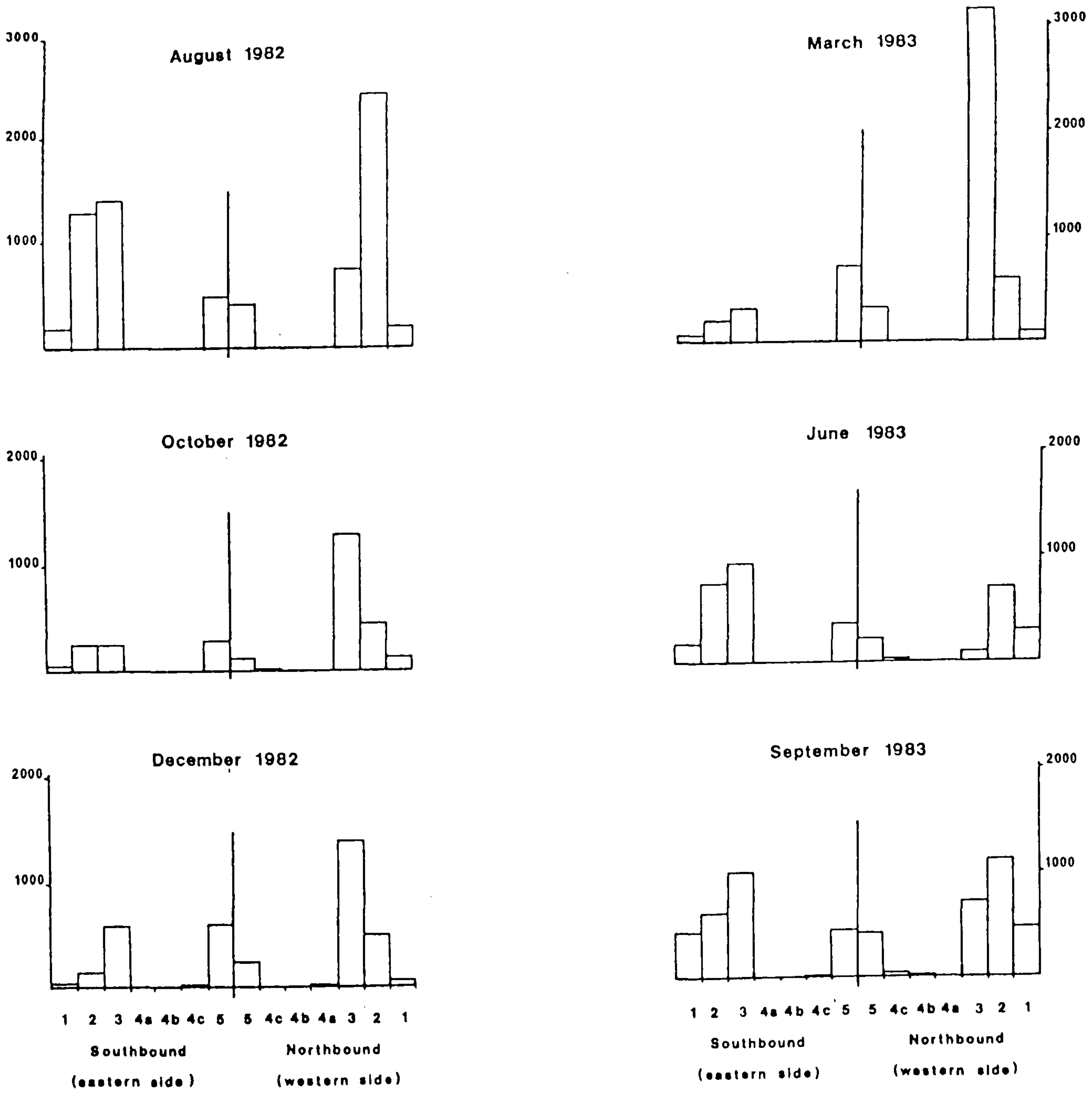


Figure 4.12. Lead loadings on the road surface at site A (mg m^{-2}).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface
5. outside gutter

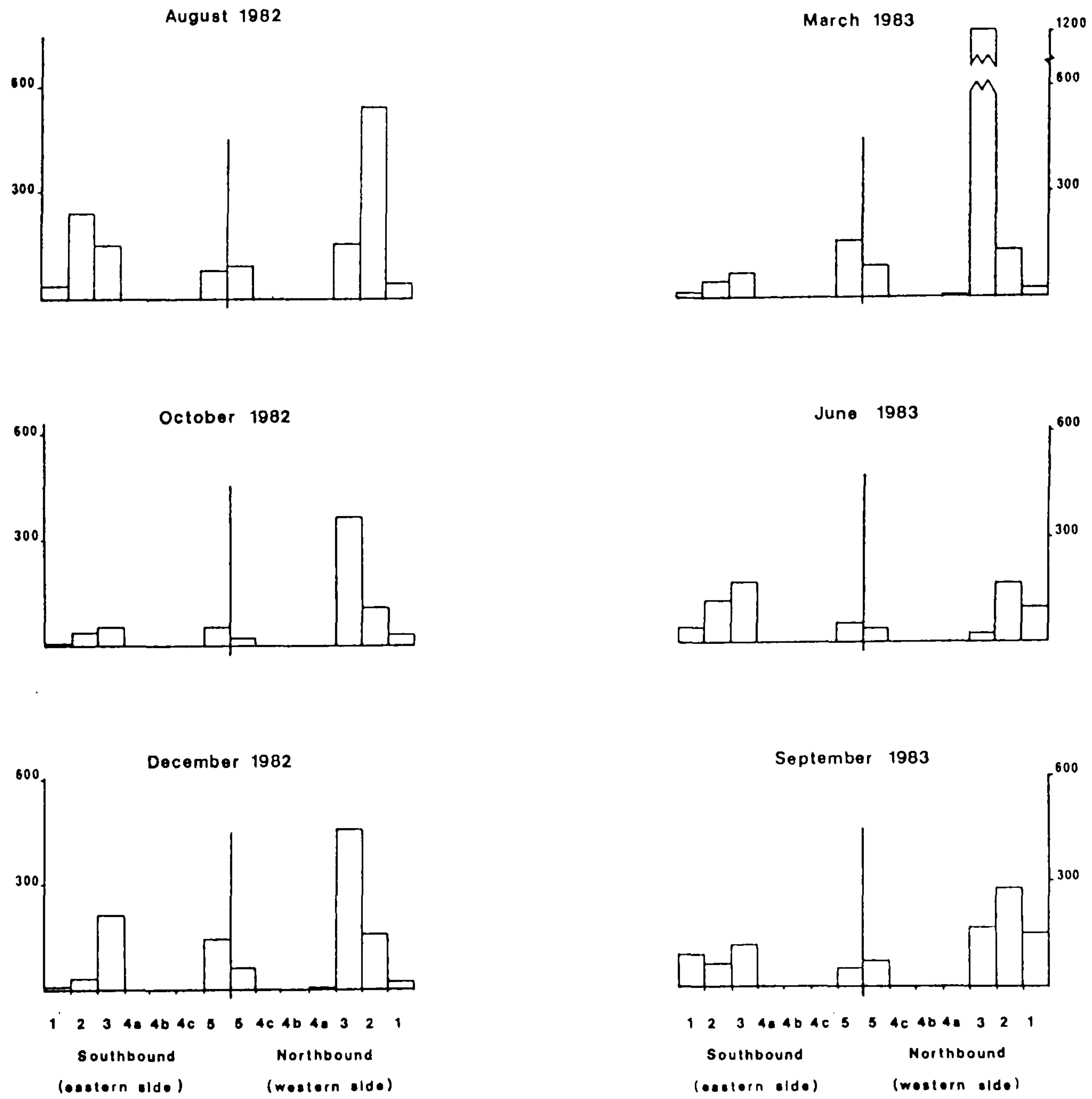


Figure 4.13. Zinc loadings on the road surface at site A (mg m^{-2}).

particularly the coarser particles.

There is very little change in the metal loading distribution patterns between sampling visits. The most obvious temporal change occurs between the August and October 1982 visits for the inside gutter and kerbside samples on the northbound carriage-way. These show a reversal in the pattern of enhancement. The October 1982 metal distribution patterns are maintained during the December 1982 and March 1983 samples, but the original distribution pattern is again observed during the June and September 1983 sample visits.

Metal loadings at sites B and C show much lower levels than site A, consistent with the considerably reduced traffic flows at these sites (Figures 4.14 to 4.17). Although the majority of the metals are deposited in the gutters there is no obvious directional preference at the residential side street. This would be expected in view of the much lower traffic speeds on this road, so the main dispersive mechanism for metals will be the wash-off processes which will occur equally to both gutters during storm events. The road surfaces of this site show slightly higher metal loadings than the road surfaces at site A due to the ability of the coarser surfaces to provide a higher resistance to the removal of particle associated pollutants. In general all road surfaces exhibit high metal concentrations in conjunction with low metal loadings, which indicates the presence of a small amount of highly contaminated material in the form of metal containing particles in this area. This is particularly so for Pb, which is emitted from vehicle exhausts as fine highly enriched particles.

The metal loadings for site B show the initial high values also observed at other sites. The distribution of loadings are most comparable with those observed at site A, with a pronounced increase in the gutter levels on the western side of the road. The road surface loadings are consistent with the low levels observed at the other two sampling sites but also show a preference for the western side of the carriage-way. There are no houses bordering this section of roadway, or any observed differences in traffic density on either side of the road as is the case at site A. This would suggest that the obvious bias of metals and sediment towards the western edges of sites A and B is connected with differences in the hydrological characteristics of the opposite carriage-ways at these sites.

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

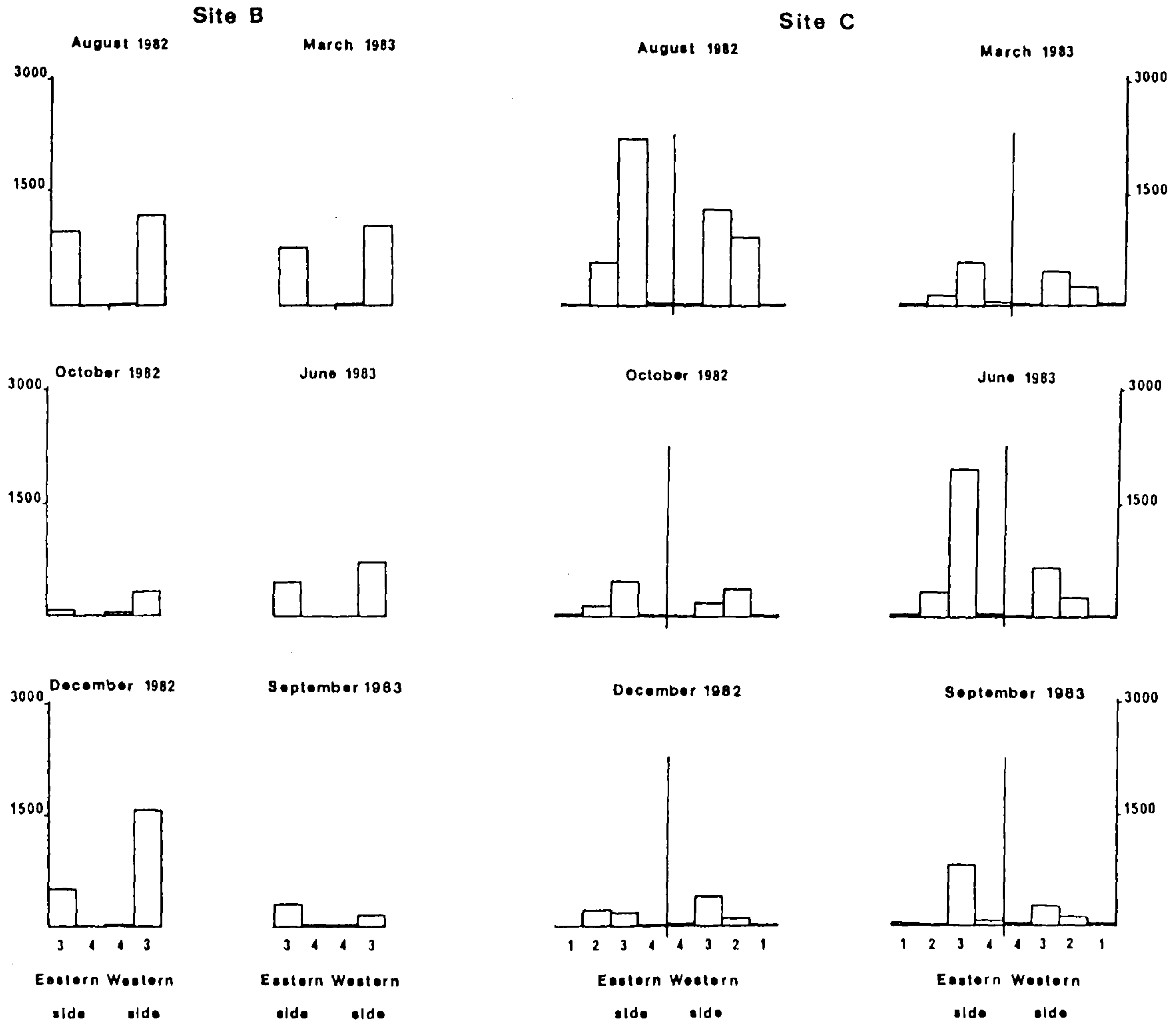


Figure 4.14. Cadmium loadings on the road surface at sites B and C (μg m-2).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

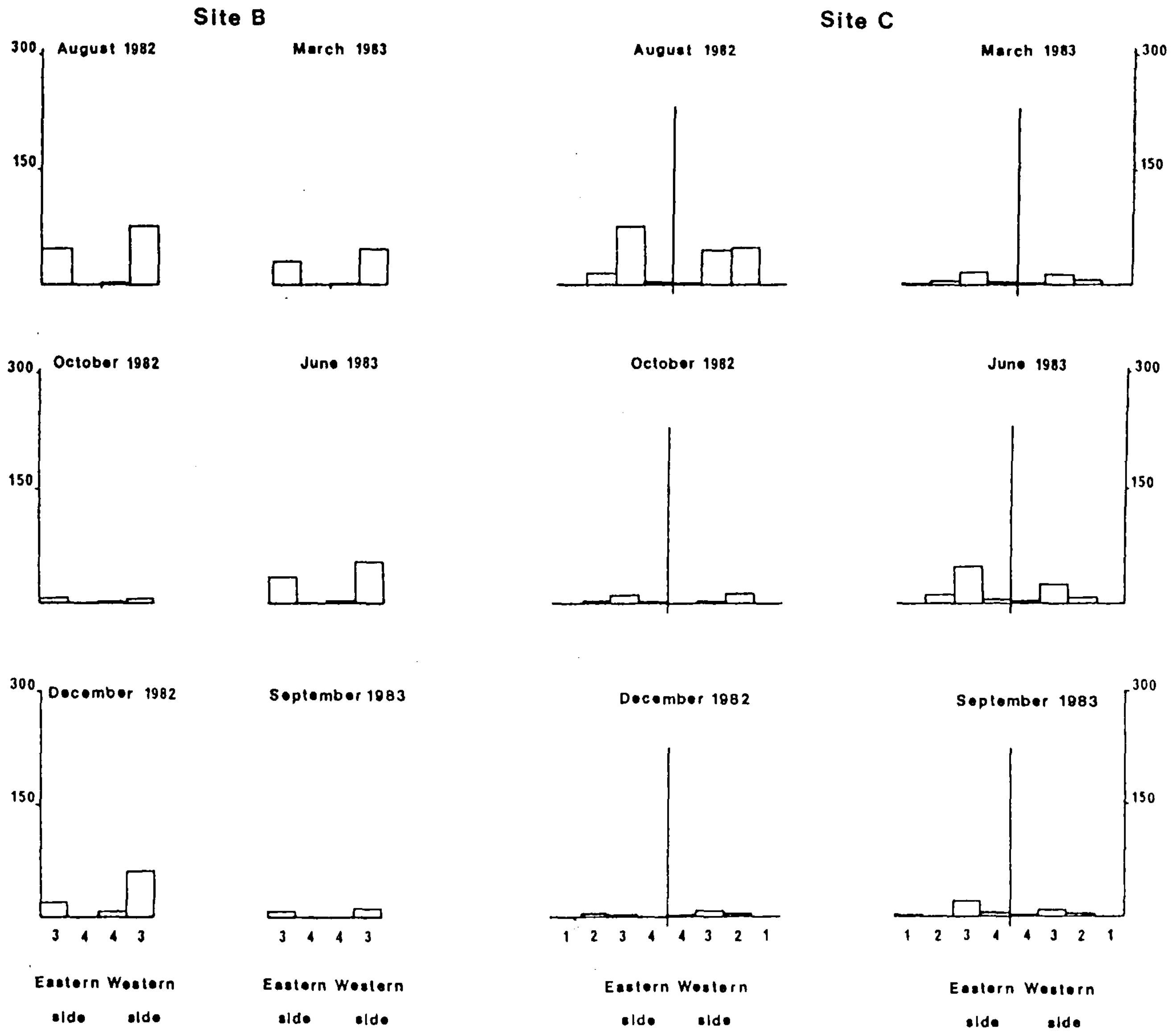


Figure 4.15. Copper loadings on the road surface at sites B and C (mg m^{-2}).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

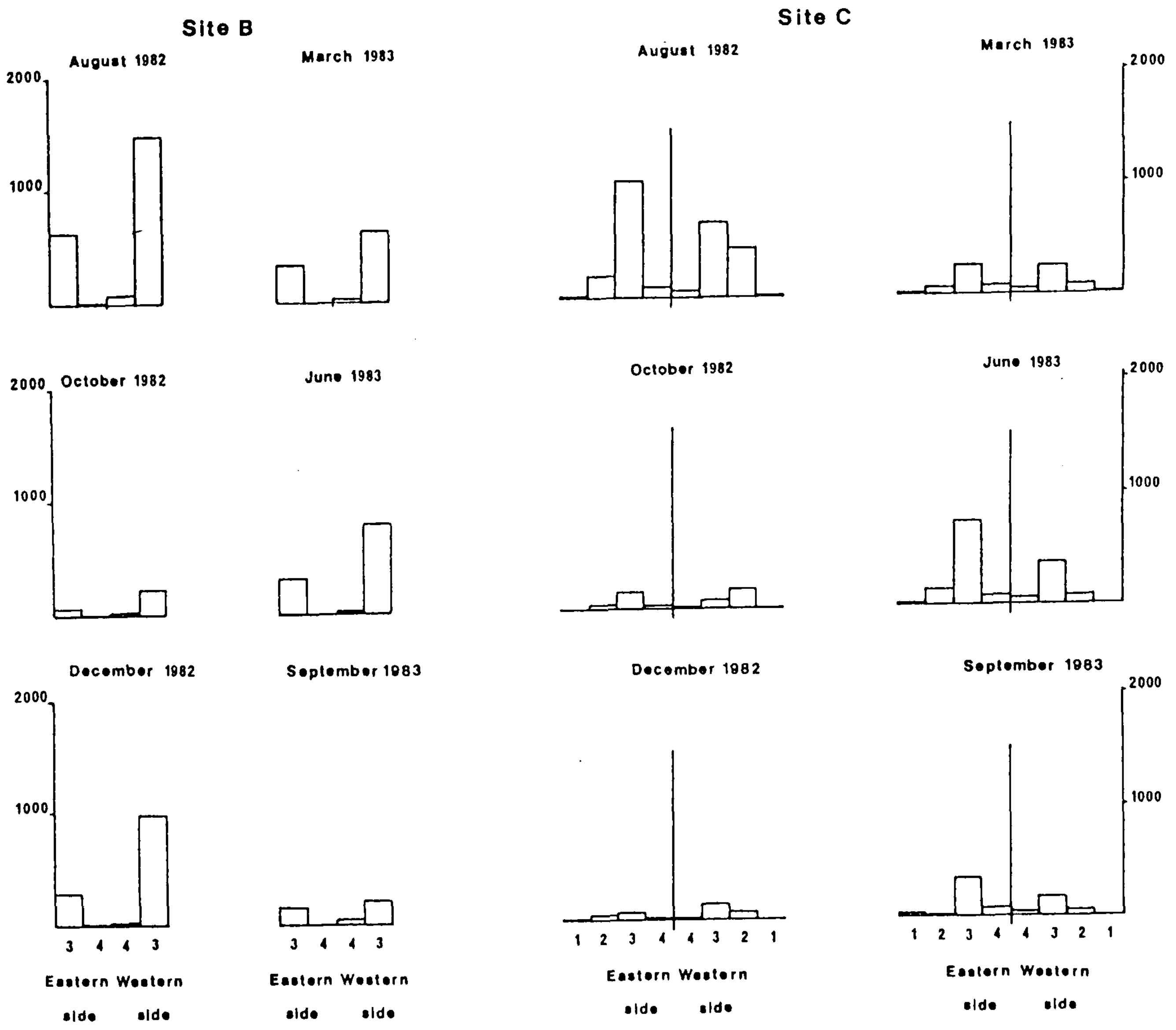


Figure 4.16. Lead loadings on the road surface at sites B and C (mg m^{-2}).

Key.

1. pavement
2. kerbside
3. inside gutter
4. roadsurface

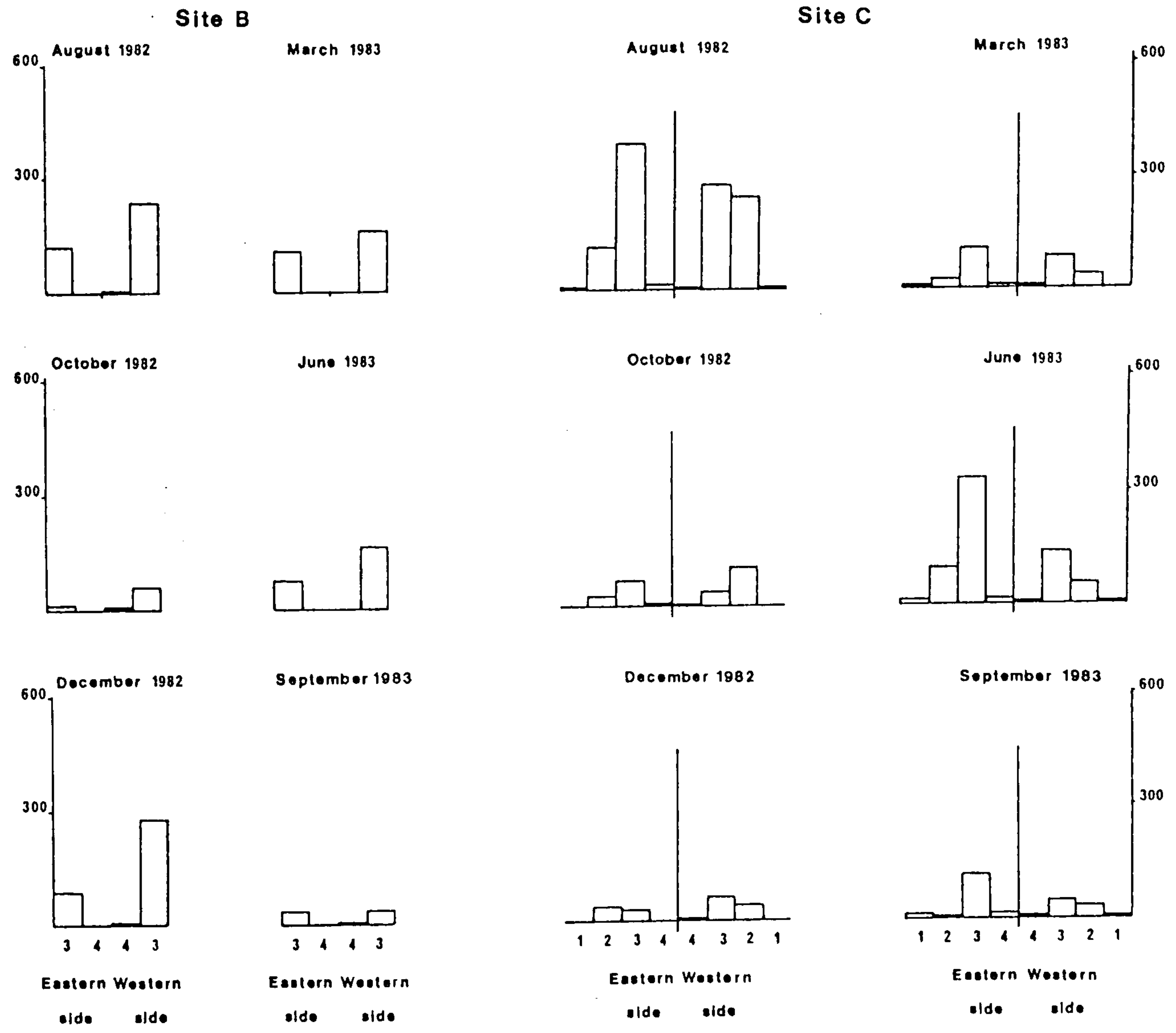


Figure 4.17. Zinc loadings on the road surface at sites B and C (mg m^{-2}).

4.3.6. The influence of municipal street cleaning on heavy metal levels in urban street sediments.

During the October 1982 sampling visit, the northbound carriage-way inside gutter at site A was swept by vacuum mechanical sweeper just after sample collection had taken place. This provided the opportunity to assess the effectiveness of street cleaning in removing heavy metals from road surfaces. An adjacent section of gutter of equivalent area was sampled using the vacuum technique immediately after the road sweeper had passed over the area. The sampled sediment was size fractionated and analysed for heavy metals using the techniques outlined in Chapter 3.

4.3.6.1. Heavy metals in the bulk sediment.

The total sediment loadings were 328.6 g m^{-2} and 136.1 g m^{-2} in the pre- and post- sweeping areas respectively. This represents an overall reduction of 58% on one vehicle pass. Metal concentrations in the bulk sediment collected after road sweeping increased by 11% for Cd and Cu, >19% for Zn and 26% for Pb compared with the sediment sampled before sweeping (Table 4.9). Road sweeping has been shown to be relatively inefficient at removing fine particles and their associated pollutants from the road surface (Sartor and Boyd 1972; Ellis 1979; Pitt 1979). The increase in metal concentrations reported in Table 4.9 may be due in part to the preferential removal of less polluted particles by the sweeper, leaving finer more contaminated sediment behind. Metal loadings in the bulk sediment decreased by 47% for Pb, 49% for Zn and 54% for Cd and Cu after sweeping had taken place (Table 4.9). These results agree with those of Malmqvist (1978) who observed that sweeping removes 65% of the metals from the road surface. Previous work in the United Kingdom has shown rotary brush sweeping to be relatively inefficient in reducing the total metal loadings when compared with alternative techniques of street cleaning such as flushing (Revitt and Ellis 1980).

4.3.6.2. Heavy metal levels in size fractionated sediment.

The removal rate of street sediment by mechanical road sweeper was not constant with grain size (Figure 4.18). The removal efficiency dropped with decreasing particle size from 85% for sediment >2000 µm to a minimum of 29% within the 125-250 µm size range. The removal efficiency then showed a marked increase for the very fine particle

Table 4.9. Metal levels in street sediments before and after street sweeping.

	Cd	Cu	Pb	Zn
Concentrations ($\mu g\ g^{-1}$)				
pre-sweeping	5.4	157.8	1230.0	461.4
post-sweeping	6.0	176.5	1555.9	551.4
Loadings ($mg\ m^{-2}$)				
pre-sweeping	1.85	53.43	416.48	156.25
post-sweeping	0.84	24.74	218.11	77.29

sizes. Sartor and Boyd (1972) and Ellis (1979) have shown that road sweeping caused a redistribution of road sediment out of the gutter and onto adjacent road surfaces, the high removal efficiencies for the finer particles may be due to this process. Alternatively the finer particles may be coagulating during the sweeping operation which includes wetting the sediment. The increase in removal efficiency for the fine particle sizes provides some evidence for this process. The results shown in Table 4.10 depict the increase in heavy metal concentrations with decreasing particle size which has been observed in several previous investigations (see Section 2.3.4). This pattern appears to be reinforced by the action of the road sweeper. Sediments less than 125 µm in diameter show a particularly marked rise in concentration for all four metals studied, whereas the metal concentrations in the coarser size fractions (>250 µm) were found to decrease in most instances. This size range (>250 µm) has been identified in previous work as that in which street sweeping is most effective (Revitt and Ellis 1980).

Prior to sweeping the highest metal loadings for all metals occurred in the 250-500 µm size range with a bias towards the coarse grain sizes (Table 4.10). After sweeping this grain size still remained dominant in terms of metal loadings distribution, but with a noticeable shift in bias towards the finer sizes. This is reflected in the following reductions in metal loading median sizes: 250 to 175 µm for Cd; 210 to 175 µm for Cu; 180 to 135 µm for Pb and 200 to 165 µm for Zn.

Street cleaning carried out by mechanical sweeper appears to produce pollutant enriched sediments of finer particle size than pre-

Table 4.10. Metal levels in size fractionated street sediment before and after road sweeping.

	Size range (μm)	Cd		Cu		Pb		Zn	
		Pre-sweeping	Post-sweeping	Pre-sweeping	Post-sweeping	Pre-sweeping	Post-sweeping	Pre-sweeping	Post-sweeping
Concentrations ($\mu g\ g^{-1}$)									
	>2000	3.8	3.7	18.1	26.3	44.4	192.6	72.0	93.7
	1000-2000	5.3	4.8	195.6	70.4	661.9	628.5	646.8	395.8
	500-1000	5.6	6.0	221.0	204.6	1731.5	1085.9	475.5	681.4
	250-500	5.9	6.0	215.8	244.1	1970.5	1905.9	676.9	608.1
	125-250	7.4	6.7	228.7	201.7	2082.1	2561.4	647.6	663.3
	63-125	7.2	12.0	246.3	250.5	2406.9	2982.0	769.1	946.3
	38-63	9.2	11.3	240.3	307.9	2226.4	3024.3	897.7	1247.3
	<38	10.1	12.5	250.0	309.0	2344.8	3198.1	1112.5	1275.0
Loadings ($mg\ m^{-2}$)									
	>2000	0.39	0.08	1.85	0.60	4.55	4.40	7.38	2.14
	1000-2000	0.21	0.07	7.69	0.98	26.03	8.76	25.44	5.52
	500-1000	0.33	0.15	12.93	5.11	101.27	27.11	27.81	22.53
	250-500	0.46	0.24	16.73	9.96	152.74	77.74	52.47	24.80
	125-250	0.31	0.20	9.44	5.93	85.93	75.29	26.73	19.50
	63-125	0.09	0.08	3.05	1.65	29.76	19.70	9.51	6.25
	38-63	0.04	<0.01	1.17	0.22	10.79	2.20	4.35	0.91
	<38	0.02	<0.01	0.58	0.28	5.40	2.91	2.56	1.16

swept road sediment. As a control practice for reducing the surface sediment pollutant levels street cleaning can be seen to be reasonably efficient. Overall approximately 50% of the metal mass in the gutter was removed by one passage of the machine. As a considerable proportion of the total street sediment metal is found in the gutter (see Section 4.3.5) this represents a significant removal of metals from the street environment. Although sweeping causes a reduction in the total amount of dust and heavy metals present, it actually appears to enhance the concentration levels of metals.

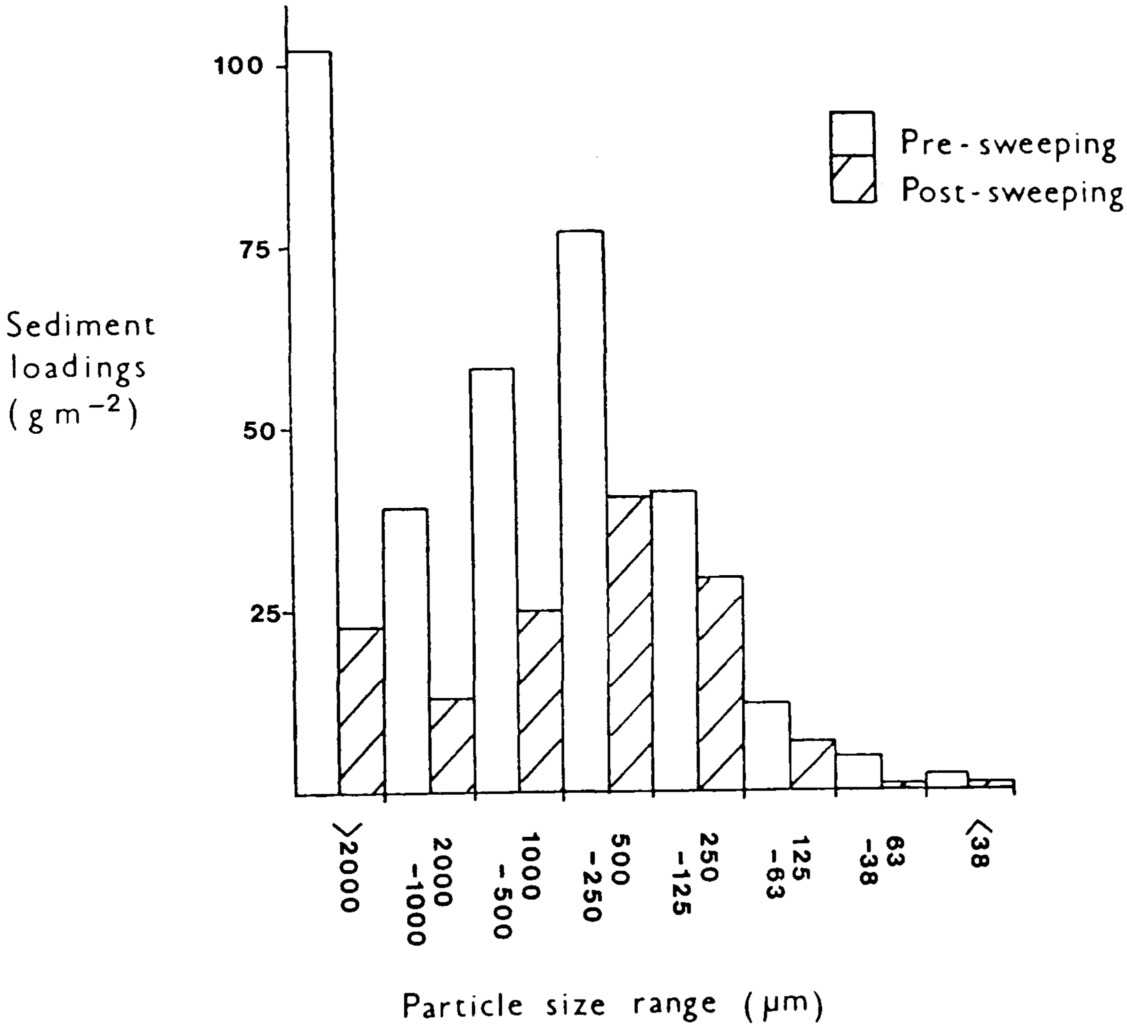


Figure 4.18. The effect of municipal road sweeping on sediment grain size loadings.

4.3.7. Representative sampling of urban street sediments.

The choice of sampling location for road sediment will obviously depend on the objectives of the monitoring programme being undertaken. If the objective is to assess the possible contamination of stormwater runoff by street sediments then the samples taken from the gutter and road surfaces are of particular importance. For routine monitoring to assess the health effects of road sediment contamination then the pavement/kerbside samples are of interest, as children are more likely to come into contact with these sediments.

The results of the surveys described in this Chapter have shown that quite marked differences in concentrations and loadings can exist within a few metres of roadway. In order to establish an overall assessment of heavy metal levels along a particular section of highway it is therefore necessary to take into account the higher concentrations of metals found on the road surfaces, and the high loadings found in the gutter and on adjacent pavements. Because these areas have such high loadings relative to the road surface the contribution of the latter to the overall heavy metal loadings is minimal, and when calculating overall metal concentrations at a particular site the the road surfaces can be seen to have little effect for major roads, such as site A. In situations where road surface sediment and metal loadings represent a significant, albeit minor, proportion of the total loadings at a particular sampling site, then the road surfaces obviously need to be taken into account by taking full width transects. Full width transects will also account for pockets of sediment which build up in hollows, cracks and where the kerb or a wall act as a barrier to lateral dispersion of resuspended dust.

It can also be seen from this work that in addition to the short term fluctuations in heavy metal levels observed by previous workers, large seasonal variations in metal levels can be found. The recommended three monthly sampling period (Schwar 1983) is obviously not long enough to account for this fluctuation in levels. These considerations must be assessed in relation to available manpower, and the practicalities of sampling on major urban roads which involves cordoning off sections of the roadway to allow safe sampling.

4.4. Conclusions.

The major findings of this section of the research project can be summarised as follows:-

a) The overall heavy metal levels observed in this study are comparable with those from previous studies. Metal concentrations and loadings for all metals decreased with decreasing traffic density but not proportionally. Metal loadings showed the closest relationship to traffic density. At all three sites the metal concentrations exceeded the Greater London Council guidelines for Pb in street dust.

b) A seasonal pattern in the heavy metal loadings and concentrations was observed. Reduced levels of metals were recorded during the winter months. This may be due to the increased frequency of street cleaning, and the increased and more intense rainfall occurring during these months. Rainfall intensity was found to be a factor affecting temporal variations in metal levels.

c) The concentration patterns observed in this study are not uniform for all metals. Copper and Pb were found to exhibit increased concentrations for the road surfaces at sites B and C, which are of low traffic density. For Cd and Zn the peak concentrations occurred in the gutter samples at these sites. At the high traffic density site no obvious spatial distribution in metal concentrations was observed.

d) A major factor which influences the distribution of metal loadings across highway and adjacent surfaces is the dispersive effect of fast moving traffic. Vehicle induced resuspension of surface dusts has been shown to be a major mechanism for the lateral dispersion of sediments on roads with heavy traffic densities. Resuspension will dominate on a major trunk road after only a few days of consecutive dry weather, whereas at sites B (intermediate traffic) and C (residential site) resuspension will seldom dominate due to the low traffic flows. This is consistent with the observations that metal loadings show less spatial variation on the side street than on the major road, but metal concentrations show the reverse trend.

e) Street cleaning practices have been shown to increase the metal concentrations in street sediments. It is suggested that this may be due to the preferential removal of larger particles. Loadings of all metal were substantially reduced after road sweeping had taken place.

As a consequence of the spatial and temporal variations in metal levels described above, it can be concluded that in order to collect representative samples of road sediment it is necessary to carefully interpret local site conditions with particular reference to the objectives of the investigation being undertaken.

CHAPTER 5. PHYSICO-CHEMICAL ASSOCIATIONS OF HEAVY METALS IN URBAN STREET SEDIMENTS.

5.1. Introduction.

The environmental and health effects of metal pollutants in urban street sediments are dependent on the mobility and availability of the metals. Total metal concentrations alone are not a true indication of the potential toxicity or environmental mobility of a particular metal. The transport pathways and toxic effects of particulate associated heavy metals are dependent on a number of complex factors including the particle size spectrum of the sediment, and the chemical form in which the metals occur as well as their concentration and loading. The affinity of fine particles for heavy metals is well documented (see Section 2.3.4). Measurements on metal size distributions indicate that approximately 50% of the metal content in road sediment can be associated with particles of <43 µm diameter (Sartor and Boyd 1972). However, only particles larger than 250 µm are removed efficiently by conventional street cleaning procedures (see Section 4.3.5). The finer more contaminated particles which remain are more readily flushed into the stormwater system. This preferential removal of fine particles by runoff processes is confirmed by the high maximum metal concentrations which have been observed in stormwater suspended solids compared with those which are generally found in road surface sediments (see Section 2.5.5).

The particle size associations of heavy metals in street dusts are also an important consideration in health studies. Hand to mouth activity is an important pathway by which metals are ingested by children (see Section 2.6.3). In measurements of the quantity of Pb on the hands of school children most of the Pb containing particles were found to be <10 µm in diameter (Duggan et al. 1985).

The ease of solubility of metals is strongly dependent on the chemical forms with which the metals are associated in urban street sediments. Most investigations of heavy metals in street sediments have concentrated on source identification, and the determination of total metal levels. Comparatively few studies have been made of the chemical forms of metals in street dust (see Section 2.4). Speciation studies of Pb in road dust have been carried out using X-ray powder diffraction (Olsen and Skogerboe 1975; Biggins and Harrison 1980). This technique gives detailed information on chemical structure but is only applicable to crystalline compounds, which represent only a few percent of the total metal present in street dust.

A technique of wider applicability is the use of a sequential extraction procedure to examine chemical associations of metals in street dust. A number of such experimental procedures have been applied to the study of metals in aquatic sediments, soils and street dusts (see Section 2.4). The procedures are designed to selectively remove metals from the various components of the sediment with which they are associated. The trace metal distribution in any extraction scheme is operationally defined by the method of extraction rather than by some fundamental property of the metal complex. There is, therefore, some overlap between extractants and problems of re-adsorption have been raised (Rendell et al. 1980). Nevertheless, the schemes provide detailed information about the mode of occurrence, biological and physico-chemical availability, mobilisation and transport of trace metals.

The objective of the study described in this Chapter was to determine the chemical associations of Cd, Cu, Pb and Zn in street sediments, and to investigate variations in chemical association with particle size. In addition the influence of factors such as pH, organic matter content and cation exchange capacity on the distribution of metals in the various chemical phases is also assessed. The implications of the results are discussed with respect to the environmental mobility and bioavailability of the metals in urban street sediments.

The sequential extraction techniques chosen for use in this study are those developed by Tessier et al. (1979), which provide a realistic comparison with the ease of release of metals into solution under various environmental conditions. The scheme has been used in a number of similar investigations (Harrison et al. 1981; Fergusson and Ryan 1984). Unlike other comparable sequential extraction procedures the scheme used includes a separate carbonate fraction. Harrison et al. (1981) noted that the carbonate fraction was particularly important in street dust because of the generally higher calcite content of this type of sediment. The extraction scheme allows the partitioning of metals into five fractions which are in order of relative ease of release of the metal: exchangeable; carbonate; Fe-Mn oxides; organic and residual phases.

5.2. Sample Collection and Experimental Procedure.

Samples of street dust were collected from two sites located in North West London (Figure 5.1). Sites A and B were located on the southbound hard shoulder of the M1 motorway and the gutter of the southbound carriage-way of the A41 Hendon Way, respectively. Sample collection took place in November 1981, and was undertaken using a dustpan and brush. The sites were chosen to represent areas of different surface type (Table 5.1). In order to obtain a sufficient quantity of road sediment for the experiment a 5 m length of gutter was swept.

Table 5.1. The sampling site characteristics.

	Site	Traffic type	Remarks
A	M1 motorway southbound carriage-way Edgeware, N.W. London.	$48000\ \mathrm{day}^{-1}$ H.G.V., P.S.V., vans cars, average speeds 55 mph. Concrete surface.	Samples taken from hard shoulder adjacent to gully pot.
B	A41 Hendon Way southbound carriage-way Hendon, N.W. London.	$20000\ \mathrm{day}^{-1}$ H.G.V., P.S.V., vans cars, average speeds 45-55 mph. Asphalt surface.	Sample taken from gutters of dual carriage-way.

On return to the laboratory the samples were air dried, and then size fractionated using: 1000; 500; 250; 125; 63 and 38 μm stainless steel sieves. The following determinations were performed on each of the size fractions.

5.2.1. Total metals.

Total metal levels in the size fractionated sediment were determined using a HNO_3-$HClO_4$ extraction as outlined in Section 3.7.

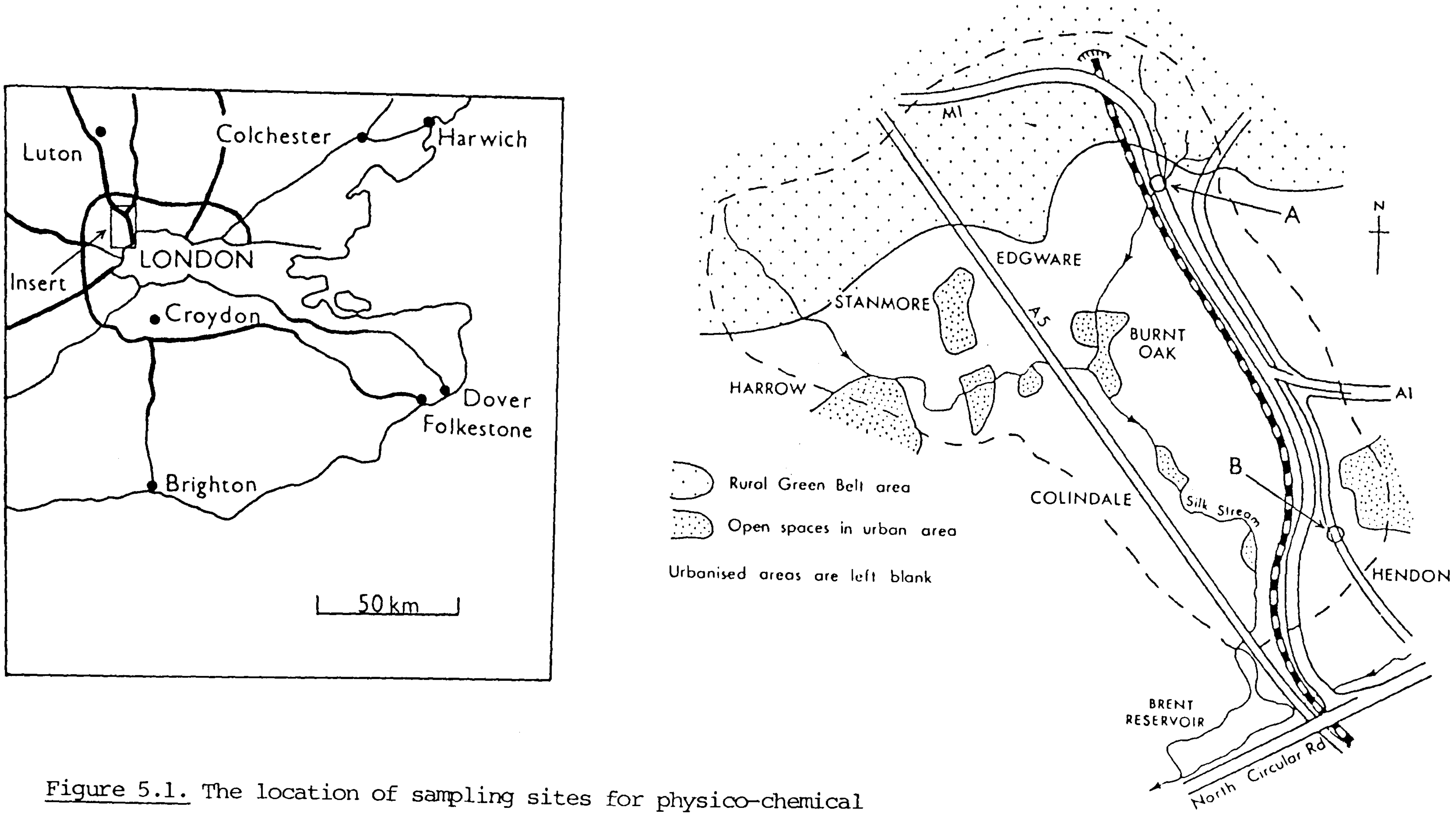


Figure 5.1. The location of sampling sites for physico-chemical speciation experiments on street sediments.

5.2.2. pH.

The pH of the road sediment was determined using the technique outlined in British Standard BS 1377 (1975). A suspension of 30 g of sediment in 75 ml of distilled water was equilibrated overnight, and the pH determined electrometrically.

5.2.3. Organic matter content.

The organic matter content in each size fraction of road sediment was determined by the Walkley-Black method described in British Standard BS 1377 (1975). A 0.5 g subsample of road sediment was digested with 10 ml of 1N $K_2Cr_2O_7$ and 10 ml of H_2SO_4 for 30 minutes. The excess dichromate was then titrated against 0.5N ferrous ammonium sulphate using di-phenylsulphonate indicator.

5.2.4. Cation exchange capacity.

The C.E.C. of the size fractionated sediments was determined using the method outlined in M.A.F.F. Booklet RB425 (M.A.F.F. 1981). The sediment was leached with 1M CH_3COONH_4. Excess CH_3COONH_4 was removed from the sediment with ethanol. The exchanged NH_4^+ ions corresponding to the C.E.C. of the sediment were then extracted with KCl and determined titrimetrically.

5.2.5. Chemical associations of heavy metals.

The chemical associations of the metals in size fractionated sediments were determined using the sequential extraction procedure described in detail by Tessier et al. (1979). Extractions were performed on duplicate 1 g subsamples in 50 ml polypropylene centrifuge tubes. A shaking water bath was used as necessary. Following each extraction the mixture was centrifuged at 3000 rpm for 30 minutes and the supernatant liquid decanted into polythene volumetric flasks, acidified to pH <2, and stored at 4°C prior to analysis. The chemical extractants and analytical conditions for each stage in the procedure are described below.

a) Exchangeable fraction.

The sediment was extracted at room temperature for 1 hr with 8 ml of 1M $MgCl_2$ solution at pH 7, with continuous agitation.

b) Bound to carbonates fraction.

The residue from (a) was leached at room temperature with 8 ml of 1M CH_3COONa adjusted to pH 5.0 with CH_3COOH. Continuous agitation was maintained throughout the extraction time of 5 hr.

c) Bound to Fe-Mn oxides fraction.

The residue from (b) was extracted with 0.04M $NH_2OH.HCl$ in 25% (v/v) CH_3COOH. The extraction was performed at 93 ± 3^oC with occasional agitation for 6 hr.

d) Organic matter fraction.

The residue from (c) was extracted with 3 ml of 0.02M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2 by addition of HNO_3. The mixture was heated to 85 ± 2^oC for 2 hr with occasional agitation. A second 3 ml aliquot of 30% H_2O_2 (at pH 2) was then added, and the sample heated at 85 ± 2^oC for a further 3 hr with intermittent agitation. After cooling, 5 ml of 3.2M CH_3COONH_4 in 20% (v/v) HNO_3 was added to prevent adsorption of extracted metals onto the oxidised sediment. The mixture was diluted to 20 ml and agitated continuously for 30 minutes.

e) Residual metals fraction.

The residue from (d) was first digested in a Teflon beaker with 2 ml of concentrated $HClO_4$ and 10 ml HF. The mixture was heated to dryness and a second addition of $HClO_4$ (1 ml) and HF (10 ml) made. The mixture was then evaporated to near dryness. Finally, $HClO_4$ (1 ml) alone was added and the sample evaporated until the appearance of white fumes. The residue was dissolved in 1M HNO_3 and diluted to 25 ml.

Between each successive extraction the residue was washed with 8 ml of de-ionised water, after further centrifugation for 30 minutes this second supernatant layer was discarded. All glassware and plastic vessels were previously soaked overnight in 10% HNO_3 and carefully rinsed in de-ionised water. The reagents were analytical grade or better.

5.2.6. Selection of a representative sample of collected sediment.

Highway dusts are a heterogeneous mixture of particulates with widely varying composition. Appropriate procedures must be employed to ensure that the final results are representative of the bulk sample, and have not been significantly affected by the presence of a small number of particles of anomalously high composition. Initial results from the sequential extraction experiment produced widely varying results for replicate subsamples for larger sediment particle sizes. The two usual methods of reducing the variation in results are by using a larger sample mass, and by grinding the sample prior to analysis. Since the aim of this study was to assess the characteristics of heavy metals in street sediment in their naturally occurring environmental situation, it was considered preferable not to grind the samples. Simple calculations (Table 5.2) show that a 1 g dust sample is adequate for analysing dust of diameter <1 mm, but inadequate for sediment sizes above this. Using quantities of dust in excess of 10 g caused problems with the handling and quantity of extractants required for the experiment. Therefore for dust >1 mm in diameter 5 g of sediment was used.

5.2.7. Metal analysis.

Metal analysis was performed by flame atomic absorption spectrometry for Cu, Pb and Zn. Cadmium analysis was carried out using a carbon furnace attachment. Standard calibration procedures were used with standards prepared using the relevant components of the extraction solution. The details of the analytical instrumentation are given in Chapter 3.

5.3. Physico-chemical Associations of Heavy Metals in Road Sediment.

5.3.1. Metal levels in the bulk sediment.

The total metal levels, determined by HNO_3-$HClO_4$ extraction (Table 5.3), are similar to those reported by other workers for motorway and major roadway sampling sites (see Section 2.3, Table 2.10). Previous work, described in Chapter 4, on samples of road sediment taken close to sites A and B has also shown comparable results to those reported in this investigation. Ellis and Revitt (1982) have reported metal concentrations for the two sites (Table 5.3). The metal concentrations observed in this study show the same spatial distributions to the earlier study and in both cases the motorway site (site A) has elevated Cd, Cu, and Zn levels. In contrast the Pb concentrations observed on the A41 (site B) are higher than those at site A,this may be the result of differences in driving mode. Less Pb is emitted from cars cruising on motorways than those travelling on

Table 5.2. The effect of particle size on the number of particles in a subsample.

	Particle size range (µm)						
	>1000	500-1000	250-500	125-250	63-125	38-63	<38
a) typical particle size (µm)	2000	750	375	188	94	47	24
b) mass of 1 particle assuming $\rho = 3$ g cm^{-3}	$1.3x10^{-2}$	$6.8x10^{-4}$	$8.4x10^{-5}$	$9.0x10^{-6}$	$9.8x10^{-7}$	$2.0x10^{-7}$	$2.5x10^{-8}$
c) No. particles in 1 g	78	1481	$1.2x10^{4}$	$1.1x10^{5}$	$1.0x10^{6}$	$5.0x10^{6}$	$4.0x10^{7}$
d) Mass of Pb (µg) in 1 particle containing 10% Pb by mass.	1280	67.5	8.4	0.9	0.1	0.02	$2.5x10^{-3}$
e) Mass of Pb in 1 g (µg) assuming [Pb]=1000 µg g^{-1}	1000	1000	1000	1000	1000	1000	1000
f) Mass of original sample to make row e <10% row d (g)	12.8	0.675	0.084	0.009	0.001	$2.0x10^{-4}$	$2.5x10^{-5}$

urban roadways which undergo more stops and starts (see Section 2.1.4).

It has been noted in previous Chapters that comparatively few investigations have reported metal loadings on road surfaces. The total metal loadings reported in Table 5.3 are within the range of values reported in Section 4.3.5 for gutter areas of the A41 (site B of this study). The Cd and Pb loadings at both sites are considerably higher than those reported by Solomon and Hartford (1976) for a major roadway site. However, the large spatial and temporal variations in metal levels between sites, which are discussed in Chapter 4, make comparisons difficult.

The speciation of heavy metals in road dusts has been investigated by a number of workers. The results of this study of the fractionation of metals in the bulk sediment confirm those observations made by Harrison et al. (1981), Gibson and Farmer (1984) and Fergusson and Ryan (1984). No previous investigation has reported the loadings of metals in each chemical fraction on urban street surfaces. However, percentage of the total metal content in each fraction is frequently reported and this information can be derived from the data in Table 5.3. Significant inter-elemental differences have been observed in previous investigations and similar trends are shown in Table 5.3. Cadmium is the only element to show significant levels (4.3 and 9.2%) in the exchangeable fraction. This compares with the results of Harrison et al. (1981) and Fergusson and Ryan (1984) who observed a greater proportion (15-32%) of Cd associated with this fraction. Cadmium, Pb and Zn are found mainly in the carbonate and Fe-Mn oxide fractions with some 60-70% of the three metals bound in these combined fractions. These fractions can be considered as moderately available in biological and environmental terms. Harrison et al. (1981) have observed that in road sediment the Pb content of the carbonate fraction was greater when compared with soils. This has been attributed to the greater abundance of calcite in road dusts. Copper is primarily associated with the organic fraction (55-60%), with a significant proportion located in the residual phase (27-36%). This affinity for the organic phase has been observed in other street sediments (Harrison et al. 1981; Gibson and Farmer 1984 and Fergusson and Ryan 1984), in soils (McLaren and Crawford 1973) and in aquatic sediments (Gupta and Chen 1975; Tessier et al. 1979; Forstner and Salomons 1980).

There appears to be very little difference in the distribution of metals between the five fractions in the sediment collected from the

Table 5.3. Chemical associations of Cd, Cu, Pb and Zn in bulk sediment.

	Site A				Site B			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Concentration ($\mu g\ g^{-1}$)								
Exchangeable	0.7	2.3	23.1	17.1	0.3	1.4	29.9	12.2
Carbonate	1.6	11.2	612.2	344.3	3.2	9.6	1133.7	128.6
Fe-Mn oxides	3.9	16.8	1443.2	385.0	1.8	6.1	812.9	158.0
Organic	0.8	180.2	517.6	140.2	1.7	75.3	568.2	61.8
Residual	0.3	111.5	392.9	162.0	0.2	34.4	176.7	90.3
Sum total	7.3	330.1	1855.0	1048.6	7.2	126.8	2718.8	451.3
Total by HNO_3-$HClO_4$	4.0	279.5	2747.4	835.9	3.0	173.5	3241.7	404.1
Literature values Ellis & Revitt (1982)	6.0	410.0	2100.0	1876.0	5.3	280.0	1826.0	695.0
Loadings ($mg\ m^{-2}$)								
Exchangeable	0.5	1.6	16.0	11.9	0.2	0.9	19.6	8.0
Carbonate	1.1	7.8	425.0	239.0	2.1	6.3	742.0	84.2
Fe-Mn oxides	2.7	11.7	100.2	267.3	1.2	4.0	532.0	103.4
Organic	0.6	125.1	359.3	97.3	1.1	49.3	371.9	40.4
Residual	0.2	77.4	272.8	112.5	0.01	22.5	116.6	59.1
Sum total	5.1	223.6	1173.3	728.0	4.6	83.0	1782.1	295.1
Total by HNO_3-$HClO_4$	2.8	194.0	1907.4	580.3	2.0	113.6	2121.6	264.5

two sample sites in this investigation. Harrison et al. (1981), Farmer and Gibson (1984) and Ryan and Fergusson (1984) have investigated a much greater number of sample sites and also reported little overall change in metal distributions.

Although a large number of studies have reported the results of chemical fractionation experiments on aquatic sediments and soils, there is very little information with which to compare atmospheric particulates. Lum et al. (1982) used the chemical extraction procedure devised by Tessier et al. (1979) to partition metals in a reference sample of atmospheric particulates collected over 12 months near St Louis, U.S.A. The distribution of metals between chemical fractions was significantly different to those observed for road sediments. High concentrations of metals in the exchangeable fraction were observed in atmospheric particulates. The exchangeable fraction contained 87%, 39%, 46% and 24% of the total Cd, Cu, Pb and Zn respectively. X-ray diffraction studies have shown that for Pb the most frequently observed compound in urban air is $PbSO_4.(NH_4)_2SO_4$ (Biggins and Harrison 1979). In road sediment the most commonly observed compound is $PbSO_4$ which appears to be formed by rainwater leaching of $PbSO_4.(NH_4)_2SO_4$ (Biggins and Harrison 1980). Lead sulphate has significant solubility in 1M $MgCl_2$ and Harrison et al. (1981) have observed that 40-45% of $PbSO_4$ spiked to a soil sample was recovered in this fraction. Only a small proportion of Pb in street sediment is in the crystalline form susceptible to XRD analysis (Biggins and Harrison 1980). Therefore crystalline compounds of Pb must rapidly dissolve in water and re-deposit in the chemical forms typical of soils (Harrison and Laxen 1980). X-ray diffraction analysis of atmospheric particulates has shown double salts analogous to $PbSO_4.(NH_4)_2SO_4$ for other metals (O'Connor and Jaklevic 1981), therefore the pathway described above for Pb may also apply to other metals in the atmosphere.

The drop in Pb in petrol levels has reduced atmospheric levels of Pb substantially (see Section 2.2.1). However, the chemical associations of Pb described in Table 5.3 indicate that road sediments will remain highly contaminated with this metal. The levels of Pb in the more environmentally mobile fractions will be maintained by the slow release from the more environmentally stable phases. Road sediments will therefore continue to contribute to the exposure of young children to Pb.

It may be expected that the chemical associations of trace metals in urban street dirt would be reflected in aquatic sediments following removal by stormwater runoff. Modifications in the chemical partitioning of metals may arise due to the processes of adsorption, desorption, complexation and biological accumulation in the water column. The speciation patterns described in Table 5.3 are broadly similar to those for a range of aquatic sediments (Gibbs 1973; Tessier et al. 1979; Salomons and Forstner 1980; Forstner 1982; Calmano and Forstner 1983), although the wide range of extractants and extraction schemes employed makes direct comparison difficult (see Section 2.4.4).

5.3.2. Variations in total metal concentrations with particle size.

The variations in total metal concentrations with particle size are shown in Table 5.4. The results are similar to those observed by previous workers who have studied metal-particle size relationships (see Section 2.3.3). All four metals studied in this investigation show an increase in concentration with decreasing particle size. The differences in metal concentrations between the two sample sites reflect the spatial variations reported for bulk sediment in Section 5.3.1. Overall, site A has elevated levels of Cd, Cu and Zn when compared with site B with Pb showing the reverse trend.

Table 5.4. The distribution of heavy metal concentrations with particle size (µg g^{-1}).

	Size fraction (µm)						
	>1000	500-1000	250-500	125-250	63-125	38-63	<38
Cd Site A	1.7	2.0	3.0	3.4	7.9	10.2	8.9
Site B	1.1	1.3	2.4	3.6	5.2	7.8	8.1
Cu Site A	79.2	144.9	364.0	418.9	525.4	545.9	477.3
Site B	102.5	100.8	148.8	217.2	264.1	299.1	348.9
Pb Site A	408.9	2469.1	2674.8	3695.8	4971.1	4668.1	4455.4
Site B	1325.7	2888.2	2331.0	3126.8	3900.6	3952.5	4174.2
Zn Site A	392.3	497.2	813.0	840.1	1205.1	1293.3	1439.1
Site B	220.1	236.7	330.5	448.5	784.9	744.1	830.3

The percentage distributions of the metals within each size fraction for both the total metal, as determined by HNO_3-$HClO_4$, and the sum total of metal in each chemical fraction are given in Table 5.5. At each site the percentage distributions of the metals are very similar, with the 125-250 µm size dominating the distribution pattern.

The most notable difference in the percentage distribution of the metals between the two sample sites is shown in the >1000 µm size fraction. In sediment taken from the site B there is considerably more metal in this fraction (7.5-9.2%) compared to that taken from site A (0.8-3.0%). This may reflect the difference in surface type between the two sites. Site B is surfaced with asphalt, whereas site A is constructed of concrete. Pitt (1979) has shown that sediments on asphalt and asphalt/chippings surfaces tend to have a greater proportion of larger particles and associated heavy metals.

Biggins and Harrison (1980) have observed that because of the greater total sediment mass in the large size fractions, in many cases the greater mass of metal is associated with larger grain sizes in street sediment. In this study it can be seen from Table 5.5 that for both sample sites more than 60% of the metal content is found in the <250 µm size fractions. This confirms work carried out by Ellis and Revitt (1982) who showed that for many metals the median grain size is in the region of 250 µm. Particles >250 µm in diameter represent those most efficiently removed by street cleaning procedures (see Section 4.3.6). Little and Wiffen (1977) have reported that 90% of the mass of Pb in air sampled at the hard shoulder of a motorway is associated with particles of 5 µm or less in diameter. The results of this survey show that only 2% of the Pb in sediment on the motorway site was in the <38 µm size fraction. This supports the view that very fine particles are not present independently but are aggregated with larger particles (Ellis and Revitt 1982).

The recovery efficiency of the sequential extraction scheme can be assessed by a comparison of the sums of the concentrations of each metal extracted in the five stages (Tables 5.6 to 5.9), with the independently determined total metal concentrations (Table 5.4). When averaged these values show that HNO_3-$HClO_4$ extracted 48±16% of the Cd; 146±94% of the Cu; 151±91% of the Pb and 86±13% of the Zn. These values do not compare favourably with equivalent determinations reported by Gibson and Farmer (1984) and Harrison et al. (1981) with the exception of Zn (Table 5.9). It was noticeable that the greatest discrepancies

Table 5.5. The percentage metal content in size fractionated sediments.

	Particle size range (µm) >1000	 500-1000	 250-500	 125-250	 63-125	 38-63	 <38
Site A							
Cd Sum of chemical fractions	3.8	9.4	20.6	30.7	20.6	12.1	2.7
HNO_3-$HClO_4$	2.7	6.9	21.5	26.5	23.3	15.6	3.3
Cu Sum of chemical fractions	1.6	5.1	7.3	56.0	18.6	9.3	2.1
HNO_3-$HClO_4$	1.4	5.5	28.8	36.0	17.1	9.2	2.0
Pb Sum of chemical fractions	0.9	5.6	23.7	40.3	18.1	9.0	2.2
HNO_3-$HClO_4$	0.8	10.6	23.8	35.7	18.2	8.9	2.1
Zn Sum of chemical fractions	3.0	8.2	24.5	33.6	18.3	9.7	2.6
HNO_3-$HClO_4$	3.0	8.3	28.0	31.5	17.1	9.5	2.6
Site B							
Cd Sum of chemical fractions	13.0	13.9	12.0	26.0	16.5	15.9	2.7
HNO_3-$HClO_4$	8.4	7.5	19.3	25.7	15.0	20.0	4.1
Cu Sum of chemical fractions	18.7	9.1	9.7	25.7	15.1	17.8	3.9
HNO_3-$HClO_4$	9.2	10.5	21.6	28.0	13.8	13.9	3.2
Pb Sum of chemical fractions	2.5	11.5	17.1	32.0	17.2	15.3	4.5
HNO_3-$HClO_4$	7.5	18.9	21.3	25.4	12.8	11.6	2.4
Zn Sum of chemical fractions	8.3	11.7	19.5	28.6	18.0	10.7	3.1
HNO_3-$HClO_4$	8.4	10.6	20.6	24.8	17.6	14.8	3.3

between extraction methods were observed in the larger size fractions. The percentage distributions of the metals within each size fraction are very similar for each extraction technique (Table 5.5). This would suggest that differences in concentration levels are due to random variations within the heterogeneous road surface sediments. The greater differences for larger size fractions support this because fewer particles are undergoing extraction, around 80 in 1 g of >1000 µm sediment compared with 4 x 10^7 in 1 g of <38 µm sediment (Table 5.2). Therefore the effects of a small number of particles of anomalously high metal concentration are more noticeable.

5.3.3. The speciation of heavy metals in size fractionated sediments.

The results reported in Tables 5.6 to 5.9 show the speciation distribution patterns of Cd, Cu, Pb and Zn between the different size fractions. The variations in pH, organic matter content and C.E.C with road sediment particle size are given in Table 5.10. The concentrations of metals in almost all fractions exhibit a significant relationship of increasing concentration with decreasing particle size. This is confirmed by statistical analysis using least squares fit computation to obtain values of the correlation coefficient r. The correlation coefficient provides a guide to the significance of any relationship between two variables. The results of the correlation analysis are given in Table 5.11. At both sites Pb shows the most significant negative correlation with particle size, followed by Zn, Cd and then Cu. Similar observations have been made by Salomons and Forstner (1980) for size fractionated aquatic sediments. This trend may be related to the sources of these metals, Pb is emitted from vehicle exhausts as small particles (see Section 2.1.4), whereas the other metals tend to be associated with larger particles on emission. Salomons and Forstner (1980) also suggested that the deposition of coatings on inert materials is responsible for the relatively high metal contents of the non-residual fractions within coarse grained sediments. At both sample sites, Cu in the residual phase shows no significant relationship with particle size. Copper was the only metal examined in this study to show a marked affinity for the residual fraction (see Section 5.3.1). Correlation analysis provides an indication of the strength of a relationship between two variables but does not give any indication of what form that relationship might take. For this type of assessment regression analysis with examination of residuals is required (Tiley

Table 5.6. Chemical associations of Cd in size fractionated road sediment ($\mu g\ g^{-1}$).

	Size fraction (μm)						
Fraction	>1000	500-1000	250-500	125-250	63-125	38-63	<38
Site A (M1)							
Exchangeable	0.8	0.4	0.6	0.9	0.9	0.8	0.6
Carbonate	1.1	1.4	1.4	1.9	2.7	2.7	2.3
Fe-Mn oxides	2.8	3.2	3.1	4.2	6.6	9.1	7.0
Organic	<0.05	0.3	0.3	0.6	2.3	2.3	3.5
Residual	<0.05	<0.1	0.2	0.2	1.4	0.8	0.6
Sum total	4.7	5.4	5.7	7.8	13.8	15.7	14.1
Site B (A41)							
Exchangeable	0.1	0.3	0.1	0.3	0.5	0.8	0.6
Carbonate	2.1	1.3	1.9	4.4	6.6	5.6	3.9
Fe-Mn oxides	1.2	0.8	0.7	3.3	3.7	3.3	5.5
Organic	2.1	2.6	0.6	0.3	2.0	4.4	2.2
Residual	0.6	0.5	0.1	<0.1	<0.1	<0.1	0.2
Sum total	6.0	5.5	3.4	8.3	13.0	14.1	12.4

Table 5.7. Chemical associations of Cu in size fractionated road sediment ($\mu g\ g^{-1}$).

	Size fraction (μm)						
Fraction	>1000	500-1000	250-500	125-250	63-125	38-63	<38
Site A (M1)							
Exchangeable	0.5	1.7	1.0	2.8	4.7	4.1	4.2
Carbonate	1.8	3.4	4.7	13.9	28.3	22.0	19.1
Fe-Mn oxides	7.6	8.0	4.5	17.4	28.0	62.5	73.3
Organic	28.4	56.4	36.7	294.5	367.1	327.5	278.5
Residual	46.0	52.2	36.7	260.8	89.6	85.1	75.5
Sum total	84.3	121.7	83.6	589.4	517.7	501.2	450.6
Site B (A41)							
Exchangeable	0.4	0.5	0.7	1.5	2.7	5.0	4.6
Carbonate	3.4	2.1	4.6	9.8	22.7	34.3	31.5
Fe-Mn oxides	4.0	0.9	3.6	11.4	5.5	13.4	18.6
Organic	84.0	25.0	19.6	90.7	149.3	194.1	220.6
Residual	61.5	35.3	20.6	32.2	31.3	33.3	39.4
Sum total	153.3	63.8	49.1	145.6	211.5	280.1	314.7

Table 5.8. Chemical associations of Pb in size fractionated road sediment ($\mu g\ g^{-1}$).

	Size fraction (μm)						
Fraction	>1000	500-1000	250-500	125-250	63-125	38-63	<38
Site A (M1)							
Exchangeable	4.5	10.7	18.0	38.4	21.2	21.6	18.7
Carbonate	53.8	160.6	393.5	977.6	906.1	810.8	622.5
Fe-Mn oxides	153.2	478.9	983.1	1774.3	2622.8	2804.8	2923.9
Organic	100.4	218.3	686.2	620.5	519.9	363.2	309.8
Residual	126.1	344.6	380.2	436.6	499.6	380.6	521.5
Sum total	438.0	1213.1	2461.0	3847.4	4569.6	4381.0	4396.4
Site B (A41)							
Exchangeable	2.3	13.6	14.2	26.1	37.4	49.1	42.7
Carbonate	40.4	488.4	433.1	1167.5	1503.3	1563.8	2974.8
Fe-Mn oxides	125.2	422.8	407.5	714.0	1033.7	1035.9	1276.2
Organic	72.4	138.1	284.9	607.6	782.1	743.7	826.0
Residual	54.6	118.0	121.0	139.6	163.4	144.9	151.0
Sum total	294.9	1180.9	1260.7	2654.8	3519.9	3537.4	5270.7

Table 5.9. Chemical associations of Zn in size fractionated road sediment ($\mu g\ g^{-1}$).

	Size fraction (μm)						
Fraction	>1000	500-1000	250-500	125-250	63-125	38-63	<38
Site A (M1)							
Exchangeable	9.8	12.4	11.6	22.2	24.7	22.5	22.1
Carbonate	46.4	100.7	371.0	454.2	438.7	342.5	333.5
Fe-Mn oxides	190.6	283.8	264.2	273.0	813.1	941.5	1152.6
Organic	104.3	101.9	114.9	182.4	147.3	150.6	154.5
Residual	128.9	125.9	131.8	192.3	197.1	193.5	180.1
Sum total	480.0	624.7	893.5	1124.1	1620.9	1650.6	1842.8
Site B (A41)							
Exchangeable	3.9	6.6	7.6	15.0	24.3	28.6	34.2
Carbonate	41.0	82.9	94.4	154.6	360.2	132.2	225.0
Fe-Mn oxides	111.5	92.6	130.4	202.8	274.3	167.4	317.9
Organic	37.6	32.3	34.7	103.1	121.0	148.7	154.0
Residual	49.1	78.5	83.5	103.3	117.4	124.5	143.0
Sum total	243.1	292.9	350.6	578.8	897.2	601.4	874.1

1985). An examination of the scatter plots of metal concentration against particle size for the data in Tables 5.6 to 5.9 shows that in most instances this relationship is non-linear (Figures 5.2 and 5.3).

Table 5.10. Variations of pH, organic matter content and cation exchange capacity in size fractionated road sediment.

	Particle size range (µm)	pH	Organic matter content (%)	C.E.C. meq/100 g
Site A	>1000	7.6	10.6	21.4
	500-1000	7.7	3.5	13.8
	250-500	7.7	3.3	7.7
	125-250	7.6	7.5	11.0
	63-125	7.5	19.6	33.7
	38-63	7.4	12.0	52.1
	<38	7.6	28.0	88.5
Site B	>1000	7.7	7.1	20.7
	500-1000	7.6	5.0	21.5
	250-500	7.8	4.4	14.4
	125-250	7.9	8.0	20.1
	63-125	7.5	18.8	39.3
	38-63	7.5	21.2	47.3
	<38	7.6	21.7	48.7

Metal concentrations increase with decreasing particle size for a number of reasons. An important consideration is the increase in specific surface area (i.e. m^2kg^{-1}) of the particles as particle size decreases. As a measure of this relationship, correlation analysis of metal concentrations with particle radius^{-1} has been carried out (Table 5.11). Overall, metal concentrations in the samples from site B (Hendon Way) show highly significant positive correlation with radius^{-1}. Copper concentrations in all but the residual phase show a more significant relationship with surface area than with particle size at this site. For samples collected at site A (the motorway), Pb and Zn show a less significant relationship with radius^{-1} than for particle size. A notable exception to this being for the Fe-Mn oxide fraction where r =

Table 5.11. Correlation matrix for particle size, particle surface area (radius^{-1}), cation exchange capacity, organic matter content and pH with heavy metal concentrations.

		Site A					Site B				
Metal	Chemical association	Particle size	Radius^{-1}	CEC	Organic matter	pH	Particle size	Radius^{-1}	CEC	Organic matter	pH
	exchangeable	-0.332	0.100	-0.022	0.228	-0.657	-0.732*	-0.879****	0.932****	0.908****	-0.694*
	carbonate	-0.876****	0.908****	0.780**	0.629	-0.802**	-0.775**	0.584	0.696*	0.790**	-0.431
Cd	Fe-Mn oxides	-0.785**	0.797**	0.893****	0.630	-0.855***	-0.780**	0.861***	0.824**	0.861***	-0.311
	organic	-0.773**	0.710*	0.950****	0.894****	-0.575	-0.080	0.512	0.667	0.574	-0.839***
	residual	-0.682*	0.733*	0.554	0.621	-0.705*	0.915****	0.466	-0.349	-0.453	-0.037
	exchangeable	-0.862***	0.901****	0.797**	0.719*	-0.694*	-0.790**	0.975*****	0.952*****	0.951*****	-0.578
	carbonate	-0.853***	0.925****	0.715*	0.682*	-0.769**	-0.801**	0.959*****	0.965*****	0.978*****	-0.616
Cu	Fe-Mn oxides	-0.701*	0.652	0.994*****	0.778**	-0.621	-0.716*	0.885****	0.728*	0.744*	-0.109
	organic	-0.858***	0.990*****	0.690*	0.614	-0.757**	-0.670*	0.933****	0.951*****	0.967*****	-0.553
	residual	-0.381	0.006	-0.154	-0.034	-0.159	0.612	-0.092	0.018	-0.021	-0.090
	exchangeable	-0.715*	0.224	-0.021	0.042	-0.247	-0.910****	0.894****	0.890****	0.910****	-0.532
	carbonate	-0.893****	0.506	0.267	0.370	-0.602	-0.800**	0.922****	0.844***	0.847***	-0.373
Pb	Fe-Mn oxides	-0.944****	0.884****	0.734*	0.726*	-0.689*	-0.906****	0.902****	0.884****	0.905****	-0.489
	organic	-0.588	-0.051	-0.287	-0.177	0.044	-0.950****	0.830**	0.808**	0.871***	-0.356
	residual	-0.883****	0.588	0.452	0.505	-0.181	-0.919****	0.606	0.587	0.624	-0.316
	exchangeable	-0.888****	0.702*	0.536	0.625	-0.687*	-0.859***	0.961*****	0.940****	0.957*****	-0.531
	carbonate	-0.892****	0.394	0.155	0.269	-0.343	-0.702*	0.473	0.588	0.668	-0.432
Zn	Fe-Mn oxides	-0.750*	0.962*****	0.921****	0.849***	-0.624	-0.766**	0.733*	0.706*	0.771**	-0.263
	organic	-0.808**	0.538	0.352	0.425	-0.492	-0.857***	0.912****	0.898****	0.934****	-0.433
	residual	-0.863***	0.665	0.481	0.573	-0.754*	-0.937****	0.891****	0.828**	0.847***	-0.400

Level of significance	
*****	$\rho = 0.001$
****	$\rho = 0.01$
***	$\rho = 0.02$
**	$\rho = 0.05$
*	$\rho = 0.1$

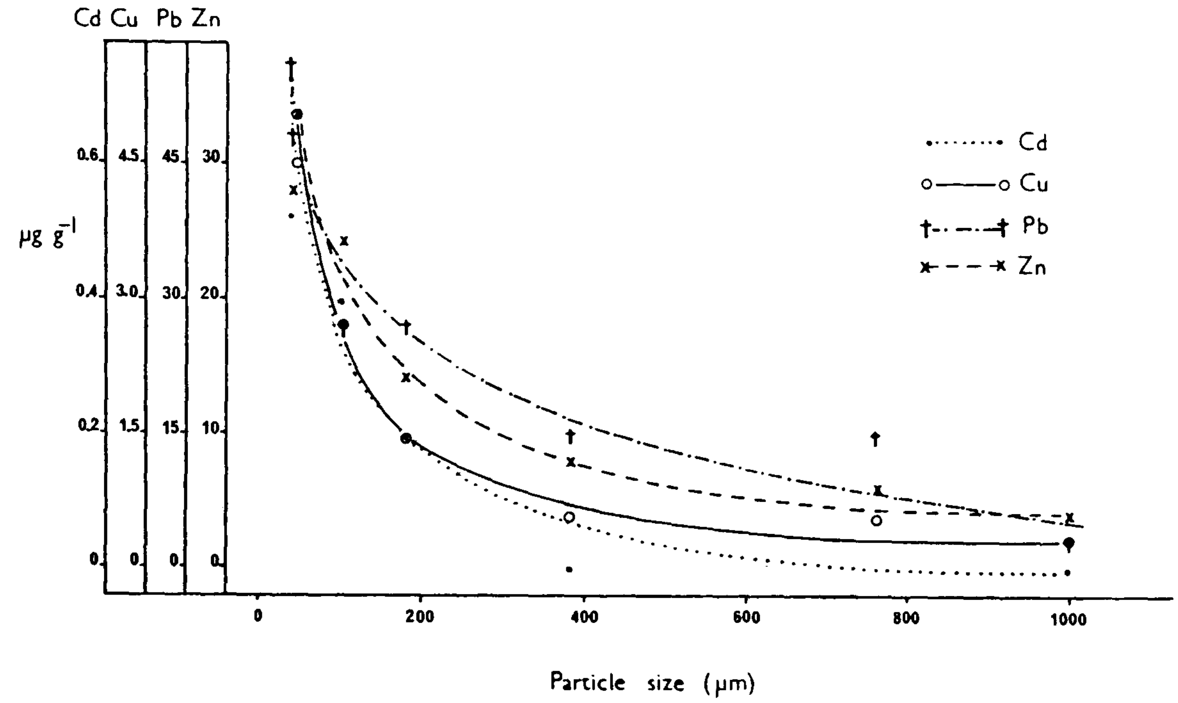


Figure 5.2. Variations in heavy metal concentration in the exchangeable fraction with particle size at site B.

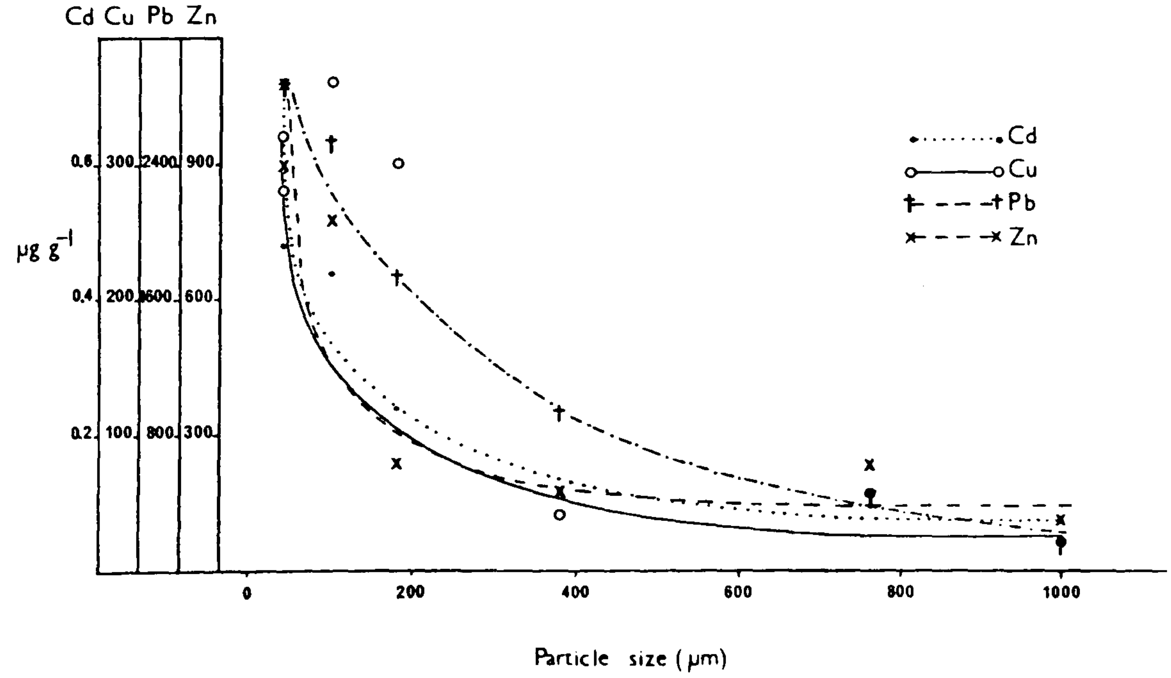


Figure 5.3. Variations in heavy metal concentration in the Fe-Mn oxide fraction with particle size at site A.

0.884 and 0.962 for these metals respectively. As surface area increases the number of exchange sites may be expected to increase. This is confirmed in Table 5.10, which shows that for both sample sites C.E.C. increases with decreasing particle size. It may be expected that metal concentrations in the exchangeable phase would correlate with C.E.C. There are considerable intersite differences in the strength of this relationship. For site A, only Cu shows a significant correlation coefficient between C.E.C. and metal concentration in the exchangeable phase (r = 0.797). In sediment collected from site B all metals show correlation coefficients with a significance of $\rho = 0.01$ or less. The form of this relationship is illustrated in Figure 5.4.

The organic matter content of the sediments was also found to increase with decreasing particle size, the very fine size fractions exhibiting particularly high levels (Table 5.10). Organic matter content can also be seen to correlate with metal concentrations in most fractions in samples from site B, but to show a much weaker relationship with metal concentrations at site A (Table 5.11). In particular Cu, which is widely recognised as showing a strong affinity for organic matter, shows a highly significant correlation coefficient (r = 0.967) at site B but does not show a significant correlation coefficient at site A (r = 0.690). The pH of the sediment was found not to show any variation with particle size (Table 5.10), and hence shows generally poor correlation with metal concentrations in the various fractions (Table 5.11).

Although the metal concentrations in all fractions increase with decreasing particle size the percentage chemical association patterns shown in Figures 5.5 and 5.6 show some independent trends. The percentage of metal associated with the exchangeable phase appears to vary independently of particle size. Cadmium shows the greatest overall affinity for the exchangeable phase in all size fractions, followed by Zn, Cu and Pb in that order. The higher levels found for Cd and Zn are consistent with the results obtained from rain water leachate experiments on road surface sediments taken from these two sites. Laboratory simulations of stormwater runoff conditions over a 28 day period have shown that Cd has the highest extraction efficiency followed closely by Zn, with Pb being retained to the greatest extent by highway sediments (Ellis and Revitt 1982).

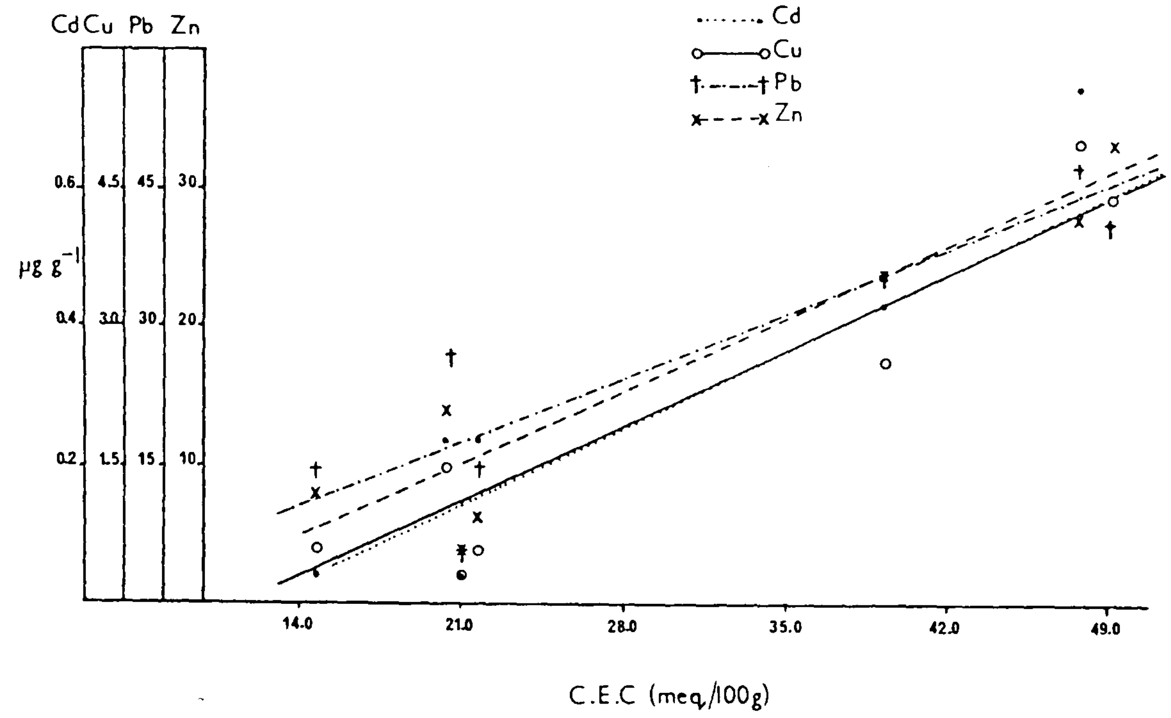


Figure 5.4. Variations in heavy metal concentration in the exchangeable fraction with cation exchange capacity at site B.

Cadmium also exhibits the highest affinity for the carbonate fraction. For the sediment collected at site A there is a slight reduction in the percentage of Cd associated with this phase, whereas at site B the sediment levels increase to >50% in the 63-250 µm size ranges then fall off to 35%. The Pb association (42%) in the carbonate fraction is similar to that of Cd but demonstrates a markedly lower affinity for the coarser compared to the finer particles, particularly in the samples collected at site B. This trend is reversed for Pb levels in the Fe-Mn oxide phase at this site. The total sediment affinity for Pb in the combined carbonate and Fe-Mn oxide fractions at 67% is similar to that for the chemical associations of Pb in non-sized fractionated road sediments (Harrison et al. 1981) and river sediments (Tessier et al. 1979; Forstner 1982).

Percentage Pb levels associated with the hydrous oxide phase in sediment collected at the motorway site (A) show a marked affinity for the fine particle sizes in contrast to those for site B. However, the levels for the combined carbonate and Fe-Mn oxide fraction follow a

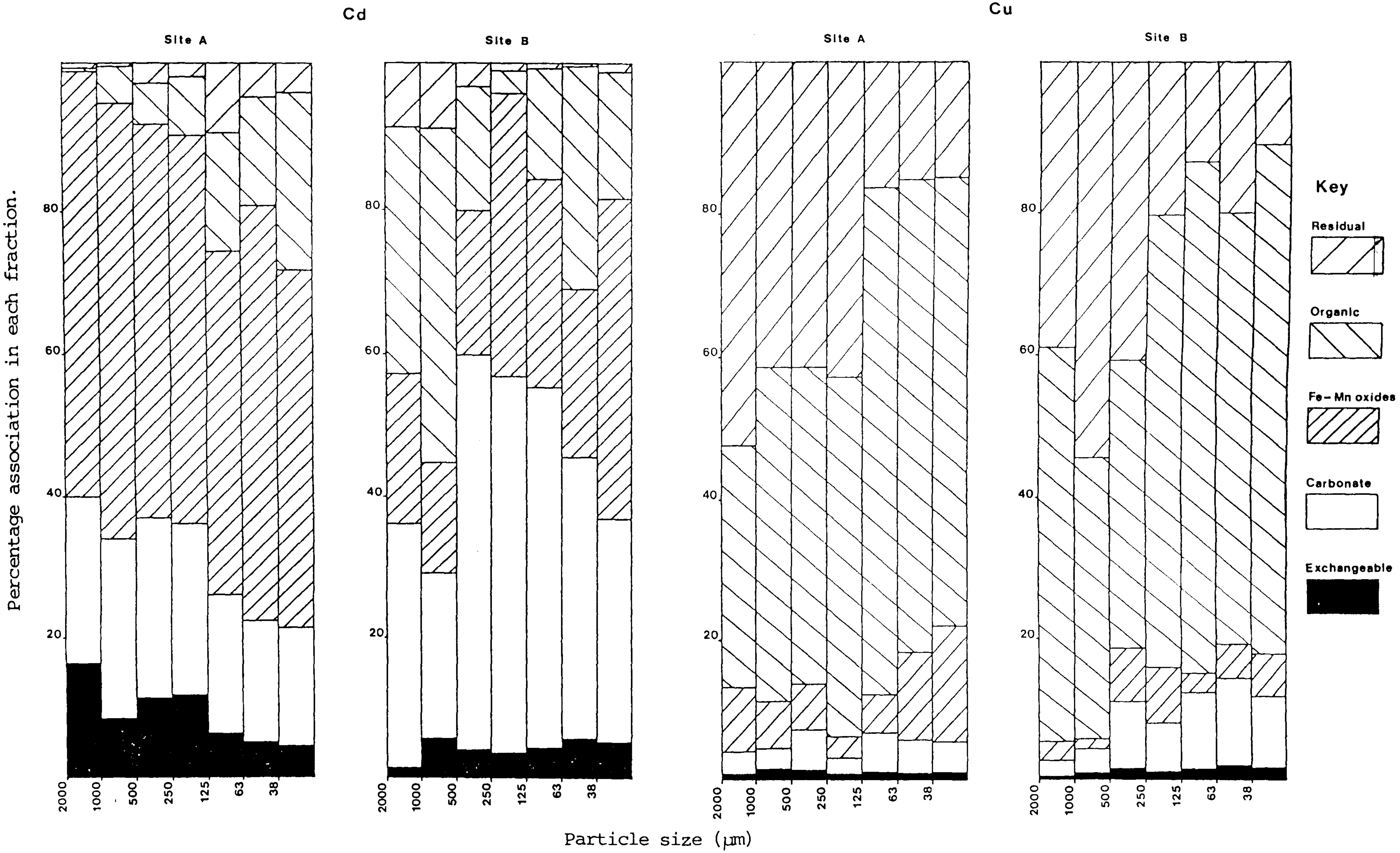


Figure 5.5. Chemical associations of Cd and Cu in urban dust.

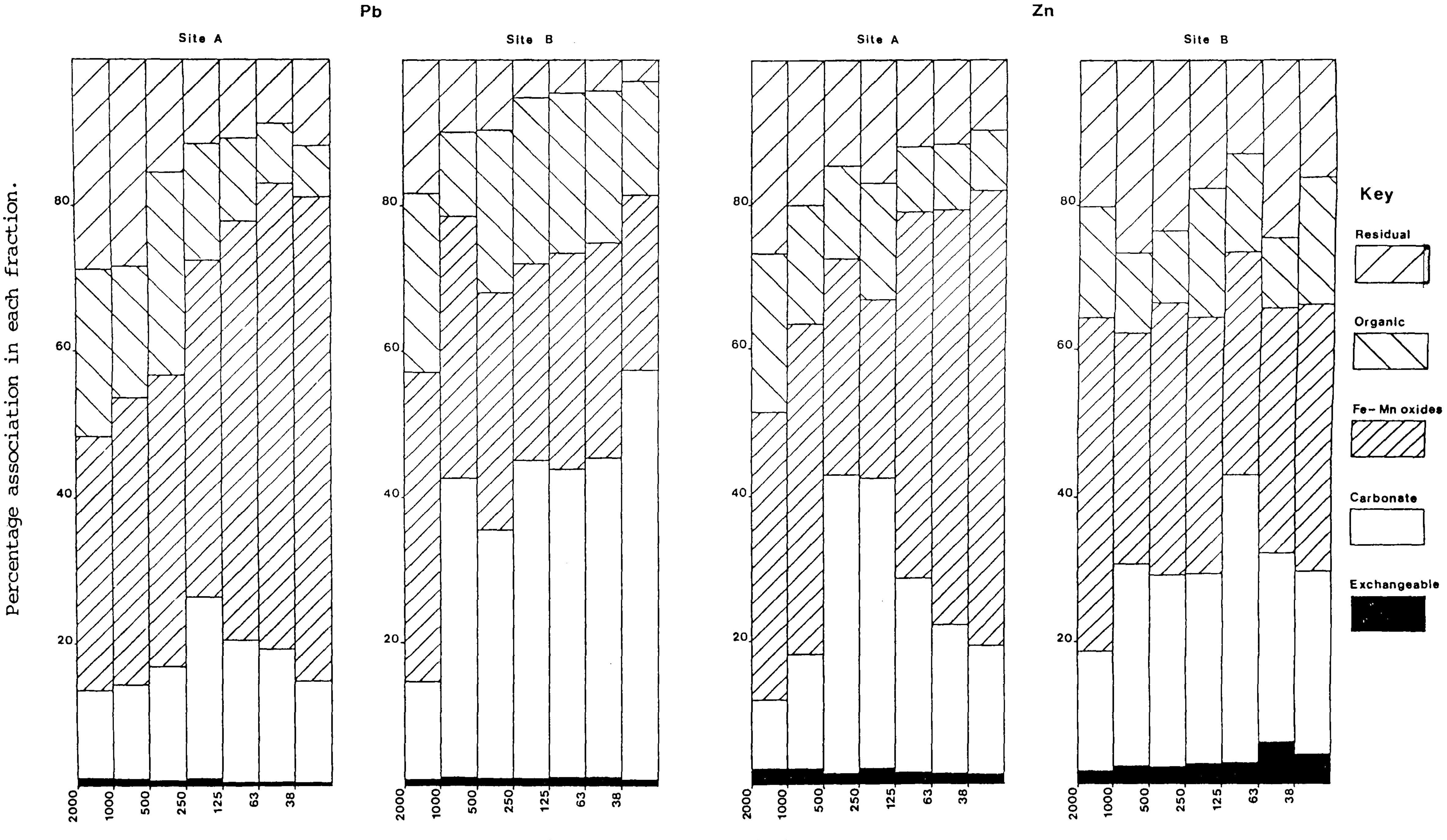


Figure 5.6. Chemical associations of Pb and Zn in urban dust.

similar pattern at the two sites.

The affinity of Cu for the organic phase increases with decreasing particle size at both sites, rising from 34% to 62% between the >1000 µm and the <38 µm particle sizes at site A, and from 55 to 70% in sediment at site B. This is despite the poor relationship shown earlier by Cu for the organic phase. For the other metals the percentage content in the organic fraction generally decreases with decreasing particle size, except for Cd in the motorway sediment which shows a marked increase.

Analysis of the residual phase shows that overall all metals show a decline in the percentage metal associated with this fraction although at both sites the concentrations show a slight increase. The general decrease in the affinity of metals for the residual phase with decreasing particle size may reflect a difference in the mineral and crystal lattice structure between the coarse and fine particles. It has been shown previously (Table 5.10) that the organic matter content rises considerably in the finer particle size ranges at both sample sites.

5.3.4. Implications for environmental mobility.

The exchangeable fraction contains metals which are specifically adsorbed and held by ion exchange mechanisms to particulate surfaces. Metals bound in this fraction are subject to sorption-desorption processes with the changing ionic composition of stormwater runoff. The neutral pH of the extraction reagent used (1M $MgCl_2$) is similar to the pH of most urban natural waters (Harrop 1983). Additionally the high cation and chloride concentrations of the extractant may be similar to stormwater runoff contaminated with de-icing salt. Therefore metals in this fraction will be indicative of the highest availability to the soluble phase of highway runoff. Figures 5.5 and 5.6 indicate that cadmium has the greatest overall affinity for this fraction (4.3-9.2%) followed by Zn (1.6-2.7%), Cu (0.7-1.1%) and Pb (0.8-1.1%). The removal of metals from the exchangeable phase is likely to be increased by elevated levels of salinity, which would occur during road salting, due to increased competition for surface binding sites by cations (Ramamoorthy and Rust 1978; Morrison et al. 1984b). Gosz (1977) has shown that road salting leads to increased total metal concentrations in runoff receiving streams.

The carbonate phase can be considered to contain metals which are moderately available for release to runoff, but which are highly susceptible to changes in pH. Such changes would occur when acidic rainfall fell on the road surface. This would lead to the breakdown of carbonates and subsequent release of metals to stormwater runoff Morrison (1985). The results of this investigation show that copper is consistently weakly associated with the carbonate fraction for all sediment grain sizes (Figure 5.5). The Zn content of this fraction in road sediment shows a similar uniform distribution with particle size but the overall level is much higher at approximately 30% of the total Zn present (Figure 5.6). Cadmium exhibits the highest affinity for the carbonate fraction, which again indicates the potential ease of removal of this toxic metal into road runoff (Figure 5.5).

Despite random variations with respect to particle size the overall Cu (at 5%) and Zn (at 35%) associations for the oxide phase are very similar to those for the carbonate phase (Figures 5.5 and 5.6). Concentrations of these two metals show an increased affinity for the lower size ranges particularly at site A. Cadmium shows a lower overall affinity at 25% of the total metal content. Although like Zn and Pb this metal exhibits overall levels approaching 70% in the combined carbonate and Fe-Mn oxide fractions (Figures 5.5 and 5.6).

The majority of the Cd, Pb and Zn in urban street sediments can therefore be considered to be associated with sediments in physico-chemical forms which are moderately available in environmental terms. The Fe-Mn oxide may exist in road sediments as concretions, cement between particles or as surface coatings on particles. This work confirms that hydrous Fe-Mn oxide coatings on particles of soil and road sediment are excellent scavengers of Cd, Pb and Zn (Jenne 1968; Tessier et al. 1979; Harrison et al. 1981). The hydrous oxides are thermodynamically unstable under anoxic conditions (Gambrell et al. 1981), and therefore the release of these metals to the soluble phase could occur from gully pot sediments where such conditions may exist. Morrison (1985) has shown that metal concentrations in gully pot liquors increase between storm events as a result of biological and chemical reactions within the gully pot sediment. Bacteriological activity causes a fall in the dissolved oxygen content of the gully pot liquor by 60-80% and metals bound to the Fe-Mn oxide fraction are released as these oxides are reduced.

The high affinity of Cu for the organic fraction, shown in Figure 5.5, can be considered theoretically to represent a form which is of limited availability to the soluble phase of highway runoff. The Cu may be bound to various forms of organic matter including detritus and coatings on mineral particles, and will only be released into the soluble phase under strong oxidising conditions. This may explain why the overall Cu extractions efficiency found in experimental leachate studies on sediments from site B was the same as that for Zn (Ellis and Revitt 1982), and therefore higher than would be expected in view of the high overall affinity of Cu for the organic phase. Zinc is predominantly associated with carbonate and Fe-Mn oxide phases and would therefore be expected to be more readily available to stormwater runoff. The high bacterial levels found in street surface runoff (Ellis 1979; Sartor and Boyd 1972) would be expected to lead to the breakdown of some of the organic material and hence result in further mobilisation of Cu from sediments (Morrison et al. 1984b).

The residual fraction represents metals held within the crystal lattice and can be considered to be completely environmentally immobile. Of the metals studied here Cu shows the greatest affinity for this phase.

The chemical associations of metals in essentially neutral highway sediments, indicates that their overall availability to the soluble phase of stormwater runoff is in the order Cd>Zn=Pb>Cu. This order will be particularly susceptible to variations in pH as well as to changes in oxidising and reducing conditions and cation concentrations, which can occur as runoff travels from the road surface through the underground drainage system to receiving waters.

5.3.5. Implications for human health.

Dilute HCl (0.07M) has been used by a number of workers as a leaching agent to enable assessment of Pb uptake by young children who ingest street dirt by sucking dirty fingers or other contaminated objects (Duggan and Williams 1977; Harrison 1979; Farmer and Gibson 1984). This is commonly considered to approximate to human stomach acidity. Gibson and Farmer (1984) observed that results from this extractant are broadly equivalent to the sum of the combined exchangeable, carbonate and easily reducible oxides (0.1M $NH_2OH.HCl$) fractions. As a measure of the potentially available metals in the samples collected during this investigation the sum of the exchangeable and carbonate phase are given in Table 5.12. An easily reducible oxides fraction was not determined in this investigation, instead a more concentrated $NH_2OH.HCl$ solution was used to determine the total Fe-Mn oxide fraction. Therefore only the combined exchangeable and carbonate fractions were used to assess metal availability to humans, although undoubtedly some of the metals associated with the oxide fraction would be available for uptake.

Duggan et al. (1985) report that particles collected from the hands of school children are generally less than 10 μm in diameter. It can be seen from Table 5.4 that the concentration of metals increases with decreasing particle size, similar trends have been noted for metals associated with the different chemical fractions (Tables 5.6 to 5.9). A closer estimation of the potentially available metals would therefore be obtained by using the <38 μm fraction (Table 5.12).

Table 5.12. Potentially available metals to humans following ingestion (μg g^{-1})

		Cd	Cu	Pb	Zn
Site A	bulk sediment	2.3	13.5	395.1	360.7
	<38 μm fraction	2.9	23.6	641.2	355.6
Site B	bulk sediment	3.5	11.0	1163.6	140.8
	<38 μm fraction	4.5	36.1	3017.5	259.2

Duggan and Williams (1977) have estimated that young children ingest about 100 mg of dust per day through hand to mouth activity. The percentage of a metal ingested which is absorbed into the bloodstream depends on the physical and chemical form of the metal, the contents of the stomach and the main constituents of the diet (Heard and Chamberlain 1982). For Pb, estimates of absorption by children, including a factor for solubilisation, of up to 53% have been reported (Royal Commission on Environmental Pollution 1983; Gibson and Farmer 1984). The data in Table 5.12 suggests that for bulk sediment between 21-43% and for the <38 μm fraction 56% of the total Pb is in the combined exchangeable and carbonate fractions, and therefore is potentially available for solubilisation and absorption in the human gut. Ingestion of 100 mg per day of street dirt which is less than 38 μm in diameter would yield an average of 183 μg of Pb. Obviously this value would be reduced by less effective absorption. Duggan and Williams (1977) estimate that for children blood Pb is raised by an increment of 5 μg 100 ml^{-1} for every 1000 μg g^{-1} increase in sediment Pb. The Ninth Report of the Royal

Commission on Environmental Pollution estimated that the typical daily ingestion of Pb in dust for a two year old inner city child was 140 µg, which corresponds to a daily uptake of 74 µg Pb. This was equivalent to 70% of the total daily Pb uptake via the lungs and gut of 105 ug of which inhalation accounted for only 3%. Dietary intake contributed 47 µg Pb which is equivalent to an uptake of 25 µg Pb per day. The data derived from speciation studies described above suggests that in urban areas the value for ingestion via dust may be an underestimate. The value of 183 µg Pb potentially available for uptake through ingestion must be treated with some uncertainty because of the wide range of reported Pb in dust concentrations (see Sections 2.3.2 and 4.3.1). Furthermore, there is uncertainty over metal absorption factors and the quantities of dust ingested by children. However, the results suggest ingestion of street sediment is an important route for Pb uptake by children.

The average amounts of potentially available Cd (0.4 µg), Cu (3 µg) and Zn (31 µg), which would result from the ingestion of 100 mg of street dirt are unlikely to be cause for concern when compared with the normal dietary intake of these metals (Mertz 1981).

5.4. Conclusions.

The findings of the investigation of physico-chemical associations of Cd, Cu, Pb and Zn in road sediments can be summarised as follows:

a) The total metal levels observed in this investigation are similar to those reported by other workers for samples collected in the same area of North-West London. The metal levels also show similar spatial distributions to those previously reported in the literature and in this research project (Chapter 4).

b) The speciation of Cd, Cu, Pb and Zn in the bulk sediment confirm the distribution patterns observed in previous investigations in which multi-stage sequential extraction procedures have been used. Cadmium is the only metal to show significant levels in the exchangeable phase. Lead and Zn are found mainly in the carbonate and Fe-Mn oxide fractions. Copper was predominantely bound to organic matter but also shows the highest affinity for the residual phase.

c) Total metal concentrations were found to increase with decreasing particle size. Metal concentrations in each of the 5 fractions were also found to increase with decreasing particle size.

This may be related to the increased surface area and consequent increase in exchange sites. Organic matter content was also found to increase with decreasing particle size. The pH of the sediment was found to remain relatively uniform (pH 7.5-7.9) regardless of particle size at both sites.

d) The recovery of metals by the sequential extraction procedure has been assessed by comparison with the independently determined total metal concentration. Very poor recoveries were obtained for particle sizes greater than 500 µm, despite attempts to reduce such effects by increasing the quantity of sediment used in the experiment.

e) The majority of the Cd, Pb and Zn content in the street dusts analysed can be considered moderately available in environmental terms. Copper was found to be of limited availability. Whilst the total concentrations of the metals studied suggest an order of contamination of Pb>Zn>Cu>Cd, the results of the sequential extraction procedure indicate an order of release to stormwater runoff of Cd>Zn=Pb>Cu.

f) Because of particle size considerations, previous attempts to assess metal uptake from street dirt by young children may have considerably underestimated the contribution of this source to the intake of metals. Comparisons with published data shows that this is particularly true in the case of Pb.

CHAPTER 6. THE INFLUENCE OF LEAD BASED PAINTS ON HEAVY METAL LEVELS IN URBAN DUST.

6.1. Introduction.

Heavy metal contamination of soils and dusts arising from natural weathering or redecoration of exterior painted surfaces has been reported by a number of workers (see Section 2.1.3). Lead containing paints in particular have found extensive use in decorative and protective applications for many years. Consequently the amount of Pb incorporated into the urban infrastructure is considerable. Lead levels of 60% in the dry film are common in pre-1930 paint coats which contain substantial amounts of white basic lead carbonate (Falla 1980). Post-war white paints contain much less Pb due to a gradual substitution by TiO_2. However, high Pb paints continue to be used as primers for metal or wood surfaces, particularly red lead (Pb_3O_4) and calcium plumbate (Ca_2PbO_4).

Ingestion of paint has been identified as the most important cause of clinical Pb poisoning in children in the United Kingdom (Lawther et al. 1980). Pre-school children are particularly at risk because of their habit of mouthing non-food objects. Day (1983) reports several cases of Pb poisoning in children. All exhibited 'pica' and had been chewing paintwork in their pre-1919 homes. Workers removing Pb based paint have also been identified as being at risk (Feldman 1978). Paint stripping has been shown to produce very high Pb in air and dust concentrations especially when dry sanding is used as the removal process (Inskip 1984). This has been shown to have a marked effect not only on operators undertaking the work but also on people living in the close locality (Manton 1985). The possibility of environmental contamination by Pb derived from the renovation of painted surfaces is therefore of particular concern, especially where old paintwork is being removed by burning-off or sanding-down procedures, which often produce easily dispersed Pb bearing dust.

The contribution that Pb in old paintwork makes to the environment when school buildings are being redecorated is important for several reasons. The levels of Pb in dust produced by renovation can be very high and school playgrounds are obviously areas in which children may be directly exposed to Pb contamination. In a recent survey of schools in the London Borough of Barnet most of those samples exceeding the Greater London Council 'interim action level' of 5000 $\mu g\ g^{-1}$ were the result of careless preparation and subsequent lack of hygiene during redecoration (Benstead 1985).

The extent and degree of Pb contamination of school playgrounds during redecoration has been investigated by Rundle and Duggan (1986). In this survey two out of seven schools, both of which were built after 1949, had Pb in playground dust levels in excess of the 5000 $\mu g\ g^{-1}$ action level during redecoration. Lead in dust concentrations increased to as high as 100,000 $\mu g\ g^{-1}$ during redecoration but declined with time after the work was completed.

Little information is available from the literature on the physico-chemical associations of metals, particularly Pb, in urban dusts highly contaminated by paint flakes. Rundle and Duggan (1980) and Cooney and Blake (1982) have shown that soluble Pb concentrations in playground dusts can be relatively high compared to other urban dusts. Size fractionation of playground dusts has shown that Pb levels increase with decreasing particle size (Rundle and Duggan 1980). However, the samples studied were not grossly contaminated by flakes of paint, and the Pb levels recorded were comparable to those in other types of urban street surface sediment, as described in Sections 2.3 and 4.3.

The principal objectives of the investigation described in this Chapter are outlined below:

1) to investigate the levels of environmental Pb produced by removing paint and the physico-chemical associations of the Pb in the dust derived from this source;

2) to investigate the spatial and temporal variations in the concentrations and loadings of Pb and other heavy metals during the redecoration of a school;

3) to determine changes in the particle size distribution of heavy metals during redecoration; and

4) to examine the chemical associations of metals in dusts which are highly contaminated by paint flakes. It was anticipated that information derived from this investigation would be useful not only in assessing the environmental consequences of the dust produced by paint renovation, but would also aid in source identification.

The work is divided into two areas of investigation, first the physico-chemical properties of dust produced during paint stripping are reported. The second aspect of the work describes the variations in heavy metal levels during the redecoration of a school. This part of the investigation was carried out in collaboration with the Environmental Sciences Division of the former Greater London Council, who selected the school studied.

6.2. Physico-chemical Properties of Dust Produced During Paint Removal.

6.2.1. Removal of paintwork and collection of dust produced.

Five commonly used techniques for removing paint were applied to the removal of Pb based paint from hardboard panels taken from a 1911 house. Two of the techniques involved the use of commercial chemical strippers, Nitromors and Ronstrip. The three other paint stripping techniques used were: a hot air gun; a blowtorch; and a belt sander. The panels were placed on plastic sheeting in the laboratory and five 0.5 m^2 sections were marked out. Each section was treated with a different paint stripping technique.

During treatment, the operator wore an atmospheric sampler strapped to his chest. Airborne particulates released during paint stripping were collected on a 0.8 µm polycarbonate filter. The dust produced during each timed treatment was collected from the plastic sheeting using a dust pan and brush. The collected dust was then size fractionated using stainless steel sieves of sizes: 2000; 1000; 500; 250; 125; 63 and 38 µm. The size fractionated dusts and the airborne particulates were analysed for Pb content using the HNO_3-$HClO_4$ digestion technique described in Chapter 3.

6.2.2. Lead levels produced by paint stripping.

The results for Pb in air levels produced during the five treatments are presented in Table 6.1. The airborne level produced during the use of Nitromors is comparable to that observed on busy roads (see Section 2.2.3). The levels of atmospheric Pb produced during the use of Ronstrip, the hot air gun and blow torch are higher, but fall within the 'Threshold Limit Value' of 100 µg Pb m^{-3} for industrial exposure (H.S.E. 1984). This 'Threshold Limit Value' was only exceeded when the belt sander was used. The results reported in Table 6.1 are lower than those reported in the literature for similar surveys. This is due largely to the wide range of paint types and formulations used since the last century. Nevertheless belt sanding is confirmed as being the technique which produces the greatest quantity of airborne Pb. The relatively high levels generated by all techniques except Nitromors emphasise the need for adequate ventilation and for the operator to take basic safety precautions. These are detailed in the D.O.E. leaflet 'Lead in Paintwork', and include: proper isolation of the work area; good ventilation; and thorough clean up procedures on completion (D.O.E. 1983b).

Table 6.1. Airborne Pb levels produced during paint stripping.

Technique	Time required to remove paint from surface (minutes)	Airborne Pb levels ($\mu g\ m^{-3}$) This study	Literature values Inskip (1984)	Feldman (1978)
Nitromors	80	1.9 (1.5%)	-	-
Ronstrip	70	16.4 -	-	-
Hot air gun	57	67.1 (8.0%)	24-270	-
Blowtorch	50	19.7 (3.9%)	55-460	-
Belt sander	55	422.0 (1.6%)	4700-18600	510-550

Values in brackets represent % Pb in TSP

The Pb in dust levels produced during each treatment are given in Table 6.2. The results show that in situations where Pb based paints have been removed from surfaces an extremely high Pb in dust level may be expected in the vicinity. This has also been observed by Inskip (1984) who found that sanding-down produced the greatest fallout of Pb. This exceeded the values found for the heat removal methods by a factor of between 40 and 60. The results in Table 6.2 show that most of the Pb removed during paint stripping is present in large particles which will deposit rapidly. The most notable difference in the particle size distribution patterns is that exhibited by the belt sanding treatment compared with the other four techniques. This technique shows a peak in the mass of Pb produced by paint removal in the 250-125 μm size range, whereas in the other techniques the peak mass of Pb produced occurs in the largest size fraction (>2 mm). It may be expected therefore that belt sanding will lead to a wider spatial distribution of Pb than the other techniques used, for which Pb fallout will be close to the source. Manton (1985) has reported a rise in blood Pb levels following sanding of paintwork for both a husband and wife. Although the wife did no sandpapering, her presence in the house while redecoration was being

Table 6.2. The mass of Pb in surface dust produced by paint removal (g).

	Particle size fraction (µm)								
Technique	>2000	2000-1000	1000-500	500-250	250-125	125-63	63-38	<38	Total
Nitromors	13.4	0.60	0.29	0.20	0.069	0.014	-	-	14.6
	(9%)	(5%)	(5%)	(12%)	(7%)	(9%)	-	-	(9%)
Ronstrip	14.0	0.038	0.017	-	-	-	-	-	14.0
	(0.9%)	(0.9%)	(1%)	-	-	-	-	-	(0.9%)
Hot air gun	11.5	1.15	0.73	0.32	0.18	0.059	0.019	0.005	13.9
	(8%)	(8%)	(11%)	(14%)	(15%)	(14%)	(11%)	(10%)	(8%)
Blowtorch	11.2	0.84	0.48	0.26	0.16	0.06	0.025	0.001	13.0
	(8%)	(8%)	(10%)	(13%)	(13%)	(12%)	(9%)	(2%)	(8%)
Belt sander	0.011	0.010	1.26	4.61	5.5	1.80	0.67	0.78	14.7
	(7%)	(9%)	(8%)	(6%)	(4%)	(3%)	(2%)	(4%)	(4%)

The values in brackets represent % Pb in the dust fraction undertaken produced measureable quantities of Pb in her blood.

Although the advice contained in the D.O.E. booklet 'Lead in Paint' appears to be well founded, traditional methods of paint removal such as sanding-down and burning-off will continue to be used, particularly as power tools are being increasingly used. This is borne out by the increased times required for chemical stripping techniques (Table 6.1).

6.2.3. The chemical form of Pb in dust produced by paint removal.

The uptake of Pb from paint into the bloodstream is a function of its chemical form as discussed in Section 2.6. A variety of speciation techniques have been used to assess the biological and environmental availability of Pb compounds (see Section 2.4. and Chapter 5). X-ray diffraction has been successful in identifying a number of crystalline Pb species in urban dust, but it was not effective when applied to paint chips (Sturges and Harrison 1985). The sequential extraction of Pb under different chemical leaching conditions yields information of chemical associations and therefore on bioavailability. In addition the technique has potential for source identification (Fergusson and Ryan 1984). The scheme used in this study was that devised by Tessier et al. (1979), which has been previously described when applied to urban street dusts (Chapter 5). Paint chips derived from using the belt sander, were subjected to the extraction procedure. The results of the sequential extractions are shown in Table 6.3.

Table 6.3. Chemical associations of Pb in paint stripped by belt sander.

Fraction	Concentration ($\mu g\ g^{-1}$)	Percent Pb in fraction
Exchangeable	1253	1.9
Carbonate	3745	5.7
Fe-Mn oxides	57694	88.0
Organic	1341	2.0
Residual	1545	2.4

The exchangeable and carbonate fractions represent a small proportion of the total Pb present in the dust produced by belt sanding (7.6%). This compares with 20-40% observed in these combined fractions for road dusts (see Section 5.3.1). The concentrations of Pb in the exchangeable and carbonate fractions of paint dust amounts to 5000 µg g^{-1} which is also the 'interim action level' used by the former Greater London Council. The bulk of the Pb in paint dust was found in the Fe-Mn oxide fraction (88%). This fraction can be considered to be moderately available to biological systems.

6.3. Heavy Metal Levels In School Playground Dust During Redecoration.

6.3.1. Sample collection and experimental procedure.

Redecoration of Robert Blair Primary School, Islington was undertaken during October and November 1982. The location of the school is shown in Figure 6.1. Initial sampling took place in September 1982, when samples of peeling paintwork were also taken. Dusts were collected using the vacuum techniques described in Chapter 3. Samples were taken from a 5 m by 1 m strip close to the school building, and from a 10 m^2 area of playground approximately 10 m from the building line. Dusts were collected from the same areas of playground on consecutive visits, both during redecoration (October 26th 1982) and two months after the work had been completed (January 26th 1983).

The collected sediments were air dried and then divided into two portions. The first subsample was sieved through a 500 µm stainless steel sieve and the <500 µm fraction was used to determine total heavy metal levels and the chemical associations of metals within the dust. The second subsample was size fractionated using: 2000; 1000; 500; 250; 125; 63 and 38 µm stainless steel sieves. The total metal levels were then determined in each size fraction. Paint samples were broken down into smaller pieces, using an agate mortar and pestle, before analysis of their metal content.

Total metal levels in the paint, the bulk and the size fractionated sediments were determined using a modified version of the procedure outlined in Section 3.7. Dry ashing at 350 °C was used as it has been shown to give better repeatability for the determination of metals in paint samples (Hausknetch et al. 1982; Sturges and Harrison 1985). Perchloric acid was excluded from the acid extraction mixture as this may lead to the formation of an insoluble white precipitate with Ti in those samples containing TiO_2.

The chemical associations of metals in the sediments were determined using the sequential extraction scheme of Tessier et al.

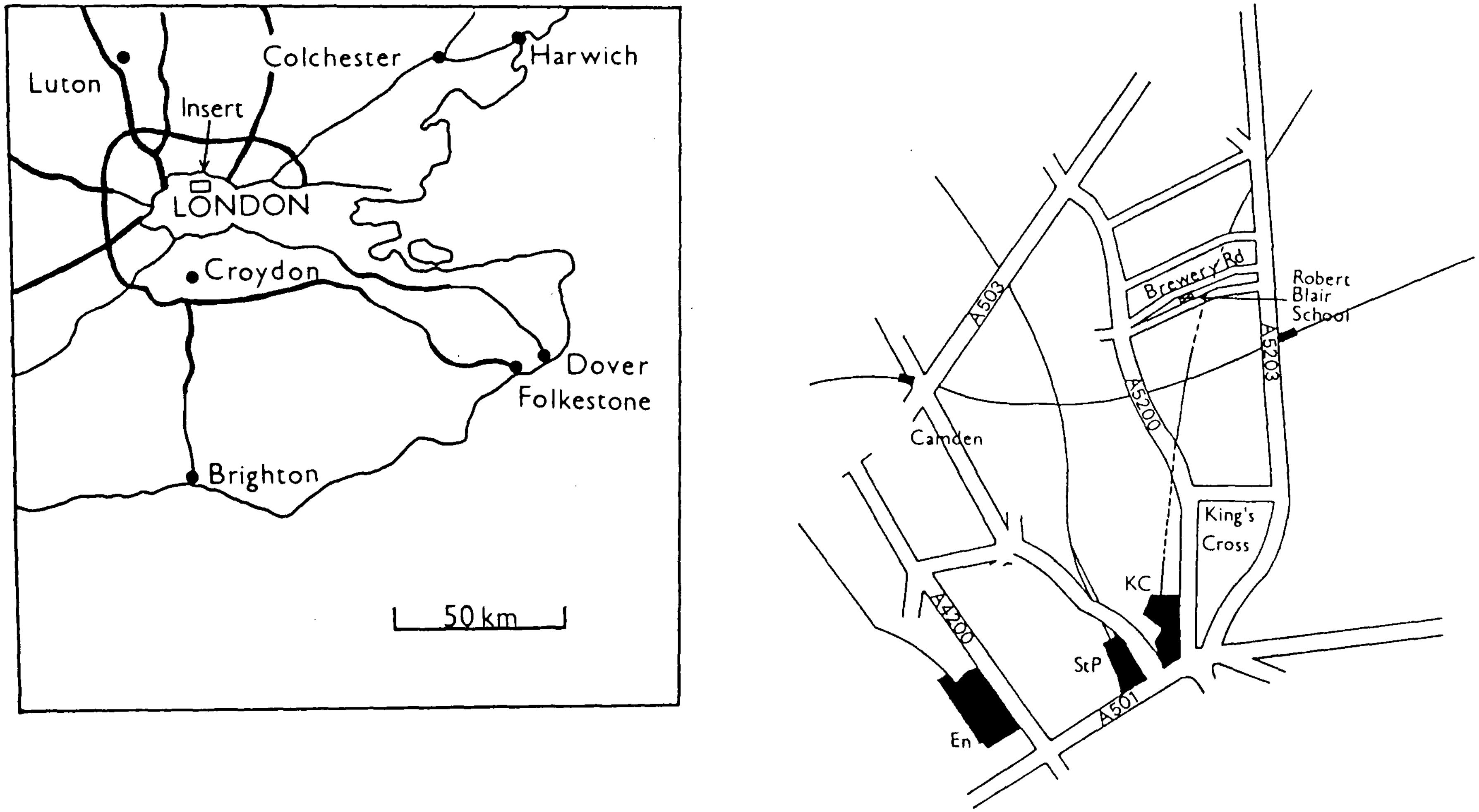


Figure 6.1. The location of Robert Blair Primary School, Islington.

(1979) described in detail in Chapter 5.

6.3.2. Total metal levels in bulk sediment and paint.

The decorators undertaking the work at Robert Blair Primary School used a blowlamp in conjunction with a scraping technique to remove the old paintwork. The exposed woodwork was sanded down to remove remaining traces of old paint prior to the application of new paint. The entire school took 2 months to repaint, but the painters only worked for 3-4 weeks on the building face adjacent to the areas sampled. The area immediately under that part of the building being painted was cordoned off to prevent children climbing the scaffolding used by the painters. The decorators were asked to sweep up paint flakes after stripping down was finished. Although this was carried out, how soon after stripping was not determined. On the third sampling visit, 2 months after the redecoration was completed, large paint flakes were still visible in the playground.

The concentrations of Cd, Cu, Pb and Zn in paint taken from the windows above the sample area are shown in Table 6.4. The paint comprises approximately 13% Pb, probably as basic white lead carbonate in the lower paint layers. In addition the paint contains trace quantities of other metals, notably Zn.

Table 6.4. Metal concentrations in paint taken from the windows at Robert Blair Primary School (µg g^{-1}).

Cd	Cu	Pb	Zn
1.1±0.7	100±77	128061±9457	4003±885

The concentrations and loadings of Cd, Cu and Zn in the bulk sediment (<500 µm) collected before, during and after redecoration are shown in Figure 6.2. The concentrations of Cd at both sample sites are comparable with levels recorded in other urban street surface sediments (see Section 4.3.1). Copper and Zn concentrations in pre-decoration sediments collected close to the building are elevated relative to levels in sediments recorded in other residential urban areas (see Section 4.3.1). The concentrations of these metals are substantially reduced in the playground sample compared to sediment collected close to the building which suggests the source of these metals is the building.

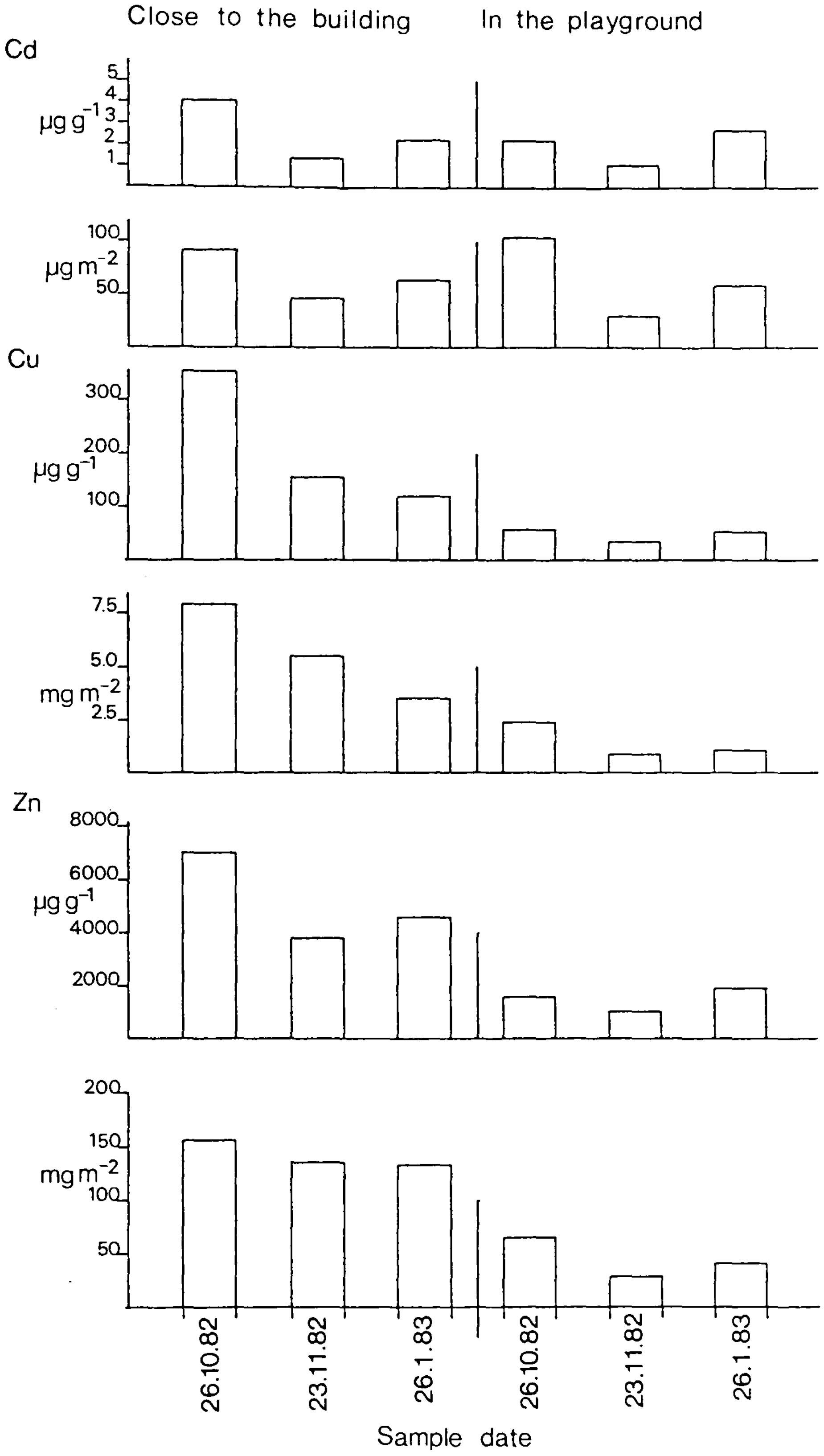


Figure 6.2. Levels of Cd, Cu and Zn in playground dust at the Robert Blair School.

High Cu concentrations were not found in the paint samples (Table 6.4), and the most likely sources of Cu are the metal fittings such as guttering and piping. Similarly the most likely source of Zn is erosion of galvanised metal construction materials.

The levels of Cd, Cu and Zn decrease during the period of redecoration although it can be seen from Figure 6.2 that concentration values decline to a greater degree than loading levels. This is probably due to the dilution effect of substantial quantities of paintflakes deposited in the playground during stripping down procedures. This dilution effect would influence the concentration levels more than loading levels, as the loading figures express the total quantity of metal in a given area irrespective of the amount of sediment. Further evidence for this is shown by the smaller decrease in concentration levels in the playground sample compared to that taken close to the wall, the area which received most of the removed paint.

The concentrations of Cd, Cu and Zn increased in samples collected on the third visit, except for Cu in sediments close to the wall. Loadings show a similar temporal pattern to concentrations, with the exception of Cu and also Zn close to the building. Zinc loadings at this site are similar both during and after redecoration.

6.3.3. Lead levels in bulk sediment during redecoration.

The concentrations and loadings of Pb in playground samples for bulk sediment collected before, during and after redecoration of the school are shown in Figure 6.3. Lead concentrations before redecoration are similar to those recorded in other surveys of playground dust in urban areas. Rundle and Duggan (1980) in a survey of twenty eight school playgrounds determined a mean Pb value of 1230 $\mu g\ g^{-1}$. Beeching and Lovell (1983) report a range of Pb in playground dust concentrations of 218-1900 $\mu g\ g^{-1}$ for two schools in Exeter. Lead concentrations up to 61000 $\mu g\ g^{-1}$ have been found in playground areas close to deteriorating paintwork (Cooney and Blake 1982).

In this survey elevated Pb levels were found close to the school building. These are probably due to flaking of paint from the window sills and frames. The Pb concentration of 4318 $\mu g\ g^{-1}$ close to the wall before redecoration is higher than the G.L.C. guideline limit of 500 $\mu g\ g^{-1}$ but lower than the G.L.C. 'interim action level' of 5000 $\mu g\ g^{-1}$. Lead loadings in samples collected before redecoration show a smaller decline with distance from the wall compared to the Pb

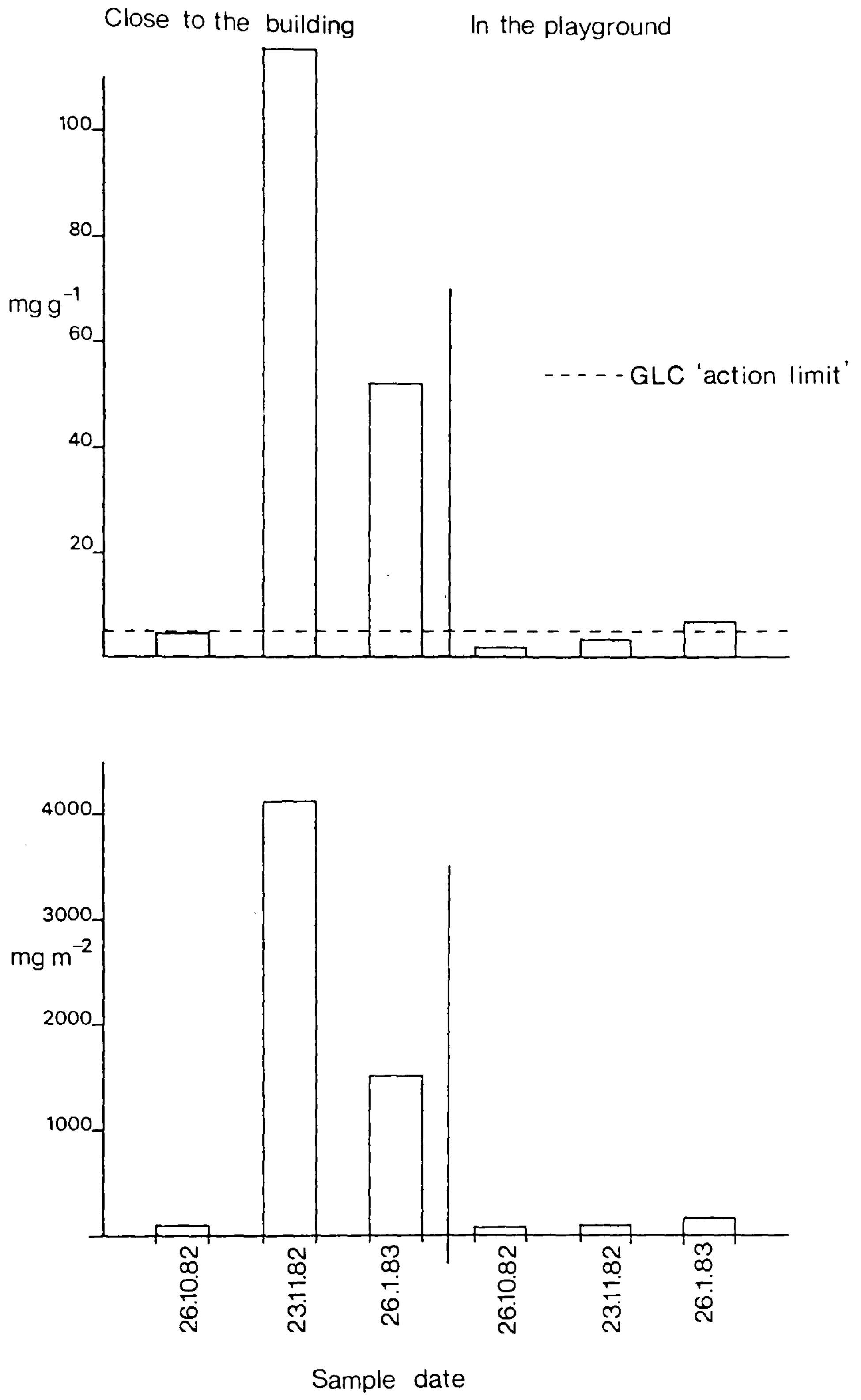


Figure 6.3. Levels of Pb in playground dust at the Robert Blair School.

concentration values. Considerably more sediment was collected from the playground area which may explain this discrepancy. The playground surface was composed of coarse asphalt and chippings and was therefore able to retain fine sediment in pockets and indentations, whereas the surface close to the wall was smooth concrete.

During the period of redecoration the Pb concentrations and loadings in playground dust close to the school building were found to increase dramatically. Lead concentrations of 11.6% in the playground dust had increased to twenty three times the Greater London Council 'interim action level', and lead loadings demonstrated an elevation of forty times relative to the pre-decoration levels. A less dramatic increase in Pb concentrations and loadings is observed in playground dust away from the wall, and the resulting concentrations remain below the G.L.C. 'interim action level'. Rundle and Duggan (1986) have noted similar increases in Pb in playground dust during redecoration of schools. In an investigation involving seven schools, the highest Pb in dust concentrations were found to vary enormously from school to school (490-100,000 $\mu g\ g^{-1}$) depending on the Pb content of the paint being removed.

Lead concentrations close to the school building dropped by half on completion of the redecoration process. This is probably the result of clean-up operations by the painters when they had finished their work. However, the Pb concentrations remained ten times the G.L.C. 'interim action level' of 5000 $\mu g\ g^{-1}$. The decorators cleaned up by sweeping, which has been shown to be a relatively inefficient sediment removal technique for all but larger particle sizes (see Section 3.2). Fine particles of paint probably remained on the surface. Lead loadings dropped to about a third of the previous high value recorded while decoration was taking place. Away from the building, concentrations and loadings of Pb continued to increase by about twofold after redecoration. A mean Pb concentration of 6620 $\mu g\ g^{-1}$ was observed after redecoration, which exceeds the ' interim action level'. This marked increase in concentration can be attributed to the dispersal of fine particles of paint by wind, and by the trampling action of children in the playground. Rundle and Duggan (1986) found a decline in Pb concentrations after redecoration in most school playground dusts. The time taken for levels to fall varied from school to school and the number of days that Pb concentrations remained above the 'interim action level' of 5000 $\mu g\ g^{-1}$ ranged from 30 to 500 days.

6.3.4. Heavy metal-particle size relationships in playground dusts.

Very little information is available in the literature on the heavy metal distributions with respect to particle size in playground dusts contaminated with paint flakes. As discussed earlier, street dusts show an increase in metal concentration with decreasing particle size (see Section 2.3.5 and Section 4.3.5). Rundle and Duggan (1980) observed a similar trend for Pb concentrations in a number of playground dusts, although these were not grossly contaminated by paint flakes. Sturges and Harrison (1985) have examined various size fractions of street dust using a microscope to investigate the particle size distribution of paint flakes. The amount of paint found in the dust reached a maximum of 0.7% by weight, and was concentrated mainly in the >250 μm size fraction. No surveys have examined the particle size distributions of heavy metals in school playgrounds during redecoration work.

The heavy metal concentrations within the various particle size ranges for dusts collected during this investigation are shown in Figures 6.4 to 6.7. Distinct spatial variations in the heavy metal-particle size distributions can be seen as well as temporal changes in the distribution patterns during the school redecoration.

Before the redecoration process began Cd and Cu concentrations showed an increase with decreasing particle size at both sampling sites. The sample taken close to the building shows a distinct split in the metal concentration distribution pattern for Cu. The 250-2000 μm size ranges show markedly reduced concentrations compared with the <250 μm size ranges. Zinc concentrations at the building line show a peak in their distribution pattern which occurs in the 63-125 μm particle size range. This may be associated with the weathering of galvanised metal fittings used on the school building. At the sample site away from the wall the Zn concentrations in each fraction are lower than those at the wall site, but show a typical increase in value with decreasing particle size. Lead concentrations close to the school wall exhibit an unusual particle size distribution pattern with concentrations falling with decreasing particle size. The Pb distribution pattern may be related to the peeling of paintwork, which comes off the window frames and sills in large pieces. The playground samples exhibit the typical metal-particle size relationship shown by other types of urban street dust (see Section 2.3.4).

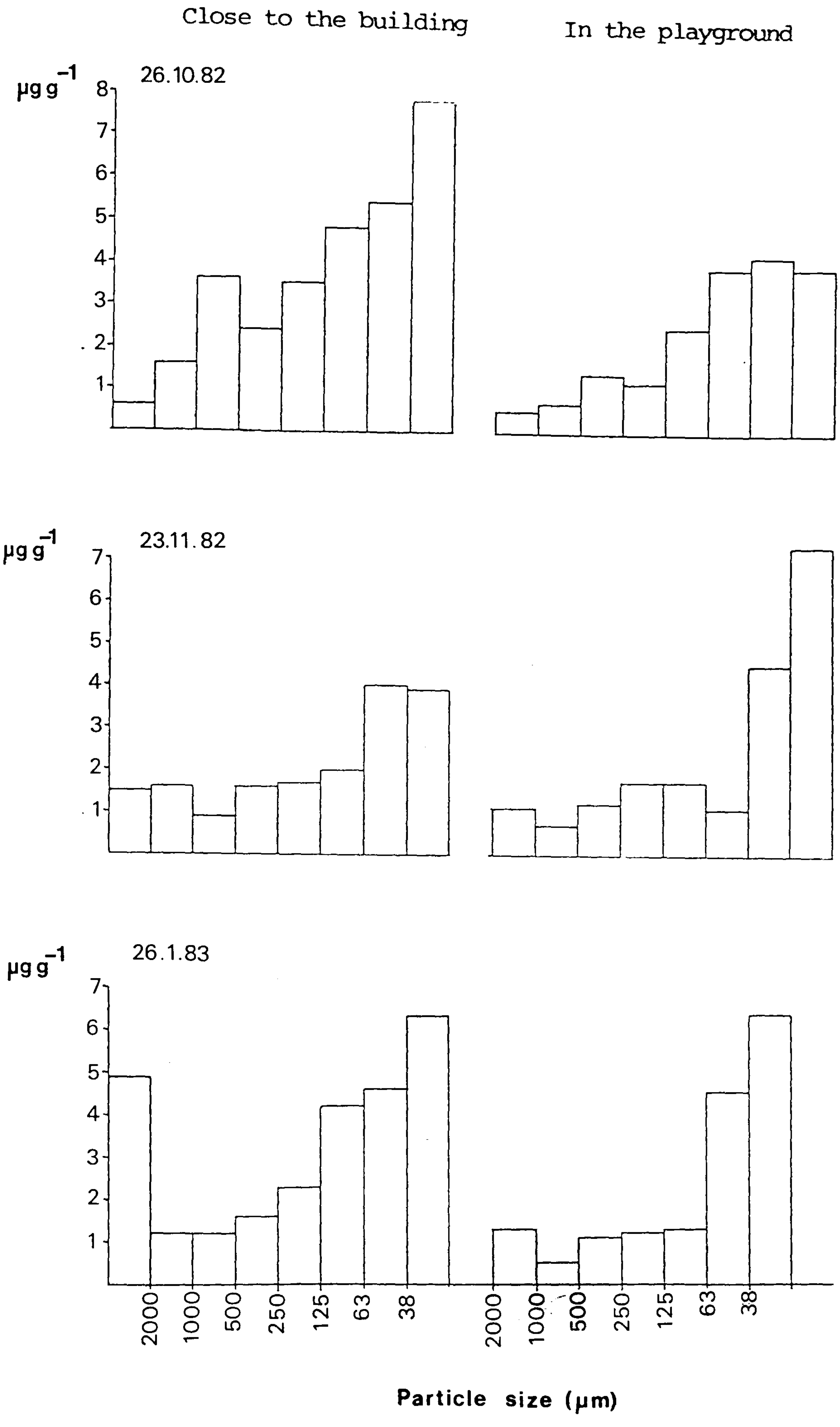


Figure 6.4. The variation of cadmium concentrations with particle size in playground dusts.

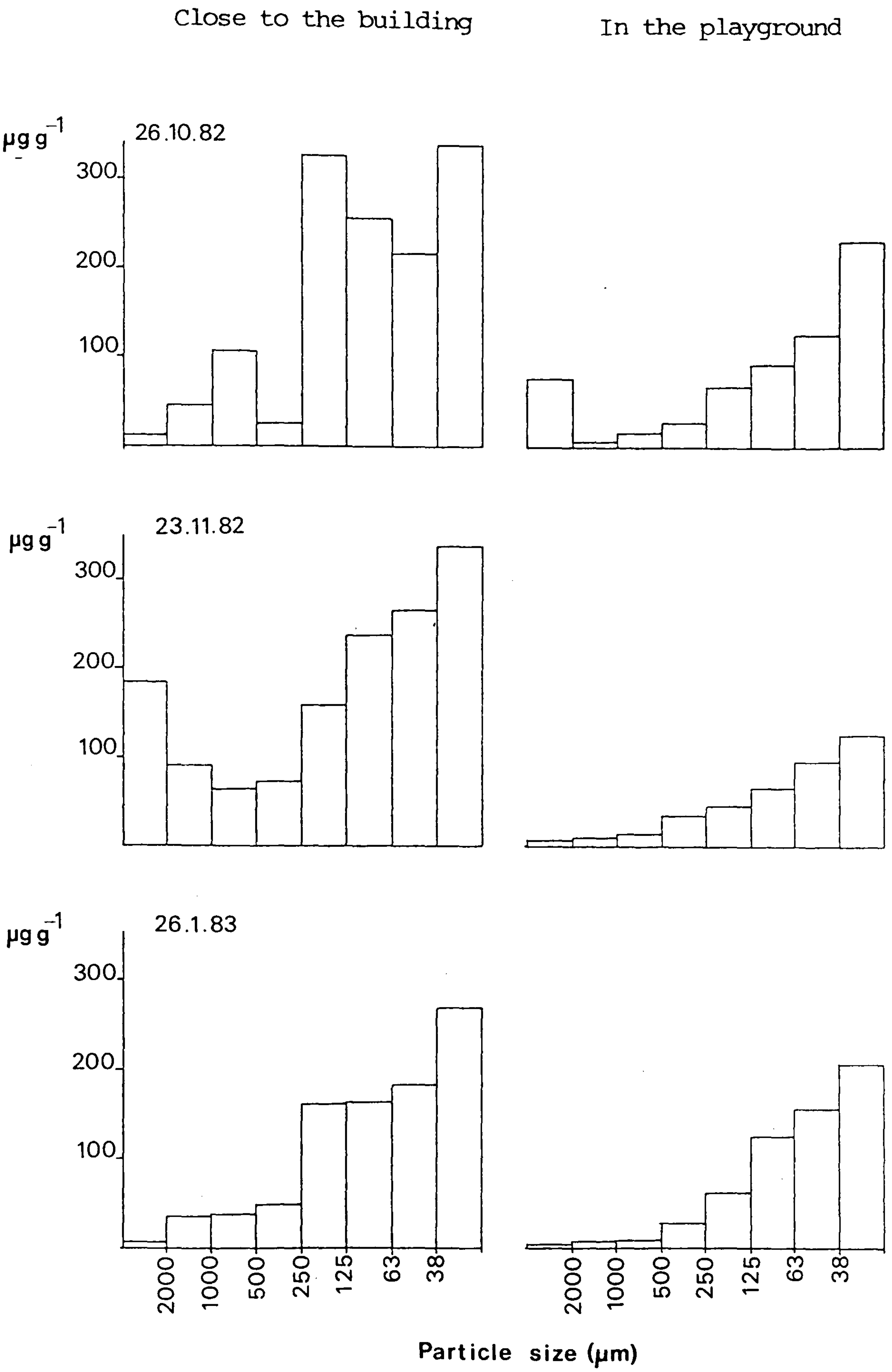


Figure 6.5. The variation of copper concentrations with particle size in playground dusts.

The distribution patterns for all metal loadings with particle size before redecoration reflect, at both sites, the distribution of sediment within the various particle size ranges (Table 6.5). The majority of sediment, and hence metal content, was found in the 63-500 µm size ranges. An enhanced Pb loading in the coarse grain size (>2000 µm) of sediment sampled close to the building was recorded. This reflects the elevated Pb concentrations found in this particle size range, due to the deposition of weathered paint chips.

While the redecoration process was being undertaken the Cd, Cu and Zn concentrations in each particle size fraction declined slightly (Figures 6.4, 6.5 and 6.7). However, the normal distribution pattern of increasing concentration with decreasing particle size remained unchanged. Only for Zn, in the sample taken close to the school building, was the distribution of concentrations with particle size altered. Concentrations of Zn in the 63-500 µm size range were reduced in this sample relative to the pre-decoration sample.

The distribution of Pb concentrations with particle size for the sample taken at the building line clearly changed during the redecoration of the school. The Pb concentrations in each size fraction increased many times. The largest enhancement in concentration was observed in the 63-500 µm particle size range where Pb concentrations increased to 160,000 µg g^{-1}. Whereas the pre-decoration samples showed decreasing Pb concentrations with decreasing particle size the sediment collected during redecoration shows a peak in Pb concentrations in the 125-250 µm size range. This can be attributed to the input of large quantities of paintflakes into the sample area. It has been noted earlier that using a blow torch for paint removal can generate large quantities of paintflakes in the larger size fractions. Additionally, a peak in the percentage Pb content of the dust produced was observed in the 125-250 µm size range (see Section 6.2, Table 6.2). Away from the school building the Pb concentrations in playground dust show no change in the distribution pattern with particle size. Concentrations are enhanced in each size fraction but not to the same extent as the samples taken close to the wall.

Lead loadings in the various particle sizes for the sample taken close to the school building during redecoration show a similar trend to the pre-decoration sample. However the loadings are greatly enhanced in each size fraction (Table 6.5). Cadmium, Cu and Zn loadings

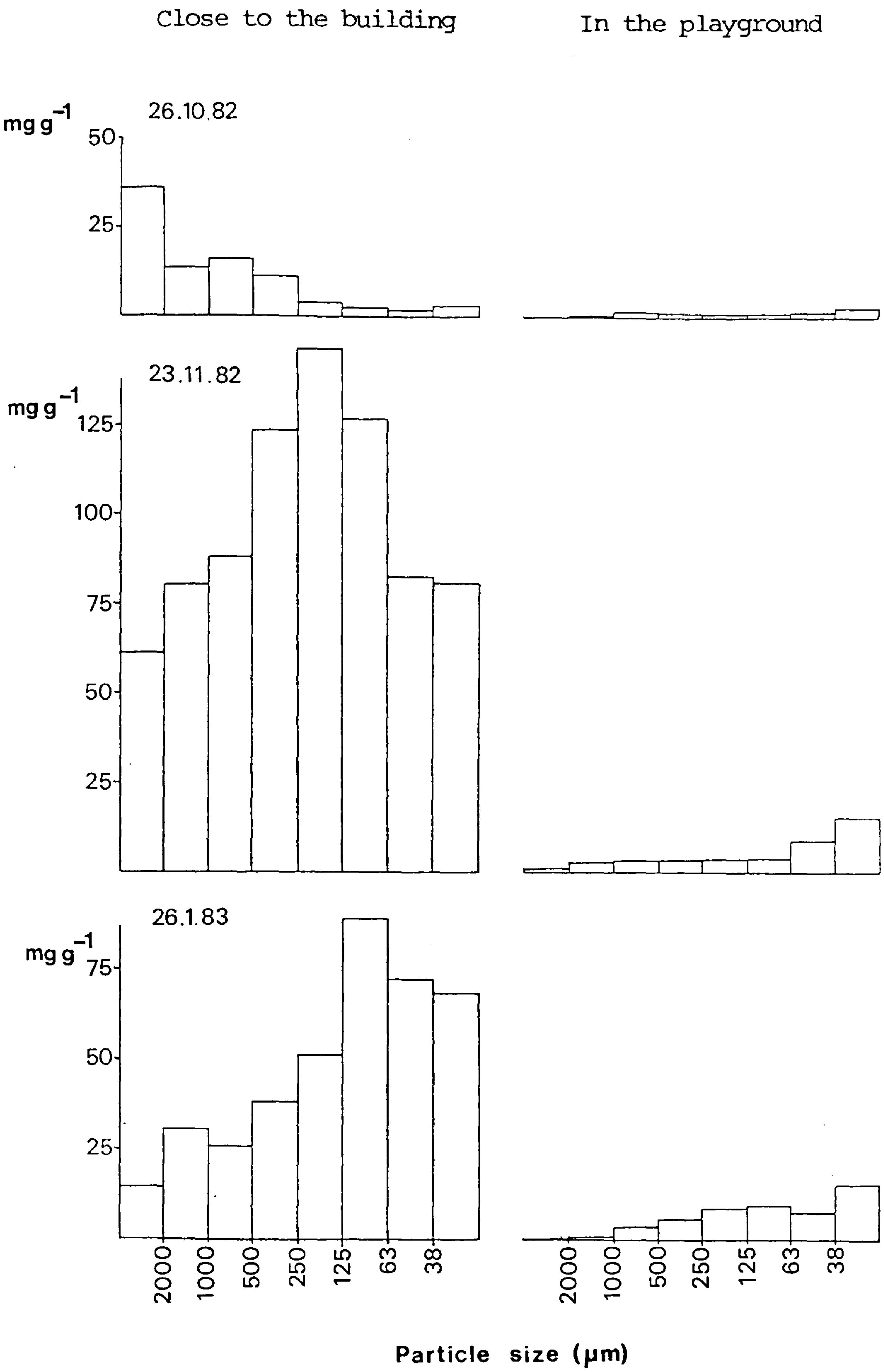


Figure 6.6. The variation of lead concentrations with particle size in playground dusts.

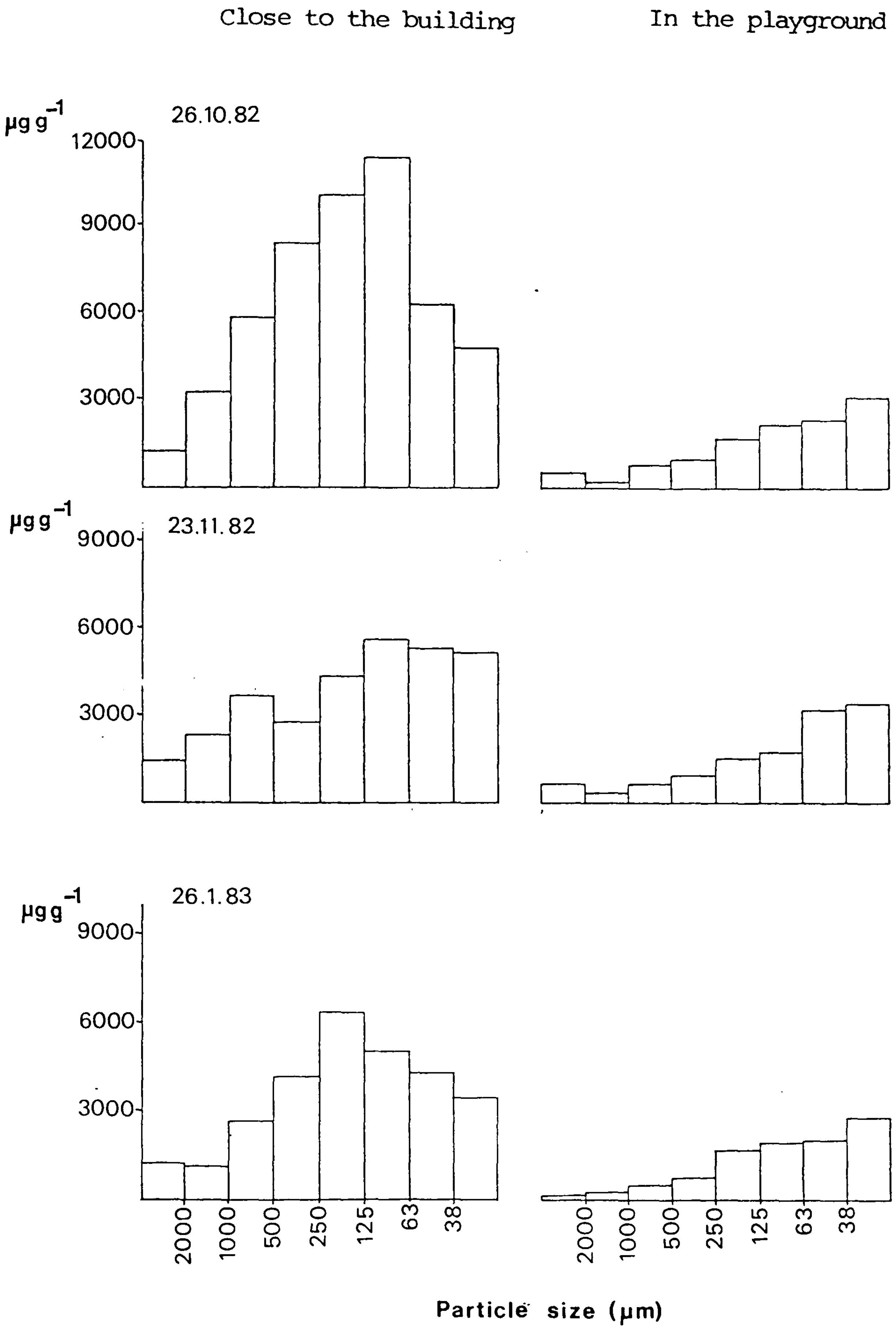


Figure 6.7. The variation of zinc concentrations with particle size in playground dusts.

also retain the same overall distribution with particle size as the pre-decoration sample, but unlike Pb show reduced loadings. Away from the school building all four metals show a uniform pattern of loadings. For Cd, Cu and Zn the loadings in each size fraction are generally reduced whereas for Pb the loadings are enhanced in the larger size ranges (>125 µm) compared with the pre-decoration sample.

After redecoration the Pb concentrations in sediment sampled close to the building decrease in particle sizes larger than 63 µm. This is the result of clean-up operations, which were undertaken using a dust pan and brush and can be seen to be more effective in removing the larger particle sizes (see Section 3.2). The <63 µm size fraction remained unaffected by this process with the Pb concentrations increasing with decreasing particle size. Away from the wall the distribution of Pb concentrations with particle size after redecoration was complete, show little change.

The concentration levels of Cd and Cu in each size fraction in the samples taken close to the school building increased slightly. The Zn concentrations in this sample appeared to be returning to a similar distribution pattern with particle size as in the pre-decoration sample. Although the concentrations in each size fraction were reduced, a distinct peak in concentration could be seen in the medium particle size range (63-250 µm). Away from the wall the distribution of Cd, Cu and Zn in the various particle size ranges remained unchanged when compared with the previous two sample visits.

The Cd, Cu and Zn loadings in the sample taken close to the school building after redecoration was completed show similar distributions with particle size to the pre-decoration samples. All metal loadings for this sample show a marked decline in the loadings in the larger particle sizes (>125 µm) when compared with the previous sample taken during redecoration. This is probably due to the clean up operation as previously noted (Section 6.3.3). Lead loadings in the fine size fractions (<125 µm) show a slight enhancement over the previous sample, probably the result of breakdown of larger particles by weathering and the trampling action of children. All metals show a similar distribution of loadings with particle size for the playground sample. Although similar in pattern to the previous samples the levels in each size range are generally lower.

Table 6.5. Heavy metal loadings in size fractionated playground dust (mg m^{-2}, except Cd µg m^{-2}).

		Close to the building			In the playground		
	Sample date	26-10-82	23-11-82	26- 1-83	26-10-82	23-11-82	26- 1-83
	Size range (µm)						
Cd	>2000	1.0	12.3	9.6	0.2	1.8	0.9
	1000-2000	2.6	7.6	2.4	2.2	3.2	1.3
	500-1000	10.8	7.0	5.7	10.6	10.2	4.1
	250-500	13.1	11.9	10.5	15.4	14.7	2.7
	125-250	14.1	6.8	11.9	29.1	5.3	1.3
	63-125	15.6	3.0	15.3	16.7	0.3	1.4
	38-63	12.6	3.8	12.1	4.7	0.3	1.3
	<38	6.9	3.9	8.2	0.6	0.5	-
Cu							
	>2000	0.02	1.53	0.02	0.04	0.01	<0.01
	1000-2000	0.07	0.44	0.07	0.02	0.04	0.01
	500-1000	0.32	0.51	0.19	0.11	0.11	0.03
	250-500	0.14	0.52	0.33	0.36	0.30	0.06
	125-250	1.32	0.64	0.84	0.78	0.14	0.06
	63-125	0.83	0.36	0.59	0.39	0.02	0.04
	38-63	0.51	0.25	0.48	0.48	<0.01	0.03
	<38	0.30	0.34	0.35	<0.01	<0.01	<0.01
Pb							
	>2000	60.1	505.1	28.9	<0.1	3.9	0.1
	1000-2000	21.0	384.1	63.0	1.9	26.8	2.5
	500-1000	46.8	686.2	68.4	12.0	55.9	14.5
	250-500	58.2	919.7	251.4	18.4	56.0	12.9
	125-250	16.3	589.2	266.6	15.8	22.2	8.5
	63-125	8.1	190.3	324.4	5.6	2.1	2.9
	38-63	4.9	76.0	190.7	2.6	1.3	1.6
	<38	2.8	82.8	88.8	0.4	2.2	0.3
Zn							
	>2000	2.0	12.0	2.3	0.3	1.1	0.2
	1000-2000	5.2	11.1	2.2	0.7	1.6	1.4
	500-1000	17.4	28.1	12.6	5.5	5.3	3.3
	250-500	45.7	20.8	27.4	18.4	8.2	3.1
	125-250	40.6	17.6	32.8	19.7	4.7	3.1
	63-125	36.2	8.4	18.0	9.1	0.5	1.1
	38-63	14.7	5.0	11.3	2.6	0.2	0.8
	<38	4.2	5.1	4.5	0.5	0.2	0.1

6.3.5. Chemical associations of heavy metals in playground dusts contaminated with paint flakes.

The results of the sequential extraction experiment are shown in Figures 6.8 and 6.9 which show the percentage metal content in each of the chemical fractions for the paint and playground dust samples. The concentrations of metals in each fraction are given in Tables 6.6 to 6.9. The results indicate some important differences in the chemical partitioning of metals between highway dusts and playground dust contaminated with paint flakes.

The total concentrations derived from the sum total of metal in each fraction for a particular sediment or paint show similar trends overall in their spatial and temporal variations to the total metal levels obtained by HNO_3 acid digestion. (Table 6.4 and Figures 6.2 to 6.3). The Zn concentrations obtained from the sequential extraction procedure are reduced relative to the total metal determination, but show similar overall temporal trends.

The Cd fractionation in both playground dust samples shows substantial proportions of this metal in the exchangeable phase which represents the highest metal availability. It has been previously noted that this metal has the greatest overall affinity for the exchangeable fraction of road dusts, with up to 5% of the metal associated with this fraction (see Section 5.3.1). However, the playground dusts and paint examined here show substantially greater levels associated with this phase.

For Cu, Pb and Zn the percentage of metal associated with the exchangeable phase is also elevated for the paint sample when compared with the road dusts examined earlier in Chapter 5. The samples of playground dust taken before redecoration show a similar percentage metal content to road dusts for the exchangeable fraction. During redecoration the percentage of metal in this fraction increases. Lead concentrations close to the building line of 4202 $\mu g\ g^{-1}$ in the exchangeable phase approach the 'interim action limit' for total Pb. Away from the wall the playground dusts are more comparable with road dust with respect to the Pb and Zn content of the exchangeable fraction.

The carbonate phase contains metals which are moderately available but which would be highly susceptible to release with changes in pH, such as would be found if the dust were ingested. The Cd content of the carbonate phase is reduced in playground dusts and the paint samples compared with highway sediments. The percentage contents of Cu,

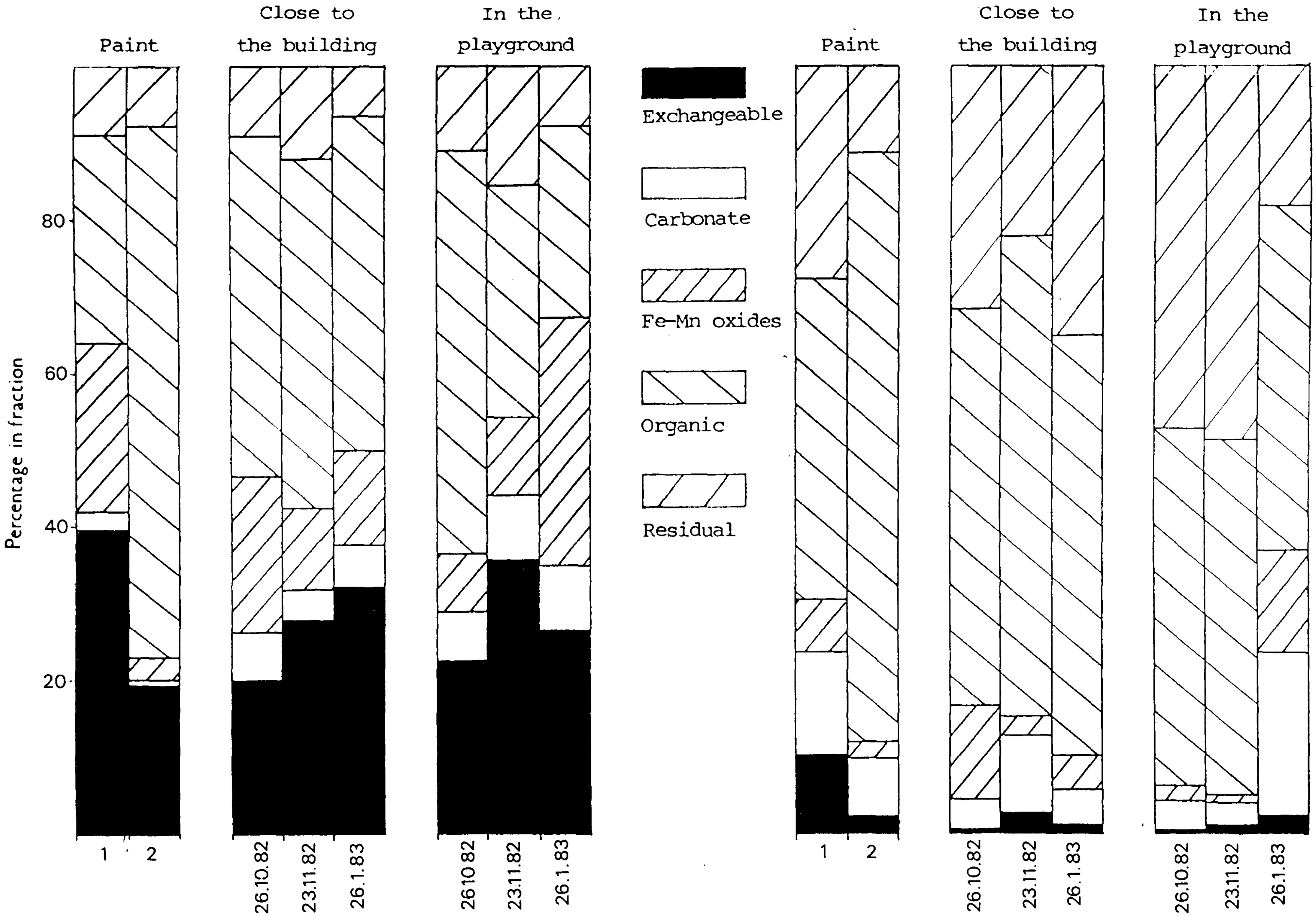


Figure 6.8. Chemical associations of Cd and Cu in paint and playground dusts.

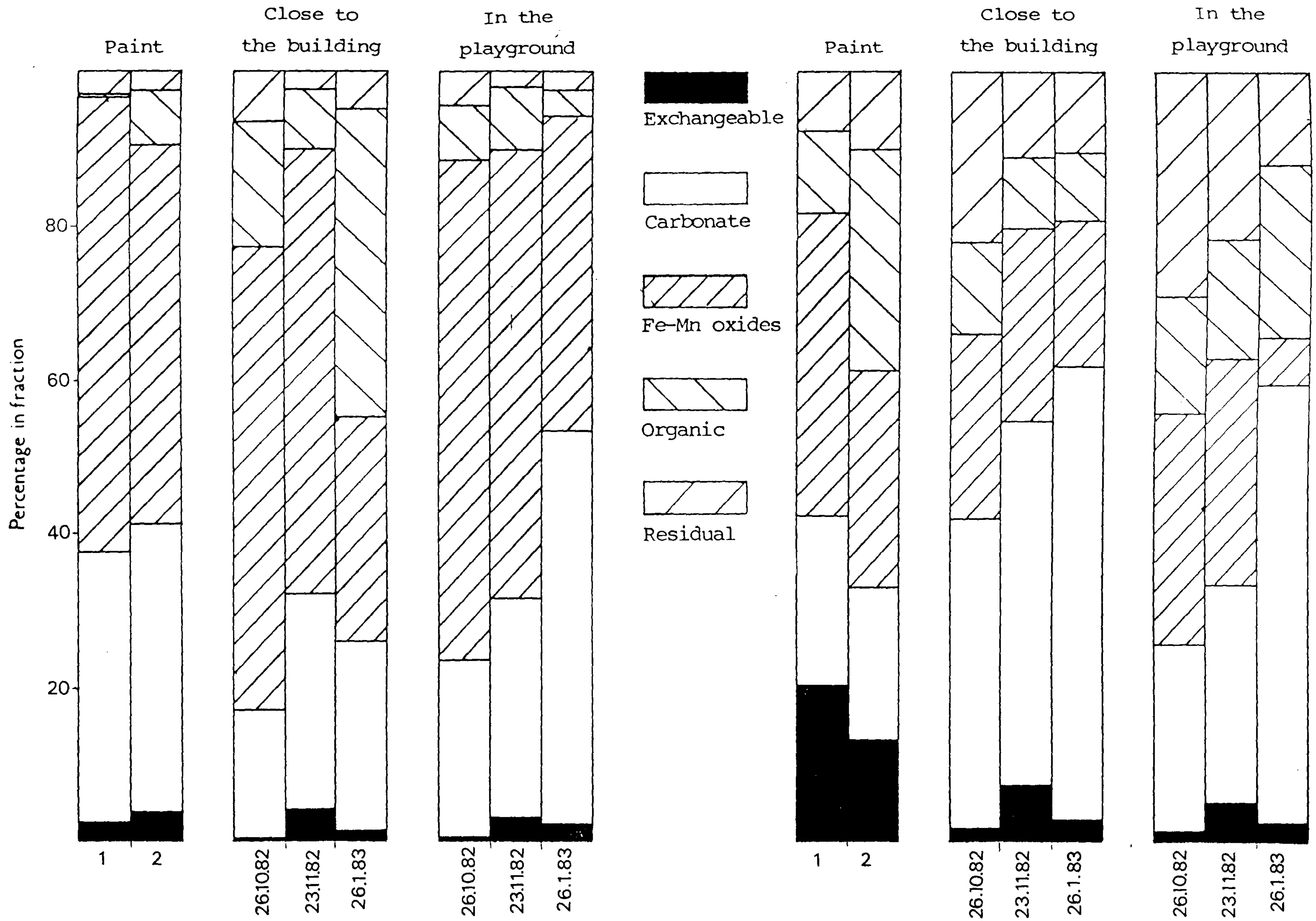


Figure 6.9. Chemical associations of Pb and Zn in paint and playground dusts.

Pb and Zn in this fraction are similar to those previously noted for other urban sediments. However, as with the exchangeable fraction the concentrations of Pb and Zn are elevated, particularly for the sample taken close to the building line, while redecoration is being undertaken. It would be expected that if the Pb in paint was in the form of basic Pb carbonate then levels of this metal in the carbonate phase would be elevated relative to other fractions. However, the percentage distribution of Pb in the playground dusts and paints show a similar overall distribution to those in other urban sediments.

The distribution of metal in the Fe-Mn oxide phase of playground dusts and paints are similar to those observed for road sediments. Copper shows the lowest affinity for this fraction, Cd and Zn show intermediate affinity and Pb shows the greatest association with the oxide phase. The percentage content of Pb in the Fe-Mn oxide phase is slightly higher than that found in road sediments, but is lower than that recorded for the paint sample analysed earlier in Section 6.2.3 (88%). This may be due to differences in the formulation of the paint samples. Like the exchangeable and carbonate fractions the Pb concentrations are greatly enhanced in this fraction during and after redecoration.

The organic fraction metal affinity decreases in the order Cu>Cd>Zn>Pb. The high affinity of Cu for the organic fraction agrees with other analyses of metal associations in soils and sediments (see Chapter 5). The percentage Pb content in this fraction is slightly reduced when compared with road dusts although as with other fractions the metal concentrations are elevated.

The residual fraction represents metal which is environmentally immobile. Copper shows the greatest affinity for this fraction. Overall the percentage distribution of metals within this fraction is similar to that observed in road dusts.

There appear to be few consistent changes in the heavy metal distributions between the various chemical fractions of playground dust while redecoration was taking place. Exchangeable metal levels follow a similar trend which shows a peak in the percentage content during redecoration at both sites. The exception to this is Cd at the wall side site, and Cu at the playground site. Both these show a gradually increasing proportion of metal in this fraction.

For Pb the results of the sequential extraction procedure show substantial variations in the levels in each fraction. These variations

Table 6.6. Chemical associations of Cd in paint and playground dust (µg g^{-1}).

	Paint sample		Close to the wall			In the playground		
	1	2	26-10-82	23-11-82	26- 1-83	26-10-82	23-11-82	26- 1-83
Exchangeable	0.66	0.38	0.63	0.35	0.59	0.39	0.39	0.88
Carbonate	0.04	0.01	0.19	0.05	0.10	0.11	0.09	0.29
Fe-Mn oxides	0.27	0.06	0.63	0.13	0.22	0.13	0.11	1.06
Organic	0.54	1.34	1.40	0.57	0.79	0.90	0.33	0.83
Residual	0.15	0.15	0.29	0.15	0.12	0.19	0.17	0.26
Sum total	1.66	1.94	3.14	1.25	1.82	1.72	1.09	3.32

Table 6.7. Chemical associations of Cu in paint and playground dust (µg g^{-1}).

	Paint sample		Close to the wall			In the playground		
	1	2	26-10-82	23-11-82	26- 1-83	26-10-82	23-11-82	26- 1-83
Exchangeable	1.8	0.4	0.9	3.4	1.7	0.3	0.4	1.6
Carbonate	2.4	1.4	11.2	14.0	6.4	2.1	1.0	15.3
Fe-Mn oxides	1.2	0.4	33.8	3.7	6.0	1.1	0.4	9.5
Organic	7.3	14.1	139.5	84.3	75.8	26.5	16.7	31.7
Residual	4.9	2.1	86.9	30.3	49.1	26.9	17.7	13.2
Sum total	17.6	18.4	272.3	135.7	139.0	56.9	36.2	71.2

Table 6.8. Chemical associations of Pb in paint and playground dust (µg g^{-1}).

	Paint sample		Close to the wall			In the playground		
	1	2	26-10-82	23-11-82	26- 1-83	26-10-82	23-11-82	26- 1-83
Exchangeable	3546.9	4142.1	11.6	4201.6	585.6	7.3	82.9	164.9
Carbonate	46471.5	40341.3	653.0	29166.4	11132.6	328.5	796.3	4054.9
Fe-Mn oxides	82183.5	52848.9	2295.5	59638.7	13005.8	923.7	1613.8	3203.2
Organic	211.8	7746.3	624.8	8053.1	17914.2	96.7	225.7	268.5
Residual	2849.8	2556.3	255.6	2444.2	2263.8	66.8	59.5	207.3
Sum total	135263.5	107624.9	3840.4	103504.0	44962.0	1423.0	2778.2	7898.8

Table 6.9. Chemical associations of Zn in paint and playground dust (µg g^{-1}).

	Paint sample		Close to the wall			In the playground		
	1	2	26-10-82	23-11-82	26- 1-83	26-10-82	23-11-82	26- 1-83
Exchangeable	572.8	238.3	55.8	198.6	101.6	15.2	53.5	51.2
Carbonate	628.8	354.7	1341.2	1063.5	2259.1	265.0	305.1	1229.0
Fe-Mn oxides	1113.2	503.6	793.1	664.6	721.2	326.5	313.6	496.3
Organic	311.2	515.1	395.2	443.2	335.6	163.5	166.8	125.1
Residual	221.3	185.7	744.8	305.3	415.1	320.1	236.0	267.3
Sum total	2847.3	1797.4	3330.1	2675.2	3832.6	1090.3	1075.0	2168.9

are however unable to clearly distinguish between the chemical associations in paint, playground dust contaminated with paint and highway dust. Such differentiation would be expected if the Pb in paint was in the form of Pb carbonate. The sequential extraction scheme does not appear to be able to distinguish the association of Pb as Pb carbonate. The organic metal fraction is higher in highway dust (see Section 5.3.) than in any of the playground samples, but it appears that the differences are insufficient for this method to be used for source apportionment. This arises mainly from the uncertainties in the selectivity of the various extractants. The extractants are not entirely specific and there is some overlap between fractions. This may account for the large concentrations of Pb observed in the Fe-Mn oxide phase of playground dust and paint samples. The Pb content of this fraction may represent inefficient extraction by the CH_3COONa used for determination of carbonate associated metals. The technique however provides qualitative data regarding the forms of association of metals and indirectly information relevant to their environmental mobility and bioavailability.

6.3.6. Health implications of childhood exposure to paint dusts containing Pb.

The investigation described in the preceding sections has demonstrated that the redecoration of school buildings can result in very high concentrations of Pb in playground dusts. These concentrations may result in an increased body burden of Pb in children playing in the areas affected and who may inadvertently ingest dust via the hand to mouth route. Several workers have reported evidence which suggests a relationship between blood Pb and hand to mouth activity (see Section 2.6.3). Duggan et al. (1985) have reported a direct relationship between Pb concentrations in playground dust and those on the hands of children after play.

In Chapter 5 (Section 5.3.5) it was shown that the exchangeable and carbonate fractions represent the most biologically available form of metal in settled dusts. Metals associated with these fractions are easily solubilised in the human stomach. From the data presented in Section 6.3.5 the levels of Pb potentially available to children playing in the school playground have been calculated (Table 6.10.) It can be seen from this data that considerable quantities of Pb can be made available for uptake by children during and after the redecoration of school buildings. In the worst case close to the school wall the painters cordoned off the area and access was restricted to children. However following the completion of work and after the playground had been cleaned by the painters, a concentration of 11718 $\mu g\ g^{-1}$ of available Pb was present in the playground sediment. Away from the wall, levels were not so high but were enhanced relative to other types of urban street dust (see Section 5.3.5).

Table 6.10. Potentially available Pb levels in playground dust for a school undergoing redecoration.

	Close to the school			In the playground		
	Before	During	After	Before	During	After
	------ decoration -----			------ decoration -----		
Available Pb concentration ($\mu g\ g^{-1}$)	665	33368	11718	336	879	4220
Uptake per day (μg)	66	3337	1172	34	88	422

Although there is controversy concerning the level of dust ingestion, Duggan and Williams (1977) have estimated that young children ingest about 100 mg of dust per day through the hand to mouth route. The quantity of Pb ingestion of this amount of playground dust is also shown in Table 6.10 and represents the maximum quantity of Pb that could be ingested. Obviously children will not spend all of their time in a school playground and there will be contributions of dust from other areas. Nevertheless the estimates of typical daily ingestion of Pb from dust given in in Section 5.3.5 of 74-183 μg would be greatly exceeded by children playing in both areas of the playground studied.

Duggan (1980) has theoretically determined the effect on blood Pb levels of increased Pb in dust levels and has derived the relationship:

$$\Delta [Pb]_{blood} (\mu g\ dl^{-1}) = 5 \times 10^{-3}\ \Delta [Pb]_{dust} (\mu g\ g^{-1})$$

An increase in Pb in dust concentration of 5000 $\mu g\ g^{-1}$ which occurred in the school playground following redecoration would therefore produce a blood Pb level enhancement of 25 $\mu g\ dl^{-1}$. With a background blood Pb level of 10 $\mu g\ dl^{-1}$ this situation might be expected to produce a total blood Pb level of 35 µg dl^{-1}. A much greater change in sediment Pb concentration of 48000 µg g^{-1} occurred close to the school building and under such conditions a much larger rise in blood Pb levels may be predicted. Potentially harmful Pb in blood levels can therefore be produced if playground dust is contaminated by Pb bearing paint flakes following the exterior redecoration of school buildings.

6.4. Conclusions.

The following conclusions can be drawn from the investigations described in Chapter 6 into the influence of Pb based paint on the environmental levels of Pb:-

a) The physico-chemical associations of Pb in dust produced by five techniques of paint removal have been investigated. Belt sanding was found to produce considerably higher airborne Pb levels than the four other methods tested. The Pb levels in dust fallout produced by belt sanding also tended to be associated with finer particle sizes, and this is therefore more susceptible to dispersion. The other techniques tested produced dust of much larger particle size (>2000 µm) and fallout was confined to the work area.

b) The environmental Pb levels produced by paint stripping are potentially hazardous not only to the operator but also to persons living or working in the area surrounding the stripping process, particularly young children. Therefore basic hygiene and safety precautions should be employed including: the use of chemical strippers; provision of good ventilation; isolation of the work area; and thorough clean up on completion of the work.

c) The metal levels in playground dust following the external redecoration of a school have been investigated. Levels of Pb in playground dusts were found to be greatly increased during this process. The total Pb in dust concentrations were very high when compared with the concentrations reported for other types of urban dust. The highest levels of Pb in the bulk sediment were recorded close to the school building during redecoration, Pb concentrations exceeded the G.L.C. 'interim action level' by twenty three times. Clean up operations performed by contractors on completion of their work were found to be ineffective in reducing Pb in dust concentrations to acceptable levels.

d) In the playground itself peak concentrations of Pb were reached only after the redecoration was completed. Dispersal of Pb bearing paint chips by wind and the trampling action of children, appeared to be the cause of this trend.

e) Distinct spatial and temporal changes took place in the distribution of Pb with particle size during the school redecoration. Prior to redecoration, in sediment sampled close to the school building, Pb levels showed decreasing concentrations with decreasing particle size. This is probably due to flaking of paint off windows and sills. In the playground sample the previously observed metal-particle size distribution pattern of increasing concentration with decreasing particle size was observed (see Sections 2.3.4, 4.3.5 and 5.3.2). During redecoration the Pb concentrations in all size fractions increased to very high levels. The medium particle size ranges (63-500 µm) showed particularly enhanced Pb levels. Following redecoration the levels in the >63 µm particle size fractions decreased due to the clean up operations performed by the painters. In the playground sample the Pb concentrations in all size fractions increased during and after redecoration, but the usual distribution pattern was retained.

f) Studies of the chemical associations of metals in playground sediment have shown that considerable quantities of Pb occur in the combined exchangeable and carbonate fractions. This represents metal which is readily available for uptake to the bloodstream via ingestion. Following redecoration, and after clean up by the decorators, the levels of available Pb in playground dust could lead to a maximum daily uptake via the hand to mouth route of 422-1172 µg. This compares with a daily uptake of 74-183 µg calculated for urban road dust (see Section 5.3.5).

g) It was thought that the chemical speciation technique would have potential for source identification. However, differences between the distribution of metals in the various chemical fractions of different types of urban dust are insufficient for this method to be used for source apportionment.

CHAPTER 7. A MATERIALS BALANCE FOR HEAVY METALS IN THE URBAN STREET ENVIRONMENT.

7.1. Introduction.

The urban street environment represents a complex system in terms of heavy metal accumulation, transport pathways and removal processes. The levels of heavy metals in each environmental compartment are a function of many variables including the strength and nature of the contributing source, the chemical form of the metal, deposition processes and hydrometeorological conditions. In addition metal levels are influenced by factors such as resuspension and municipal cleaning practices.

The major sources of heavy metals in the urban environment and the principal pathways of these metals have been discussed in earlier sections (see Chapter 2). Vehicular sources are widely recognised as being a significant source of metals, particularly Pb, in the urban atmosphere, street sediments and stormwater runoff. Although the behaviour of Pb in the vicinity of major roads has been studied extensively (see Section 2.2), the relationship between the levels of road surface particulate metals, the atmospheric deposition and the removal rates of heavy metals by stormwater have not been as fully investigated for other metals. Harrison et al. (1985) have investigated metal fluxes for a section of motorway. This work confirmed earlier studies which showed that 90% of Pb emissions from fast highway traffic were dispersed away from the roadway. Much of this work has concentrated on major roadway or motorway catchments and very little work has been undertaken in urban/residential areas.

The objective of the work described in this Chapter was to construct a materials balance for selected heavy metals in an urban/residential street catchment. The study aims to:

a) Assess the contribution relative to the urban background of motor vehicles to airborne, street sediment and stormwater levels of heavy metals.

b) Identify and quantify the flow pathways for heavy metals in a typical street environment.

c) Determine variations in the partitioning of heavy metals between the dissolved and particulate phases of rainfall and stormwater runoff.

d) Relate metal loading rates to input and output controls.

e) Construct a simple predictive model relating atmospheric levels of heavy metals to stormwater metal concentrations in the urban environment.

7.2. The Sampling Site.

The study area chosen for this investigation is a residential area known as Chilwell Gardens, situated on the north western outskirts of Greater London. This is a sub-catchment within the 243 ha South Oxhey catchment near Watford, Hertfordshire (Figure 7.1). The site was chosen because it offers a readily definable small catchment for which the boundaries have been clearly established and the hydrological properties well documented (Harrop 1984).

7.2.1. The catchment characteristics.

The Oxhey estate is a typical post-war housing development with a population of approximately 12,500. Housing is mainly semi-detached and terraced with an overall density of 2.02-2.43 dwellings ha^{-1}. Also included within the catchment are shops, schools and a number of public buildings. There is no industrial or commercial development. A large proportion of the estate is wooded, so that the total catchment is only 19.8% impervious. Drainage is by a separate stormwater sewer system which outfalls to the Hertsbourne River, a tributary of the River Colne.

The Chilwell Gardens sub-catchment has an impervious area of 96%. The catchment consists of a section of arterial road situated in the centre of the main housing estate (Figure 7.2). Two blocks of terraced houses border the western edge of the sub-catchment, and the South Oxhey Community Centre forms the eastern boundary. Stormwater is drained from the road surface and adjacent pavements to two roadside gully pots. Roof runoff drains directly into the storm sewer downstream of the gully pots. The total catchment area is 926 m^2 of which 533 m^2 is road surface and adjacent pavements. The road carries mainly low density residential traffic (150 vehicles day^{-1}), with occasional heavier non-domestic usage serving the community centre. The road surface is of rolled tarmacadam construction, and has recently been resurfaced with stone chippings. Pavement surfaces are also rolled tarmacadam, but show signs of wear due to pavement parking and break through of tree roots. Some garage facilities exist but most cars are street parked.

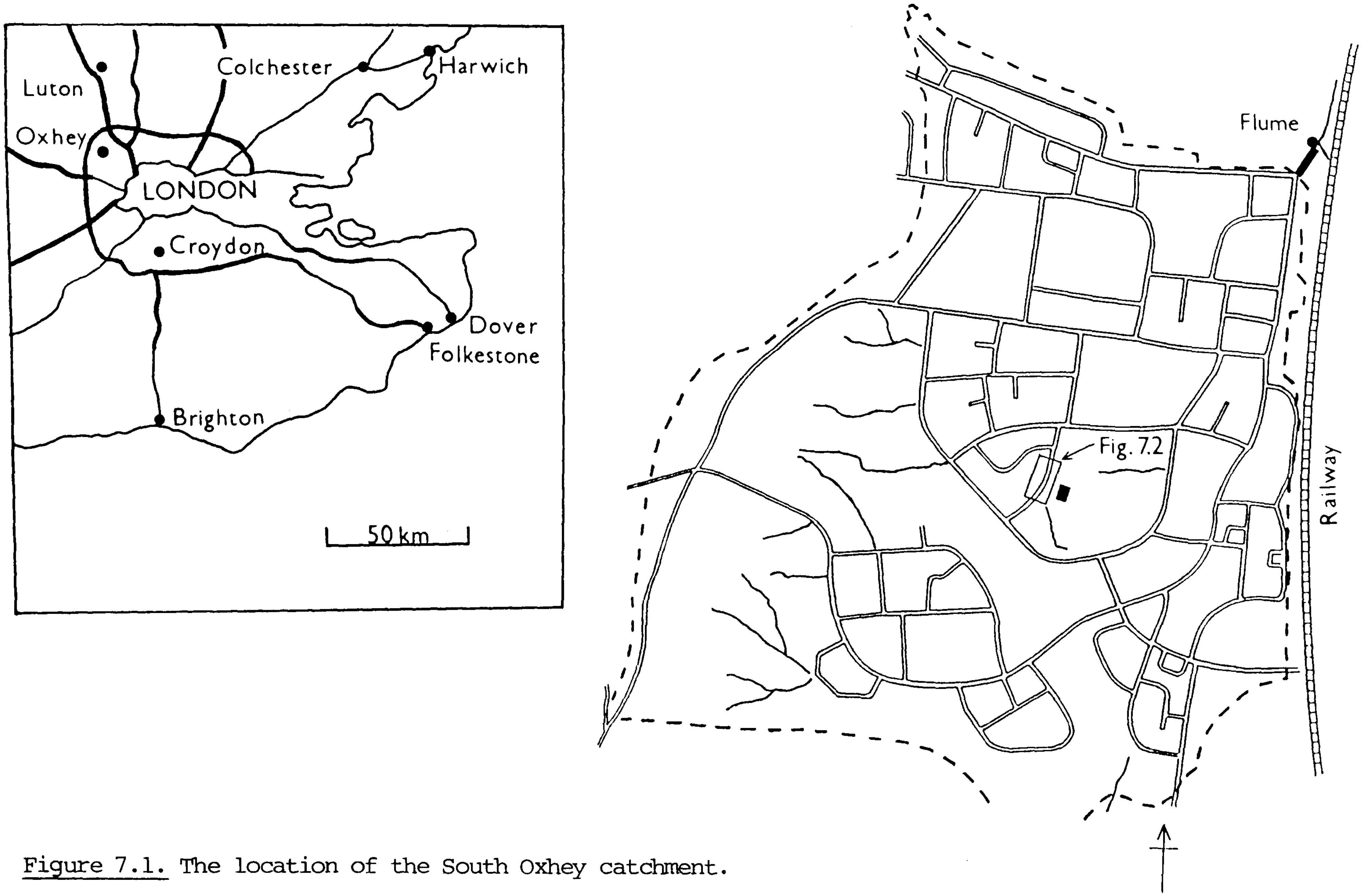


Figure 7.1. The location of the South Oxhey catchment.

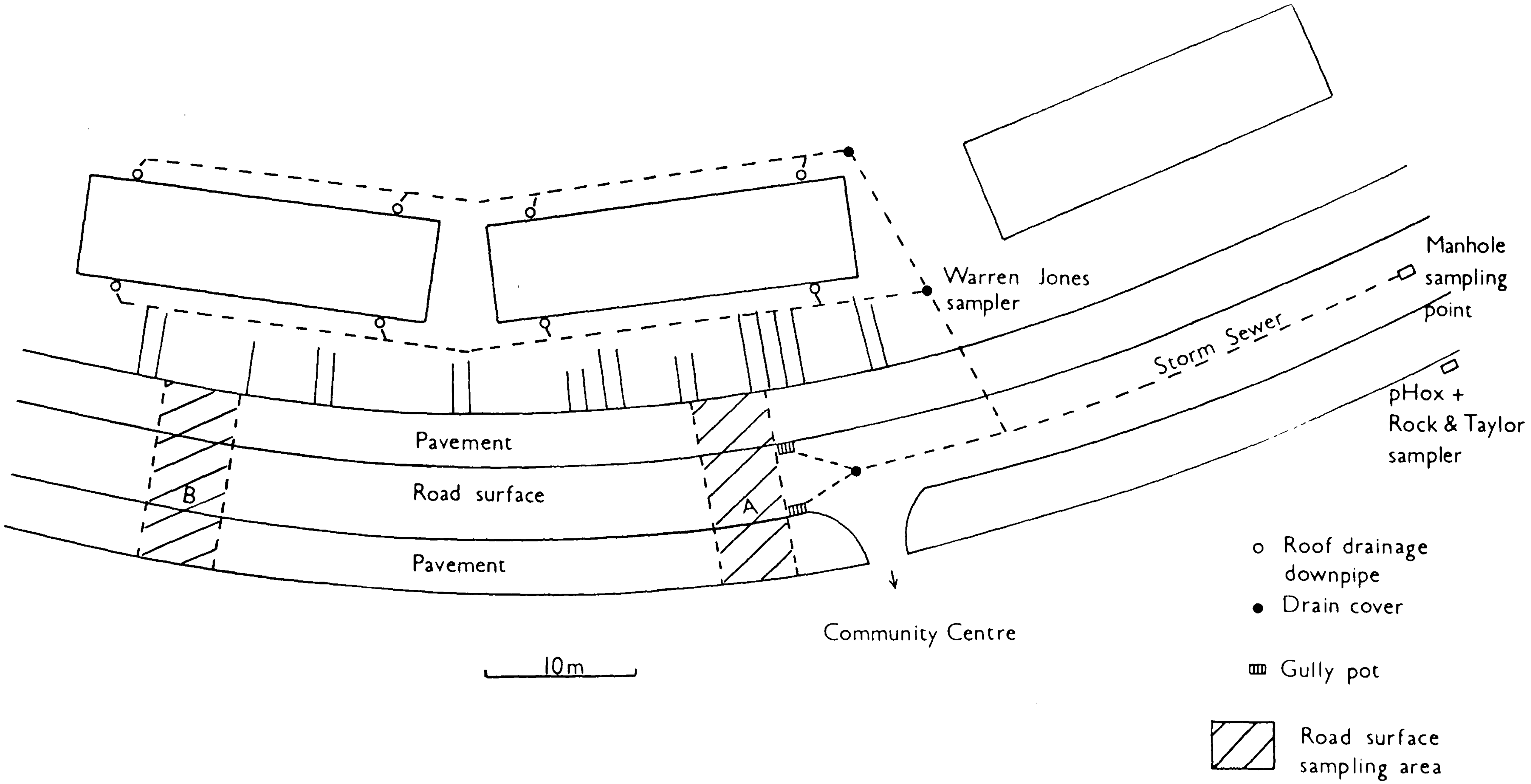


Figure 7.2. The Chilwell Gardens sub-catchment showing the sample points.

Road surfaces, adjacent pavements and roof surfaces contribute the largest proportion of surface runoff supplemented by drainage from house pavements and patios. The gardens of the houses fall back from the road and therefore might not be expected to contribute to surface runoff to any substantial extent.

7.3. Previous Research Within The Catchment.

Previous work within the Oxhey catchment has been carried out by a number of agencies since 1953. Instrumentation of the catchment commenced in 1952, when the Transport and Road Research Laboratory constructed a long throated trapezoidal flume at the outfall of the storm sewer system. This was used for gauging and modelling studies. Derived flow and rainfall data from Oxhey and eleven other sites were used between 1953 and 1959 to assess the relationship between the rate of rainfall and rate of runoff from urban areas (Watkins 1962).

The Water Pollution Research Laboratory used the Oxhey catchment for baseline studies on stormwater runoff. Samples were taken using automatic sampling equipment installed at the flume, between April 1953 and April 1954. The composition of individual samples was found to vary widely, with the maximum concentrations for BOD, permanganate value and suspended solids being 100 mg l^{-1}, 63 mg l^{-1} and 2045 mg l^{-1} respectively (Wilkinson 1956). The 'first flush' of water was generally more polluted than the rest of the storm with pollutant concentrations roughly twice as great as during the subsequent flow.

In 1977 the Institute of Hydrology and Thames Water Authority re-instrumented and refurbished the flume which had fallen into disrepair. A joint monitoring programme was undertaken to record stormwater flow and rainfall. The flume was also used by the Urban Pollution Research Centre at Middlesex Polytechnic to investigate the nature and consistency of the 'first flush' of pollutants. Confirmation of the general occurrence of the 'first flush' phenomenon was made (Ellis 1984). This occurred most frequently following a period of substantial dry weather. Delayed flushes were also recorded with suspended solids sub-peaks occurring on recessional limbs of the hydrographs, and coinciding with short lived increases in BOD in the later stages of storm flows. In addition, persistent but varying levels of turbidity were observed throughout the storm event. Ellis (1979) has suggested that such observations may be explained by sub-catchment inputs loading onto the hydrograph at different times during the storm.

Harrop (1984) carried out an investigation of the quality and quantity of stormwater runoff from the Oxhey catchment in collaboration with the Institute of Hydrology. Rainfall-runoff data was monitored at the flume, together with water quality data for the runoff events. Runoff was observed to be a significant contributor of pollutant levels to the receiving stream, particularly runoff derived from snow melt.

7.4. The Sampling and Analytical Programme.

The sampling and analytical programme used to develop a mass balance for metals in the Chilwell Gardens sub-catchment is described below. The work involved the instrumentation of the catchment to monitor levels of heavy metals in atmospheric deposition, surface dusts and runoff.

7.4.1. Atmospheric levels of heavy metals.

7.4.1.1. Total airborne suspended particulates.

Airborne suspended particulates were sampled on the roof of the South Oxhey Community Centre (4 m above ground level), using a battery powered constant flow Cassella pump. The pump had a notional flow rate of 2 l min^{-1}, and was used in conjunction with a 47 mm polycarbonate filter head. Nuclepore 0.8 µm pore size filters were used because of their high collection efficiency and low intrinsic metal content. Samples were collected over a 7 day sampling period.

7.4.1.2. Bulk deposition.

Bulk deposition was collected in a deposit gauge also located on the Community Centre roof. The deposit gauge consisted of a 16 cm diameter polythene funnel, covered with 2 mm nylon mesh to prevent entry by insects and other debris. The funnel fed into a 2 l polythene flask which was changed weekly. The collected rainwater was partitioned into dissolved and particulate associated fractions before determination of metal content (see Section 7.6).

7.4.1.3. Dry deposition.

Dry deposition was monitored using a specially constructed deposit gauge located on the Community Centre roof. The dry deposition gauge was similar to that designed and used by the Atomic Energy Research Establishment at Harwell (Pattenden 1974). The dry deposition matter was collected on Whatman 541 filter paper held horizontally 12 cm below a plastic rain cover. The deposition collector was mounted in a plastic frame 1.5 m above roof height.

7.4.2. Rainfall volume.

Rainfall volume measurements were obtained using a tipping bucket Rimco MM37 automatic raingauge. This was situated adjacent to the atmospheric samplers on the Community Centre roof. The raingauge had a bucket volume equivalent to a rainfall depth of 0.2283 mm and was linked to a data logger which recorded the number of tips every 30 s on a cassette tape. The data collected on cassette tape was processed by computer as described in Section 7.5.

7.4.3. Surface dusts.

Surface dusts were collected from the road, pavement and roof surfaces. Vacuum techniques, as described in Section 3.2, were used for all sample collection other than the roof samples. Sediments were collected monthly along two 5 m wide transects across the bottom and top of the road catchment (Figure 7.2).

7.4.4. Runoff sampling.

7.4.4.1. Stormwater runoff.

Stormwater runoff was collected at the manhole 40 m downstream of the gully pots (Figure 7.2), using a Rock and Taylor multi-purpose liquid sampler fitted with an external float switch. The switch activated the sampler at the onset of the stormwater flow in the sewer. Samples were then collected at 5 minute intervals with 2.5 minutes actual sample collection and 2.5 minutes backflush.

7.4.4.2. Stormwater flow measurement.

Stormwater flow was measured at a 90^{o} V notch weir plate using a Phox series 1000 multi-parameter water quality monitor. This had been installed in a protective cabinet close to the manhole as part of a previous research project (Harrop 1984). The flow meter was of the air reaction dip tube type. The bubbler tube outlet was fixed approximately 3 mm below the bottom of the notch of the weir. When the water level reached the external float switch, the flow meter recorded the flow at 10 minute intervals until the level fell back to zero. Data was recorded on a cassette tape using a M200L Microdata logger.

7.4.4.3. Roof runoff.

Collection of roof runoff was made using a Warren Jones WJ40 effluent sampler located in the pipe draining the roofs of the two housing blocks (Figure 7.2). This provides an initial bulk sample which is not representative of the total loadings discharged from the roof during any storm event, but does give an indication of water quality.

7.4.4.4. Gully pot liquor.

Gully pot liquor was sampled weekly, and gully pot sediment samples taken monthly. In each case grab samples were taken from both of the gully pots in the sub-catchment.

7.5. Processing of Data Held on Cassette Tape.

A suite of computer programs have been written to process rainfall and storm flow data once it has been transferred to the Middlesex Polytechnic DEC 10 computer. Recorded cassette tape data was transferred to paper tape input format using a 1180 series Tape Punch DDTM 047. Computer restrictions prevent direct input of cassette data to the DEC 10. The paper tape raw data was used to create a data file on the DEC 10 using a LRP - 300 Paper Tape Reader. Details of the equipment operation and program suite are given elsewhere (Harrop 1984).

7.6. Analytical Techniques.

Atmospheric deposition and runoff samples were separated into filterable and non-filterable fractions using acid washed 0.4 µm Nuclepore filters. Filtration was conducted as soon as possible on return of the samples to the laboratory. The filtrates were acidified ($pH<2$) with HNO_3, and stored in polyethylene sample tubes at 4^oC. Both the soluble and the particulate fractions were digested with a 9:1 HNO_3-$HClO_4$ mixture (see Section 3.7). Metal determinations were carried out by anodic stripping voltammetry as described in Section 3.8.

Road surface sediment samples were size fractionated using: 1000; 500; 250; 125; 63 and 38 µm stainless steel sieves. The total and exchangeable metal content of the sediment samples were then determined. For total metal determination, replicate subsamples were digested with a 9:1 HNO_3-$HClO_4$ mixture as described in Section 3.8. Exchangeable metals were determined by extraction with 1M $MgCl_2$ (pH 7) for 1 hour with continuous agitation as described by Tessier et al. (1979). Roof surface and gully pot basal sediment samples were sieved through a 500 µm stainless steel sieve and dried overnight at 105 °C prior to analysis. Metal determinations were performed by atomic absorption as described in Section 3.8.

7.7. The Sampling programme.

The sampling programme was initiated in April 1984 with the instrumentation of the atmospheric sampling station located on the Community Centre roof. The surface dust samples were collected at approximately monthly intervals from April 1984 to September 1984. The Phox water quality monitor had been installed for a previous project, and this was augmented by the installation of the Rock and Taylor sampler. Problems were encountered as both these units were triggered by the same external float switch. The original collar switch had to be replaced after extensive modifications had been made. This caused a delay of several months before runoff samples with flow data were obtained. A sampling period of 8 weeks from July 1984 to September 1984 was then achieved when all equipment functioned concurrently.

7.8. Heavy Metal Levels at the Chilwell Gardens Sub-catchment.

In this section the heavy metal levels in the atmosphere, road surface sediment and in surface runoff are described and compared with values in the literature. Experimentally determined levels of atmospheric heavy metal fallout are also compared with estimates of metal contributions to the catchment from automotive sources.

7.8.1. Atmospheric levels of heavy metals at Chilwell Gardens.

The mean atmospheric levels of Cd, Cu, Pb and Zn monitored from 6th July to 6th September 1984 at Chilwell Gardens are summarised in Table 7.1. The metal levels recorded in the sub-catchment lie within the range of quoted literature values for comparable urban/residential areas in the United Kingdom also given in Table 7.1.

The monitoring station for atmospheric metals was located on the roof of the South Oxhey Community Centre which is approximately 75 m from the sub-catchment. Atmospheric metal levels fall off rapidly with distance away from the roadside (see Section 2.2.2). Therefore roadside atmospheric levels of heavy metals for the Chilwell Gardens sub-catchment may be greater than those reported in Table 7.1.

Table 7.1. Atmospheric levels of heavy metals monitored at Chilwell Gardens, South Oxhey compared with literature values.

	Cd	Cu	Pb	Zn
Airborne suspended particulate metal levels (μg m^{-3})				
mean (n = 7)	1.05x10^{-3}	0.010	0.220	0.086
range	0.29-3.50x10^{-3}	0.005-0.032	0.086-0.386	0.058-0.202
Literature values				
Duggan & Burton (1983)	<1x10^{-3}	0.01-0.07	0.20-1.10	0.05-0.50
McInnes(1979)	3.8±3.1x10^{-3}	0.024±0.023	0.460±0.210	0.350±0.680
Total deposition rate (μg m^{-2} day^{-1})				
mean (n = 6)	2.03	8.37	88.17	97.89
range	0.76-3.86	2.31-18.11	25.54-155.16	25.90-186.45
Literature values				
Cawse (1974)	-	21.1-145.2	49.9-186.3	95.9-575.3
Pattenden (1974)	-	39.7-164.4	68.5-169.9	117.8-375.3
Duggan & Burton (1983)	<1.64-3.29	4.90-65.80	49.30-493.20	197.30-986.30
Dry deposition rate (μg m^{-2} day^{-1})				
mean (n = 2)	0.91	4.78	18.12	16.74
Literature values				
Cawse (1974)	-	2.7-24.7	24.1-79.5	7.9-208.2
Pattenden (1974)	-	11.7-257.7	36.0-134.3	46.3-128.7
Dry deposition velocity (m s^{-1})	0.01	0.006	0.001	0.002
Literature values				
Cawse (1974)	-	4-20x10^{-4}	2-25x10^{-4}	0.5-16x10^{-4}
Estimated wet deposition (μg m^{-2} day^{-1})	1.12	3.59	70.05	81.15

7.8.1.1. Estimated deposition of heavy metals from automotive sources at Chilwell Gardens.

The average daily traffic flow (weekday) for Chilwell gardens was observed to be approximately 150 vehicles. The average Pb content of petrol during the period was 0.38 g l^{-1} (McInnes 1986). A Pb emission rate of 0.028 g $vehicle^{-1}$ km^{-1} would result from this assuming:

a) an average petrol consumption of 27 mpg (C.O.I. 1984);

b) a 30% retention of Pb by the exhaust system (Hirschler et al. 1957; Ter Haar et al. 1972).

The daily flow of vehicles at Chilwell Gardens would therefore emit 4.2 g km^{-1} of Pb. Little and Wiffen (1978) estimate that only 9% of the emitted Pb is deposited within 100 m of the roadway, so that for Chilwell gardens the estimated deposition rate for vehicular derived Pb would be 3.78 µg m^{-2} day^{-1}. Following the reduction in December 1985 of the maximum permissible Pb level in petrol the average Pb content of petrol dropped to 0.14 g l^{-1} (McInnes 1986). At this level the estimated deposition rate for vehicular derived Pb at Chilwell would be 1.14 µg m^{-2} day^{-1}.

The value of 9% for the proportion of Pb deposited close to roads, given by Little and Wiffen (1978), is taken from a motorway study. Under such motoring conditions Pb is emitted mainly as fine particles (<5 µm diameter). During urban driving the proportion of Pb emitted in association with larger particles (5-50 µm diameter) increases, and under stop/start driving conditions Pb trapped in the exhaust system may be released (see Section 2.1.4). Therefore at Chilwell Gardens the value of 9% for the amount of Pb deposited on the road surface is likely to be an underestimate, and a higher proportion of Pb will normally be deposited. Nevertheless, the measured dry deposition rate of 18.21 µg Pb m^{-2} day^{-1} indicates that background sources of Pb dominate the local automotive sources of this metal.

Automobiles are also known to contribute Cd, Cu and Zn to the road surface sediment, but their contribution is more difficult to quantify than for Pb (see Section 2.1.4). For Cd and Zn the major automotive source is the wear of tyres. Estimates of tyre wear and concentrations of Cd and Zn in tyre rubber vary considerably (see Section 2.1.4). Christensen and Guinn (1979) estimate that Zn is released at a rate of 0.003 g $vehicle^{-1}$ km^{-1}. Using these calculations and the D.O.E. (1980) estimate of 5-6 µg g^{-1} for the Cd content of motor tyres, an emission rate for Cd can be approximated at 2.5 x 10^{-6} g $vehicle^{-1}$ km^{-1}. The bulk of tyre wear material is deposited on or very close to the road surface (Harrison and Williams 1979; Cadle and Williams 1980). Assuming that deposition of these metals will take place within 10 m of the source, at the Chilwell Gardens sub-catchment the deposition of Cd and Zn can be estimated at 0.038 μg m^{-2} day^{-1} and 45.0 μg m^{-2} day^{-1}, respectively.

The calculated deposition rate for Cd is considerably less than that recorded in Table 7.1. The D.O.E. (1980) figure for the Cd content of tyres is much lower than that recorded by Lagerwerf and Specht (1972), who reported a range of 20-90 μg g^{-1} for the Cd content of tyre rubber. This would give a roadway deposition rate of Cd at Chilwell gardens in the range 0.15-0.68 μg m^{-2} day^{-1}, which is much closer to the experimental values reported in Table 7.1. The estimated deposition rate for Zn falls within the range of experimental values reported in Table 7.1 for total deposition. However, it is 2.7 times higher than the average value of dry deposition for the catchment, and is considerably higher than the estimated deposition rate for Pb from automotive sources.

The emission of Cu from the brakes of automobiles is also highly variable. Malmqvist (1983) estimates that, of the particulates emitted from brake systems, 1.5 mg $vehicle^{-1}$ km^{-1} are deposited on the road surface. Copper may make up to 3% by weight of the brake pads (Shaheen 1975) and therefore an emission rate of 45 μg $vehicle^{-1}$ km^{-1} can be estimated. If ,like Cd and Zn, it is assumed that the maximum dispersion distance from the source is 10 m, at Chilwell Gardens the road surface deposition rate for Cu for vehicular sources can be estimated at 0.68 μg m^{-2} day^{-1}. This value is much lower than the actual Cu dry deposition rate of 4.78 μg m^{-2} day^{-1} recorded on the Community Centre roof.

From the estimates of vehicular contributions to the inputs of heavy metals into the Chilwell Gardens sub-catchment it can be seen that traffic appears to be a significant source of Zn in the sub-catchment. For Cd, Cu and Pb it is likely that the major inputs to the catchment are from sources outside the boundaries of the catchment. There are no major industrial sources of these metals in the area, and therefore the deposition values given in Table 7.1 would appear to represent fallout from the general urban background. Sampling of airborne heavy metals at the roadside was precluded because of the threat of vandalism and interference with the sampling equipment.

Obviously a number of other sources of heavy metals contribute to metal levels in the Chilwell Gardens sub-catchment. Automotive sources not estimated include leakage of engine oil and also wear and corrosion products. Domestic sources of heavy metals also contribute metals directly to the catchment. The magnitude of these other sources is difficult to quantify even to a low level of precision (see Section 2.1).

7.8.1.2. Heavy metal deposition at Chilwell Gardens.

A major pathway by which metals enter the sub-catchment is via atmospheric fallout. The transfer of trace metals to the catchment surface occurs by dry deposition and by rainfall. In this study it was not possible to sample wet deposition alone, therefore the data reported in Table 7.1 is for bulk deposition. An estimation of the wet deposition is made by subtracting the dry deposition from this value.

The deposition data reported in Table 7.1 indicates that for Pb and Zn wet deposition is by far the dominant mode of fallout, whereas Cd and Cu are deposited equally by both deposition modes. Measurements of metals in deposition given in the literature suggest that a substantial fraction is contributed by dry deposition. Galloway et al. (1982) estimate that for Cd, Cu, Pb and Zn the fraction of the total deposited by dry processes is 60% , 50%, 20% and 50% respectively. Although this is dependent on the type of sampling site (urban or rural) and climate. The type of deposition process exhibited by a metal is also dependent on physical characteristics, such as particle size and solubility, of the metal and its compounds (Cawse 1974; Galloway et al. 1982). The lower levels of Pb deposited in the dry fraction are thought to be due to the predominant association of this metal with finer particles in the atmosphere when compared with the other metals studied (see Table 2.8). Smaller particles are more easily incorporated into falling rain drops (Cawse 1974). The data in Table 7.1 also show that only 21% of Zn is deposited by dry processes yet this metal is associated with much larger particle sizes in the atmosphere (see Section 2.2.4).

The dry deposition velocities of the heavy metals have been calculated and are shown in Table 7.1. Cadmium shows the highest dry deposition velocity with Pb exhibiting the lowest. The values are similar to those reported in the literature (Table 7.1). The deposition velocity of a heavy metal is related in part to the particle size association of that metal (see Section 2.2.5.1). Lead bearing particles typically have a much smaller diameter than those of other metals (see Section 2.2.4, Table 2.8), and so remain airborne for longer periods than other metals. A number of workers have shown that a large proportion of Pb emitted from automobiles remains airborne, and is transported away from the roadside and over long distances (Katen 1974; Huntzicker et al. 1975; Ward et al. 1975; Little and Wiffen 1977, 1978).

The partitioning of metals between the dissolved and particulate phases of rainfall has also been estimated and is discussed in Section 7.9.4. Although bulk (dry and wet) deposition was collected the partitioning of metals was determined by assuming that the dry deposition fraction would be derived entirely from the particulate phase of the bulk deposition. It is realised that changes in the distribution of metals between the solid and dissolved phases of bulk deposition may have taken place in the collection bottle. Therefore the data may not reflect the true partitioning of metals in rainfall.

7.8.2. Overall average heavy metal levels in road surface sediment.

The overall average concentrations and loadings of Cd, Cu, Pb and Zn in sediment on the road surfaces and adjacent pavements at Chilwell Gardens are given in Table 7.2. Although street surface sediments were collected monthly from April to September 1984 only three sampling visits fell within the 8 week period during which both atmospheric and stormwater runoff metal levels were recorded.

Studies of the temporal variations in heavy metal levels have shown that considerable changes in the concentration and loading of metals in street sediments can take place over a relatively short period of time (see Section 2.3.3 and 4.3.2). The metal concentrations observed in this study are similar to those reported by Harrop et al. (1983) and Beckwith et al. (1985) for sediments collected from the same sub-catchment. This would indicate that the metal levels recorded during the period 6 July to 6 September 1984 can be considered to be representative for the Chilwell Gardens sub-catchment. The results are also comparable with those reported in Chapter 4 of this thesis for site C, which is also a residential side street (see Section 4.3.1, Table 4.3). Metal loadings are not reported as extensively in the literature as concentrations, which makes comparisons of experimental values difficult. The metal loadings reported in Table 7.2 are similar to those reported in Chapter 4 for site C (see Section 4.3.1, Table 4.4).

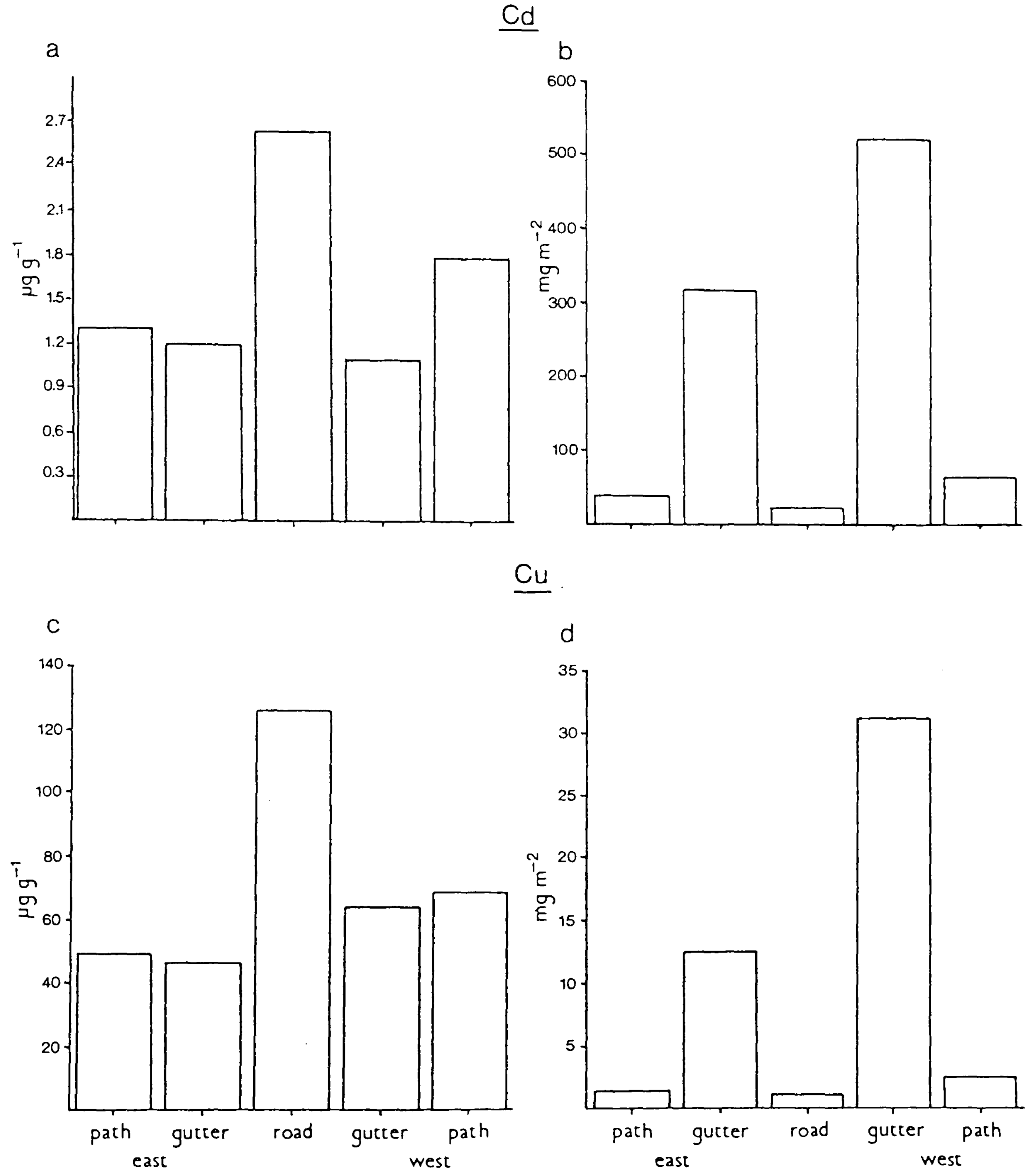
Table 7.2. Overall average heavy metal levels in settled dusts at the Chilwell Gardens sub-catchment.

	Cd	Cu	Pb	Zn
Road surface				
Concentrations ($\mu g\ g^{-1}$)				
mean (n = 30)	1.3	59.5	356.8	331.9
range	0.4-5.3	24.3-207.2	135.4-1537.8	114.9-727.6
Literature values				
Ellis & Revitt (1982)	<0.1-10.1	25.0-3170.0	128.0-8300.0	13.0-1110.0
Harrop et al. (1983)	1.2	54.0	124.0	230.0
Beckwith et al. (1985)	0.5	47.0	429.0	250.0
Road surface				
Loadings ($mg\ m^{-2}$)				
mean (n = 30)	0.08	3.53	21.15	19.67
range	0.007-8.94	0.20-89.34	1.75-530.44	0.29-722.25
Literature values				
Solomon & Hartford (1976)	0.007-0.02	-	1.30-211.00	-

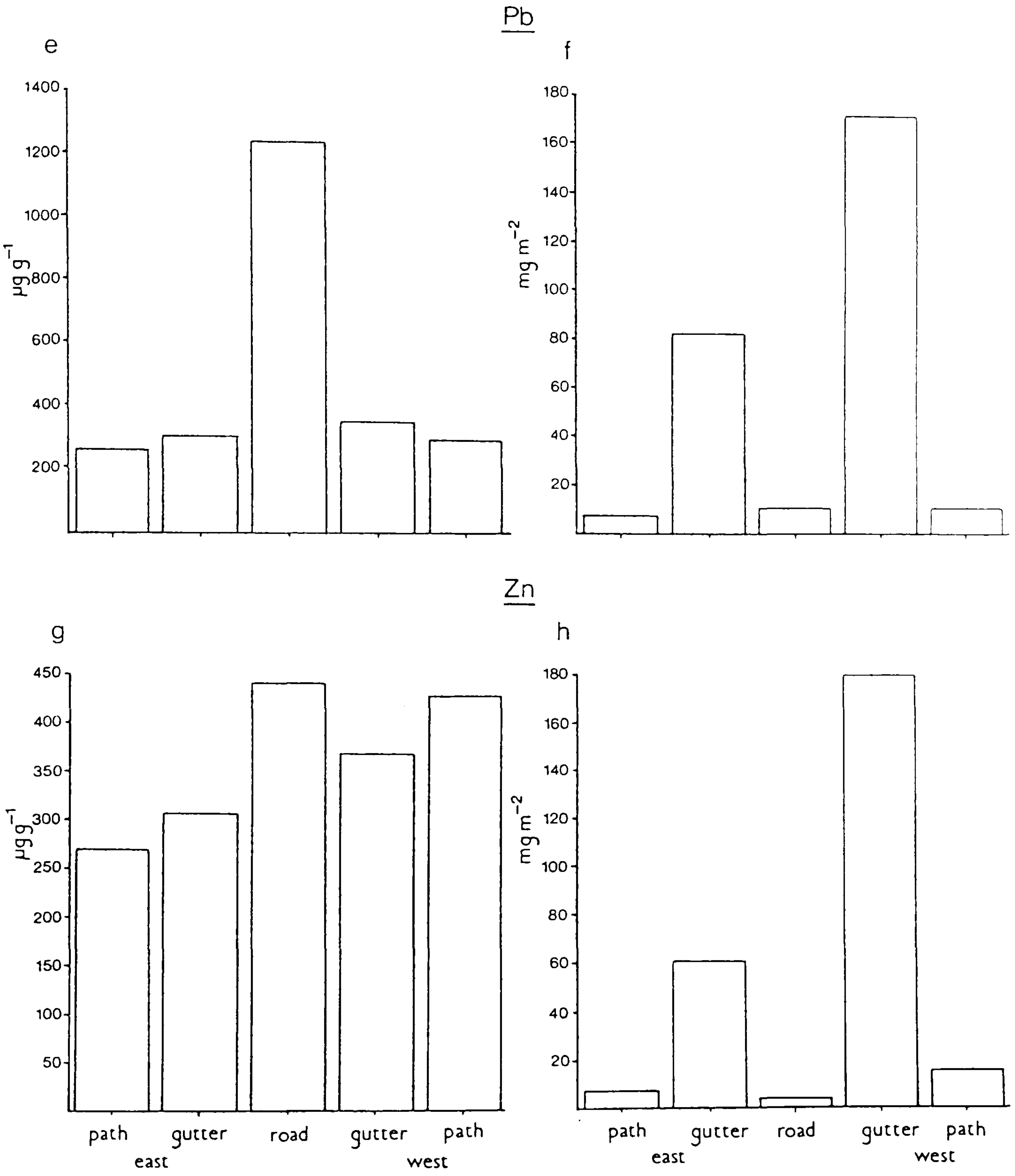
Overall road sediment metal levels at the Chilwell Gardens sub-catchment can be considered typical of those in urban/residential areas.

Road surface sediments were collected along two transects across the road surface and the average heavy metal content in each sample area is shown in Figures 7.3a-h. The concentrations of all metals increase from the pavement to the road surface. The trend is strongest for Cd and Pb, weakest for Zn, with Cu occupying an intermediate position. These spatial distribution patterns confirm those observed by Beckwith et al. (1985) for the same catchment, and are similar to those described in Chapter 4 for site C, the residential side street. All metals exhibit the same spatial distribution patterns for loadings across the road surfaces. The gutters have a markedly higher metal loading than the pavement or road surface, which have generally similar levels. The western gutter, and to some extent pavement surfaces, exhibit enhanced metal loadings when compared with the eastern side of the road. A similar trend has been observed for the sub-catchment by Harrop et al. (1983). The differences were attributed to the more intense human residential activities and car parking on the western side of the road.

Particle size is an important consideration in studies of sediment removal from road surfaces. Revitt and Ellis (1980) have shown that particles <250 µm in diameter are preferentially removed by stormwater runoff. The concentrations and loadings in size fractionated dusts are given in Table 7.3, for both total and exchangeable metals. The metal levels in the bulk sediment are also shown for comparison with Table 7.2. It can be seen that the concentrations and loadings are similar for both methods of determination. The sediments collected at Chilwell Gardens exhibit the widely reported trend of increasing concentration with decreasing particle size (see Section 2.3.4). In the bulk sediment the proportion of metal in the exchangeable fraction is 9.3%, 4.0%, 7.1% and 17.5% for Cd, Cu, Pb and Zn respectively. With the exception of Zn these values are comparable with those reported for bulk sediment in Chapter 5. The relatively high proportion of exchangeable Zn at Chilwell Gardens may be due to differences in source characteristics at this site compared to those reported in Chapter 5. However these results are in general agreement with those of Ellis and Revitt (1982), who in rainwater leachate studies found the extraction efficiencies of the metals to be in the order Cd>Zn, Cu>Pb. Exchangeable metal concentrations exhibit a similar trend to total metal concentrations in relation to particle size, although Cu, Pb and Zn



Figures 7.3 a to d. Levels of Cd and Cu in road surface sediment at Chilwell Gardens.



Figures 7.3 e to h. Levels of Pb and Zn in road surface sediment at Chilwell Gardens.

Table 7.3. Overall average heavy metal levels in size fractionated road sediment at Chilwell Gardens.

		Particle size range (μm)							
		>1000	500-1000	250-500	125-250	63-125	38-63	<38	Bulk total
Concentrations ($\mu g\ g^{-1}$)									
Cd	total	0.6	0.7	2.8	2.3	1.7	3.0	4.1	1.4
	exchangeable	0.08	0.09	0.17	0.21	0.25	0.28	0.32	0.13
Cu	total	27.6	47.2	71.0	76.5	96.7	122.3	139.1	53.0
	exchangeable	0.6	0.5	1.1	3.8	11.3	8.9	8.3	2.1
Pb	total	110.9	292.1	432.3	626.3	749.2	2012.8	1227.1	341.1
	exchangeable	6.5	11.9	36.6	41.7	82.7	62.8	73.6	24.2
Zn	total	207.2	278.9	392.1	475.8	681.7	818.6	878.0	341.4
	exchangeable	52.6	33.0	53.6	84.5	114.6	112.9	99.2	59.9
Loadings ($mg\ m^{-2}$)									
Cd	total	0.010	0.005	0.018	0.012	0.004	0.003	0.002	0.054
	exchangeable	0.0014	0.0006	0.0011	0.0011	0.0006	0.0003	0.0002	0.0052
Cu	total	0.470	0.312	0.452	0.408	0.229	0.144	0.076	2.091
	exchangeable	0.010	0.003	0.007	0.020	0.027	0.011	0.004	0.083
Pb	total	1.890	1.936	2.753	3.344	1.774	1.098	0.669	13.644
	exchangeable	0.110	0.079	0.233	0.223	0.196	0.074	0.040	0.954
Zn	total	3.531	1.848	2.497	2.540	1.614	0.964	0.479	13.475
	exchangeable	0.897	0.219	0.341	0.451	0.271	0.133	0.054	2.366

concentrations show a slight enhancement in the 38-125 µm size range. An increase in exchangeable metal concentrations with decreasing particle size was also noted in Section 5.3.3 for sediments collected from the M1 motorway and A41 Hendon Way. This trend was attributed to the increased surface area and hence increased number of exchange sites of fine particles. Metal loadings in both the total sediment and exchangeable fraction exhibit enhanced levels in the medium size range (63-500 µm). Similar observations have been made by Harrison and Biggins (1980).

In addition to road surface sediments, settled dusts were collected from the roof and guttering of the terraced houses which form part of the sub-catchment. The levels of metals in these sediments are reported in Table 7.4.

Table 7.4. Overall average heavy metal levels in roof sediment at the Chilwell Gardens sub-catchment.

	Cd	Cu	Pb	Zn
Roof surface Concentrations (µg g^{-1}) mean (n = 2)	1.1	28.4	870.8	226.7
Literature values Beckwith et al. (1985)	1.2	17.3	322.6	211.5
Roof gutter Concentrations (µg g^{-1}) mean (n = 2)	1.1	26.7	668.6	234.0
Roof surface Loadings (mg m^{-2}) mean (n = 2)	0.003	0.07	2.23	0.58
Roof gutter Loadings (mg m^{-1}) mean (n = 2)	0.12	2.80	70.20	24.57

Very few examples of metal levels in sediment collected from roofs are available in the literature for comparison with the values reported in Table 7.4. Beckwith et al. (1985) have observed similar metal concentrations to those recorded in this study for an earlier study in the same catchment. The most notable difference between the two data sets is the enhanced Pb concentration recorded in roof gutter sediments during the present investigation. The roof surface sediments show lower concentrations of Cd, Cu and Zn but enhanced levels of Pb when compared with the road surface sediments presented in Table 7.2. The differences in atmospheric particle size associations of these metals may provide an explanation for this trend. As previously noted, atmospheric Pb tends to be associated with finer particles than the other metals studied here, and hence is carried further from source. The major automotive sources of Cd, Cu and Zn are the wear products of brake linings and tyres which tend to be deposited close to source. Unfortunately determination of the particle size associations of metals in roof sediment was not carried out because of the small quantities of sediment collected.

7.8.3. Levels of heavy metals in stormwater discharged from the sub-catchment.

Four runoff events were sampled between 6 July and 6 September 1984. The storms varied in length from 35 minutes to 4.4 hours with peak flow rates of between 1.19 l s^{-1} and 3.14 l s^{-1}. The total volume of rainfall and runoff for each storm event are given in Table 7.5. In addition to those storms listed, two rainfall events were recorded by the raingauge located on the Community Centre roof, but no simultaneous runoff was captured by the stormwater sampling system.

Table 7.5. The total rainfall and runoff volume for each storm.

Date of storm	Length (min)	Peak flow rate (l s^{-1})	Rainfall volume (l)	Runoff volume (l) road	Runoff volume (l) roof
14-7-84	233	1.71	12349.5	2642.6	5271.2
8-8-84	246	1.19	3145.6	1204.8	1334.4
23-8-84	35	2.80	1864.5	406.5	781.0
6-9-84	264	3.14	6160.2	2570.4	2572.8

The average total metal concentration (dissolved and particulate associated) for all storm events are shown in Table 7.6. These values were determined by calculating the total metal mass discharged during the four recorded storms and dividing this value by the total volume of runoff in the sample period. It is clear from Table

Table 7.6. Levels of heavy metals in stormwater monitored at the Chilwell Gardens sub-catchment.

	Cd	Cu	Pb	Zn
Stormwater				
mean (4 storms)				
Dissolved (µg l^{-1})	0.87	7.65	12.76	46.22
Particulate (µg l^{-1})	0.39	1.10	14.27	10.22
(µg g^{-1})	29.9	83.1	1082.1	744.8
Total concentration (µg l^{-1})	1.26	8.75	27.03	56.44
range	0.05-3.09	0.05-14.29	0.57-150.53	0.70-65.30
Literature values				
Total concentration (µg l^{-1})				
Ellis & Revitt (1982)	0.8-8.0	7.0-1410.0	250-26000	8-4600
Suspended solids (µg g^{-1})				
Revitt et al. (1982)	0-670	160-1660	1200-8500	700-8000
Roof runoff				
Total concentration (µg l^{-1})				
mean (4 storms)	1.20	13.68	38.57	22.19

7.6 that a wide range of concentrations exist for all 4 metals. The stormwater concentrations recorded at Chilwell Gardens are low when compared with those reported in the literature (see also Section 2.5). This may be due to the nature of the catchment, Chilwell Gardens being a lightly trafficked residential highway. Differences between catchment characteristics such as location, traffic volume and geology make direct comparisons with the literature data difficult.

A feature of the data shown in Table 7.6 is the high average total concentration of Zn relative to that for Pb. Ellis and Revitt (1980, 1982) have examined the solubility of metals in rainwater and have shown the highest leachate levels are produced by Zn. In Section 7.8.2 it was noted that road sediments at Chilwell Gardens contained a relatively high exchangeable Zn content, when compared with those reported elsewhere (see Section 2.4.4 and 5.3.1). This will contribute to the elevated levels of Zn in the dissolved phase of stormwater runoff, confirmed in Table 7.6.

The concentration ranges of metals found in the suspended solids are also shown in Table 7.6. It can be seen that the concentrations of all metals in the suspended solids are highly variable, and the maximum levels are considerably higher than those reported in Tables 7.2 and 7.4 for contributing catchment surface sediment. This is particularly evident for Cd which has an average concentration of 1.3 $\mu g\ g^{-1}$ in road surface sediment and an average concentration of 29.9 $\mu g\ g^{-1}$ in stormwater solids. Previous work has suggested that hydrodynamic sorting of road sediments may take place during storm events which leads to the preferential removal of highly contaminated fine particles (see Section 2.5.7). However, a comparison of the metal concentrations in suspended sediment with the metal concentrations in size fractionated road sediment reveals the former to be elevated in comparison with even the finest road sediment. For Cd the peak stormwater sediment concentrations exceeded concentrations in the <38 um fraction of road sediment by 50 times.

The results given in Table 7.6 show that Cd, Cu and Zn are predominantly found in the dissolved phase of runoff. This phase contains 69% of the Cd, 87% of the Cu and 82% of the Zn leaving the Chilwell Gardens catchment. For Pb the the dissolved phase contains 47% of the total metal content. A similar distribution between dissolved and particulate fractions has been observed by Morrison et al. (1984b), and Harrison and Wilson (1983, 1985).

The concentrations of heavy metals in roof runoff at Chilwell Gardens are shown in Table 7.6. There are very few studies in the literature which report metal levels in roof runoff for comparison with the present investigation. Where such studies have been made comparisons are difficult because metals such as Cu have been used as roofing material (Malmqvist 1983). The roof runoff metal concentrations were determined using a Warren Jones sampler located in the pipe draining the terraced houses (see Section 7.4.4.3). This provides only a crude indication of stormwater quality from this area of the catchment. Nevertheless, at Chilwell Gardens the average concentrations of Cu and Pb in roof runoff are elevated relative to comparable values recorded for the total catchment. Lead levels in roof sediment were higher than those recorded for road sediment and so elevated Pb levels of this metal in roof runoff may be expected. Additionally, the relative concentrations of Cd and Zn in road and roof sediment are mirrored in the roof runoff levels of these two metals. The enhancement of Cu in roof runoff suggests that an additional source of this metal, such as roof fittings may be present. In Scandinavia, where Cu and Zn are commonly used in roofing and guttering, corrosion can generate significant quantities of these metals in stormwater runoff (Malmqvist and Svensson 1977; Morrison 1985).

7.9. Metal Mass Balance Studies.

7.9.1. A mass balance for heavy metals in the Chilwell Gardens sub-catchment.

The total mass of metal deposited from the atmosphere onto the Chilwell gardens sub-catchment, and the total metal mass discharged from the sub-catchment during the 8 week period commencing 6 July 1984, are given in Table 7.7. The total input mass was calculated as the product of the average deposition rate, the time period and the effective area of the catchment including the roof area of the 4 terraced houses. The total metal mass discharged in stormwater over the 8 week period was calculated by integrating the product of metal concentration ($\mu g\ l^{-1}$) and flow rates ($l\ s^{-1}$) over each of the four storms recorded in that period. Also included in Table 7.7 is an estimate of the total direct vehicle derived metal input to the catchment during the sampling period. This was calculated from the estimated daily deposition rates of metals to the road surface given in Section 7.8.1.1.

Table 7.7. The total metal inputs and outputs at the sub-catchment.

	Cd	Cu	Pb	Zn
Total metal inputs to the catchment by atmospheric deposition (g)	0.10	0.41	4.48	4.61
Total metal discharge from the catchment in stormwater (g)	0.02	0.15	0.45	0.95
Estimated direct input of metals from vehicle sources (g)	<0.01	0.02	1.13	1.34

It can be seen from Table 7.7 that for all four metals studied the mass deposited from the atmosphere greatly exceeds that removed by runoff during the sampling period. Copper shows the largest proportion of deposited metal discharged in runoff at 36% whilst Pb produces the least at 10%, Cd and Zn occupy an intermediate position with approximately 20% of the input metal discharged in stormwater runoff. Table 7.7 also shows that the for Pb and Zn the estimated input of metal from vehicular sources exceeds the total metal discharged in stormwater during the sampling period. As these are direct vehicle inputs the estimated deposition values given in Table 7.7 are for the road surface only. For Cd and Cu the direct inputs of heavy metals to the road surface are considerably lower than the total discharge of these metals.

The results shown in Table 7.7 support the view that atmospheric deposition is a major process responsible for heavy metal in stormwater. Malmqvist (1983) in a similar study of 3 catchments in Sweden found that only 4-8% of Pb entering the catchment was recorded in the stormwater outflow leaving the catchment. For Cu and Zn the proportions of total metal discharged in runoff were higher but more variable at 19-67% and 20-31% respectively.

The metal mass balances for each individual storm event are shown in Table 7.8. Overall the individual storm events show the same input-output relationship to the total mass balance for the sampling period. For storms B-D the total mass of metal deposited since the previous storm on the catchment exceeds the amount discharged. This analysis could not be extended to storm A as the period since last rainfall was not accurately known, the total metal deposition during the previous week is given for storm A in Table 7.8. The amount of metal discharged from the catchment varies greatly between storms for each metal. Copper shows the greatest variation of 5.9% to 76.6% and Pb the least (1.8 to 8.2%). Storm D shows the most efficient metal removal rate for each metal. The storm characteristics given in Table 7.5 indicate that this storm had the highest peak flow rate, more efficient hydrological scouring of the catchment surfaces may have produced the higher metal removal rates exhibited in Table 7.8 .

Table 7.8. Total metal mass balance for individual storms collected at Chilwell gardens.

Storm	Total metal deposition (g)	Total metal discharge (g)	Percent of deposited metal present in discharge
Cd			
A 14-7-84	0.008	0.011	-
B 8-8-84	0.042	0.003	7.1
C 23-8-84	0.021	0.001	4.8
D 6-9-84	0.026	0.006	23.1
Cu			
A 14-7-84	0.023	0.090	-
B 8-8-84	0.303	0.018	5.9
C 23-8-84	0.031	0.008	25.8
D 6-9-84	0.051	0.039	76.5
Pb			
A 14-7-84	0.176	0.204	-
B 8-8-84	1.771	0.138	7.8
C 23-8-84	1.477	0.026	1.8
D 6-9-84	1.052	0.086	8.2
Zn			
A 14-8-84	0.215	0.358	-
B 8-8-84	2.107	0.104	4.9
C 23-8-84	0.942	0.073	7.7
D 6-9-84	1.344	0.412	30.7

The total metal deposition data reported in Table 7.7 represents bulk deposition of metals for the 8 week sampling period. Subtraction of the total metal dry deposition from the bulk deposition data gives the mass of metal deposited during the four rainfall events recorded, assuming all rainfall events were sampled. This data is shown in Figures 7.4 a-d. The metal budget for the storm events alone indicates that of the metal deposited during precipitation events Cu shows the highest proportion (92%) of the metal in the stormwater outflow which could be considered to be derived directly from wet deposition. Lead exhibits the lowest proportion (13%), followed by Zn (22.5%) and Cd (43%). The street surfaces are therefore retaining a significant proportion of the metal deposited in wet fallout. Randall et al. (1978, 1979 and 1982), and Mance (1981), indicated that wash-out of metals during storm events was the dominant source of metals in runoff. Randall et al. (1982) also noted that atmospheric contaminants, including heavy metals, are washed out during the first stages of precipitation and so the resulting ground surface loadings of atmospheric pollutants are independent of the magnitude or intensity of the rainfall. Furthermore, the deposition rate of atmospheric pollutants by dry deposition was found to be considerably less than the deposition rate during precipitation. This is confirmed for Pb and Zn in Figures 7.4c and d, Cu shows the reverse trend (Figure 7.4b). Cadmium was deposited in approximately equal proportions by wet and dry modes (Figure 7.4a). Other workers have found that precipitation provided only a small percentage of those metals leaving an urban area as runoff (Owe et al. 1982). The relative contributions of dry and wet deposition will depend on the catchment characteristics. Owe et al. (1982) studied contaminant levels in rainfall and runoff for a car park catchment. Direct inputs of heavy metals from heavy motor vehicle activity were observed to contribute a substantial proportion of the metal pollutant loads in surface runoff.

7.9.2. Metal loadings on the catchment surfaces.

The total amount of metal on the catchment surface during the sampling period has been estimated from the metal loadings given in Tables 7.2 and 7.4. The total metal loading for roof sediment (roof surfaces and guttering) is included in this estimation. The values are shown in Figures 7.4 a-d. A breakdown of the total metal loading in the

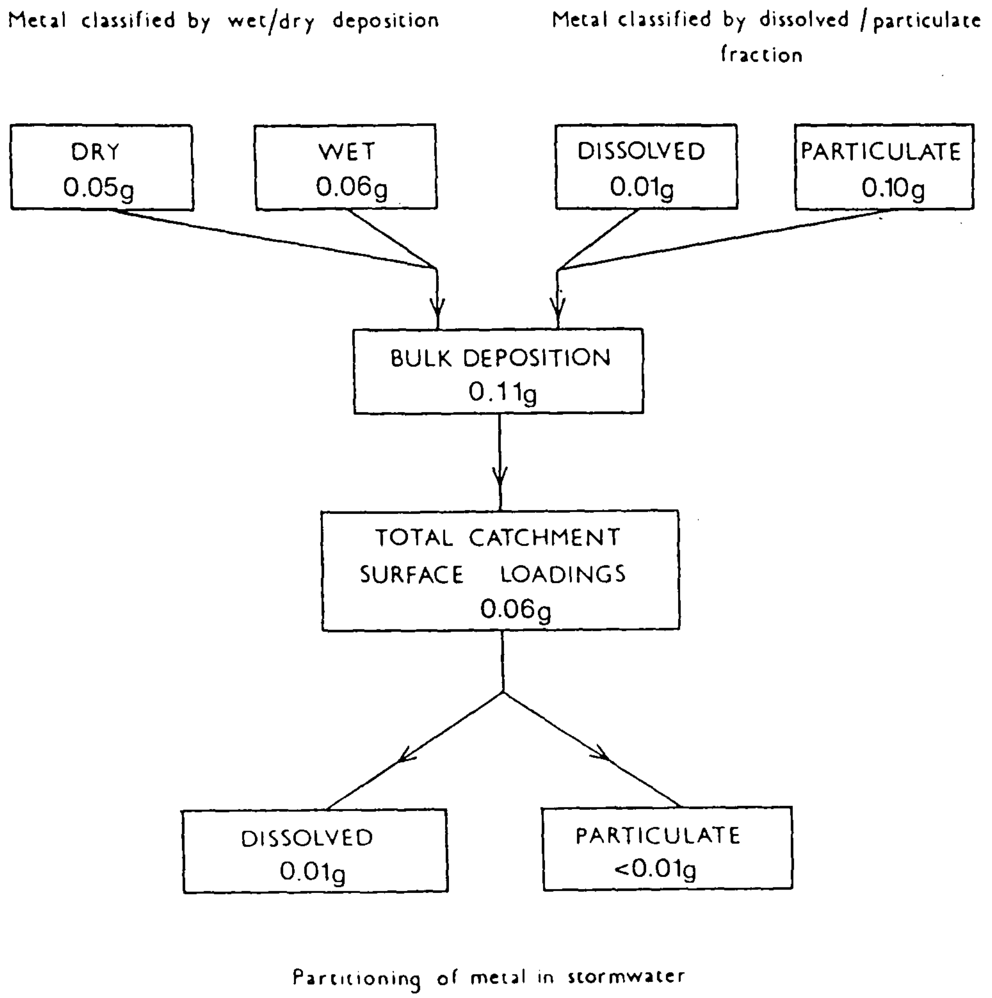


Figure 7.4a. A mass balance for Cd at Chilwell Gardens.

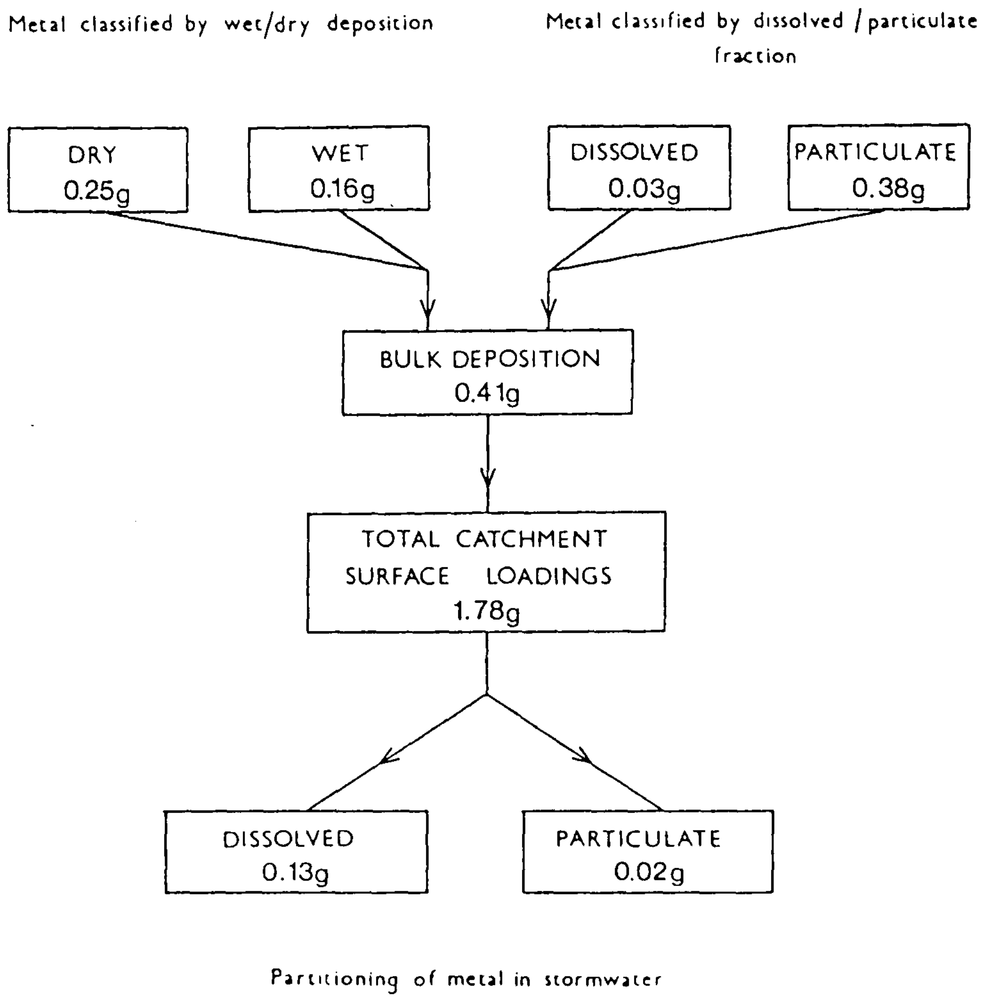


Figure 7.4b. A mass balance for Cu at Chilwell Gardens.

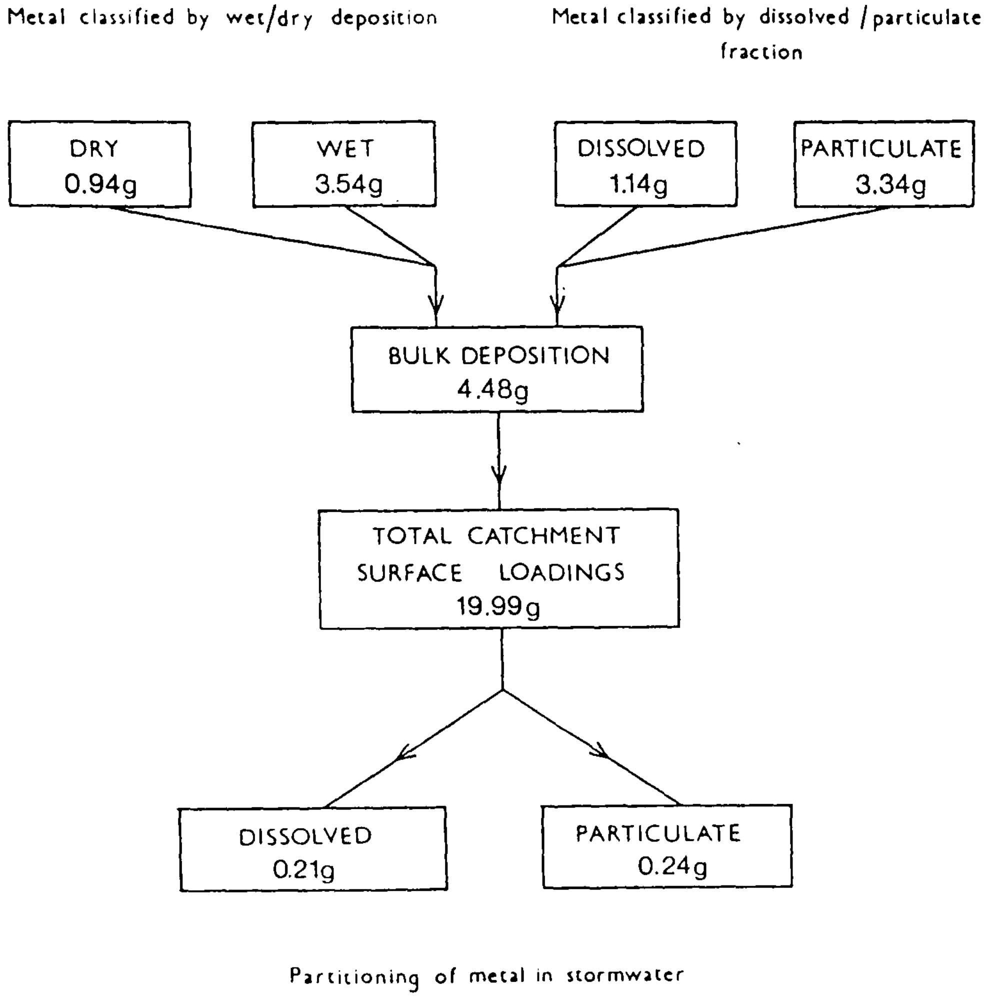


Figure 7.4c. A mass balance for Pb at Chilwell Gardens.

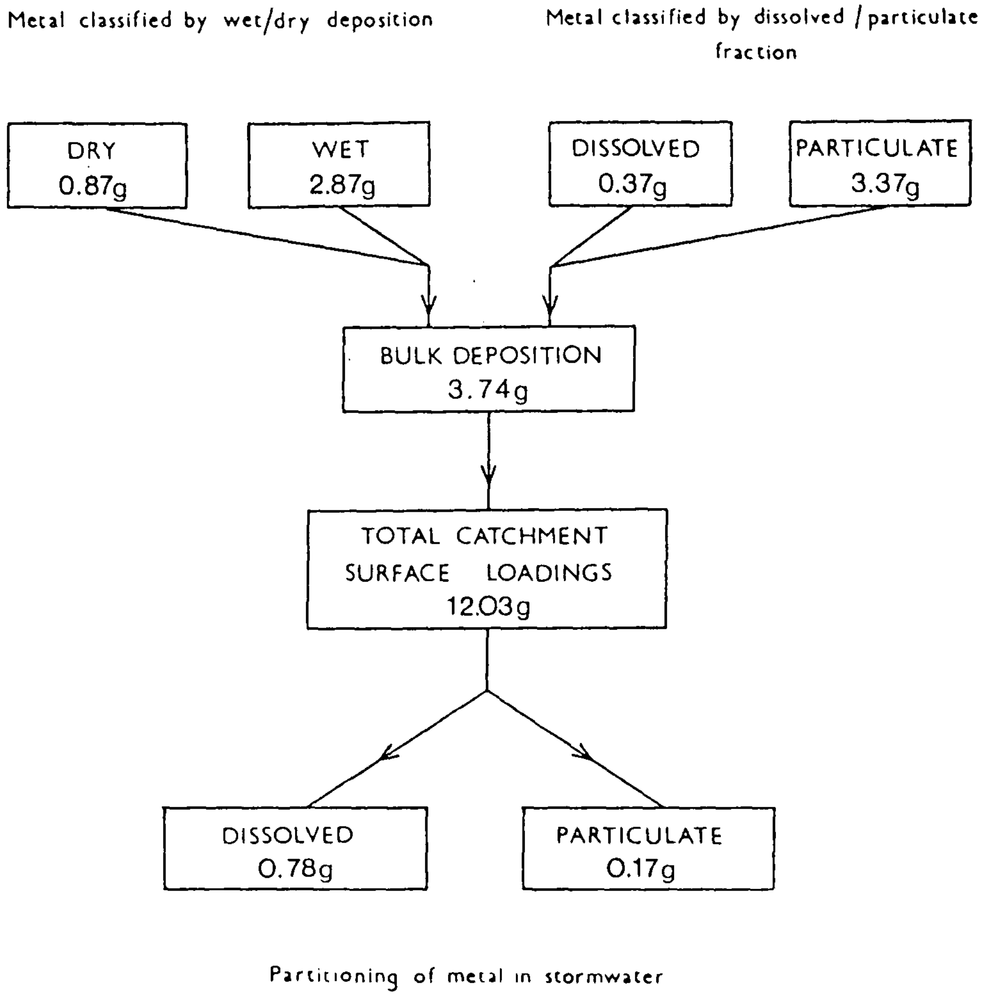


Figure 7.4d. A mass balance for Zn at Chilwell Gardens.

sub-catchment is given in Table 7.9. For all metals the total amount of metal on the road surface exceeds the loading on the roof surfaces and guttering combined. Lead shows the most equal distribution between the two parts of the catchment, Cu the least. Roof sediment represents approximately one third of the total Cd and Zn in the catchment. On the roof surfaces the bulk of the metal is found in the guttering. Overall the surface sediment represents a considerable pool of metals from which metals in stormwater runoff are derived and to which atmospheric deposition adds metals. Only for Cd does the input from deposition during the sample period exceed the total mass of metal on the street surfaces. The ratio of total metal in stormwater to the total mass on the street surface indicates that the order of ease of removal is Cd>>Cu, Zn>Pb which corresponds to the work of Ellis and Revitt (1982). However, it can be seen from Table 7.9 that the total surface loadings of exchangeable metals indicate an order of availability to stormwater runoff of Zn>Cd>Pb>Cu, which corresponds to the results of the detailed sequential extraction experiments described in Chapter 5.

Table 7.9. The total surface loadings of metals at Chilwell gardens (g).

	Cd	Cu	Pb	Zn
Road surfaces	0.04	1.41	10.61	8.83
Roof surfaces	<0.01	0.03	0.88	0.23
Roof gutters	0.01	0.26	6.57	2.30
Total	0.06	1.78	19.99	12.03
Exchangeable fraction	0.005	0.07	1.40	2.11

It has been argued that the fraction of road sediment which is most susceptible to removal by stormwater is the size range containing particles finer than 250 µm (Revitt and Ellis 1980). The proportion of metal associated with this size fraction has been calculated from the data in Table 7.3 and is presented in Table 7.10. The data given in this Table when compared with that shown in Table 7.9 indicates that of the metal deposited on the road surface approximately 30-34% is associated with particle sizes <250 µm in diameter, and therefore susceptible to physical transport off the road surface by stormwater runoff. The proportion of metal sediment loading which is available for solubilisation by stormwater runoff can also be determined from Table 7.3. Approximately 8% of the Cd, Cu and Pb, and 16% of the Zn is found in the exchangeable fraction of <250 µm sized sediment (Table 7.10).

Table 7.10. The mass of metal associated with the <250 µm size fraction.

	Cd	Cu	Pb	Zn
Total metal <250 µm (g)	0.012	0.457	3.670	2.984
Exchangeable metal <250 µm (g)	0.001	0.033	0.284	0.485

By combining the data in Tables 7.9 and 7.10, it is possible to estimate the total mass of metal on the catchment surface available to stormwater runoff by physical transport processes and solubilisation by rainfall. This estimation suggests that: 0.016 g of Cd; 0.494 g of Cu; 4.786 g of Pb; and 4.609 g of Zn, on the catchment surfaces were potentially available to stormwater during the sampling period. Comparison of these estimations with the total mass balance data given in Table 7.7 shows that for Cu, Pb and Zn the quantity of metal potential available corresponds to the total metal deposition during the sampling period and therefore exceeds the amount of metal discharged in stormwater. For Cd the amount of metal potential available approximates to that discharged in stormwater runoff. Cadmium is widely recognised as being a metal which is highly mobile in environmental terms (see Sections 2.4.5 and 5.3.4).

7.9.3. Contributions of roof runoff.

The Chilwell Gardens sub-catchment can be considered as two distinct catchment types:

a) road surface contributions (393.53 m^2);
b) roof surface contributions (533.09 m^2).

The total mass balance for the metals on the roof surfaces have been separated from the sub-catchment mass and are shown in Table 7.11. The total mass of metal deposited on the roof surfaces represents 43% of the total metal deposition on the catchment during the eight week sampling period. The total discharge in roof runoff has been calculated as the product of the roof runoff concentration (Table 7.6) and total rainfall volume for the eight week sampling period. From the data in

Table 7.11 roof runoff appears to contribute a significant proportion of Cd, Cu and Pb to the total discharge but makes a minor contribution for Zn. As with the mass balance for the whole catchment the total inputs of metals far exceed the total amounts discharged. However, whereas the road surfaces appear to act as a sink for the metals the amount of metal lying on the roof surfaces does not represent such a pool (Table 7.9). The steep slope of the roof allows greater removal efficiency of sediments, leading to a relatively enhanced contribution of total metals in the catchment runoff. The roof guttering acts as a trap for sediment and associated metals transported off the roof surfaces by rainfall.

Table 7.11. A mass balance for total metals on the roof surfaces at Chilwell Gardens.

	Cd	Cu	Pb	Zn
Total mass of metal deposited on roof surfaces (g)	0.043	0.175	1.912	1.968
Total mass of metal removed from roof surfaces in runoff (g)	0.009	0.098	0.277	0.159
Percent of deposited metal discharged in runoff	20.9	56.0	14.5	8.1
Percent of total metal output from catchment	45.0	65.3	61.6	16.7

7.9.4. Partitioning of heavy metals between the dissolved and particulate fractions of rainfall and runoff.

The total mass of Cd, Cu, Pb and Zn in the dissolved and particulate associated fractions of the deposition and stormwater runoff are shown in Figures 7.4 a-d. It must be stressed that the partitioning was carried out on samples of total deposition. The dissolved fraction therefore includes metals dissolved in rainfall and also the soluble fraction of dry deposited particulates. The particulate associated fraction includes particulates in rainfall as well as insoluble metal in dry deposition.

From the deposition values it is apparent that the heavy metals studied are mainly associated with the particulate fraction. The percentage of soluble metal in deposition collected at Chilwell Gardens is 17%, 19%, 32% and 8% for Cd, Cu, Pb and Zn respectively. From the literature the proportion of soluble metal in rainfall, although variable, is generally considered to be high with Pb exhibiting the greater tendency to associate with the particulate fraction (Cawse 1974; Ruppert 1975; Galloway et al. 1982). There may be a number of reasons for the discrepancy between the results of this study and those described in the literature. It could be that either the dry deposition values obtained from the A.E.R.E deposition collector and quoted in Table 7.1 are an underestimate; or that while the bulk deposition remained in the collection vessel prior to collection metals were adsorbed onto particulates from the dissolved phase. An accurate assessment of heavy metal partitioning in rainfall would have required a wet only deposition collector which was not available for this study.

With the exception of Pb the greater proportion of each metal leaving the sub-catchment in stormwater runoff is in the dissolved phase which represents 69% of Cd, 82% of Zn and 88% of Cu discharged during the 8 week period (Figure 7.4 a-d). For Pb, 47% of the metal is discharged in the particulate phase in stormwater. This is low when compared with levels reported by other workers, who have found Pb to be predominantly associated with the particulate phase whereas Cd, Cu and Zn are mainly found in the dissolved phase (Harrison and Wilson 1985; Morrison 1985).

It was observed from the data in Table 7.6 that stormwater sediments at Chilwell Gardens are considerably enhanced in concentration relative to the street surface sediments from which they are derived. It has been suggested that this is due in part to the hydrodynamic sorting of finer particles (Harrison and Wilson 1983; Harrop et al. 1983). Metal concentrations in stormwater solids are even higher than those found in the fine fractions of street sediments (Morrison et al. 1984b) and this is confirmed in this study (see Section 7.8.3, Tables 7.2 and 7.3). A possible explanation for these trends suggests that when acidic rainfall washes over the catchment, surface metals are transferred to the dissolved phase and on entry to the below ground system the road runoff, initially weakly buffered by surface sediment, undergoes further buffering. The pH gradually increases and metals are readsorbed on to suspended sediment. As the suspended sediment in stormwater consists of predominantly fine particles with a relative high surface area to unit mass, enhancement of metal concentration results.

7.9.5. The role of the roadside gully pot.

The roadside gully pot acts as a settling chamber for particulates transported from the road surface. The gully pot has also been shown to contribute to pollution levels in stormwater runoff by exerting a significant influence on the processes described in Section 7.9.4. The levels of metals in the two roadside gully pots at Chilwell Gardens are shown in Table 7.12. Metal concentrations in gully pot basal sediments are elevated for all metals relative to the contributing surface sediments. This has been attributed to the settling of metal rich fine particles which have been preferentially washed off the street surface (Harrop et al. 1983). However, the gully pot has been shown to be effective as a settling chamber only for particles >1 mm in diameter (Pratt and Adams 1982), and an enhancement in all particles sizes of sediment trapped in the gully pot has also been observed (Beckwith et al. 1984). The average concentrations of all four metals are elevated in gully pot liquor when compared with the stormwater levels given in Table 7.5. Metal levels in gully pot liquors have been observed to increase between storm events (Mance and Harman 1978; Morrison 1985). It is suggested that bacterial activity causes a reduction in the dissolved oxygen content of the liquor which leads to the release of metals bound to hydrous oxides (see Section 5.3.4), and to chemical reactions between the acidic liquor and basal sediment (Morrison 1985). After a storm event gully liquor is relatively clean and overlies metal rich basal sediment. Metals are then leached out of the sediment with the increase in gully pot liquor metal concentrations depending on:

a) the initial liquor concentration;
b) the initial sediment concentration;
c) the length of the dry period.

The average total metal content of the gully pot liquor during the eight week sampling period has also been calculated (Table 7.12). This data indicates that the chamber acts as a significant storage basin for metals in the catchment. With the onset of a storm event these metals will be flushed from the gully pot and will produce a peak in metal concentrations on the metal chemograph often described as the first flush (Wilber and Hunter 1980; Mance 1981; Harrop 1984).

Table 7.12. Metal levels in the roadside gully pots at Chilwell Gardens.

	Cd	Cu	Pb	Zn
Standing liquor				
Concentrations ($\mu g\ l^{-1}$)				
western gully pot	1.97	28.62	107.32	64.17
eastern gully pot	1.47	16.19	83.00	51.07
Total metal content (mg)				
western gully pot	0.39	5.72	21.47	12.83
eastern gully pot	0.29	3.24	16.60	10.21
total	0.68	8.96	38.07	23.04
Basal sediment				
Concentration ($\mu g\ g^{-1}$)				
western gully pot	4.1	66.5	542.6	371.8
eastern gully pot	3.4	46.5	526.4	282.6

7.10. Transport mechanisms for street surface sediments.

In addition to removal of sediments by stormwater other processes responsible for the removal of deposited metals are resuspension of surface sediments and municipal street cleaning.

7.10.1. Resuspension of street sediments.

Resuspension of street sediments may be induced by the passage of motor vehicles over the sub-catchment or by wind action. The basic model for vehicle induced resuspension is described in Chapter 4 (see Section 4.3.3). This model shows that for sites with low traffic densities (<30 vehicles hr^{-1}), vehicle induced resuspension is negligible. For Chilwell Gardens, which has a traffic density of 150 vehicles per day, it can be calculated that it would take several months of dry weather for vehicle induced resuspension to become a dominant removal process.

Wind induced resuspension can also be shown to be ineffectual in removing sediment from the catchment. Sehmel (1980b) reports wind induced resuspension factors in the range 10^{-10}-10^{-3} m^{-1}. Substitution of these into the model derived in Chapter 4 indicates that wind induced resuspension for the road surface dust would dominate after 1.2 years and therefore can also be considered negligible at this site.

7.10.2. The effect of street sweeping on metal removal.

Control measures such as street sweeping have been shown to remove 30-60% of the metal available to runoff (Malmqvist 1978). At Chilwell Gardens the effectiveness of street sweeping is difficult to assess. The municipal authority employ manual sweepers to clean the gutters along each road in the Oxhey catchment. The frequency of cleaning was claimed to be once per week for each street, however during the sampling programme the street sweeper was observed in the sub-catchment only on one occasion. From the data recorded in Section 4.3.6 street cleaning is shown to reduce metal loadings by approximately 50% for a single pass. The total amount of metal removed can therefore be estimated for Chilwell Gardens (Table 7.13). It can be seen from this Table that considerable quantities of metal, relative to that removed by stormwater, can be removed from the catchment by street sweeping. Manual street sweeping has been reported to be more effective than mechanical road sweeping (Ellis 1979). Street sweeping in areas such as Chilwell Gardens, particularly of the road gutters, is not always practical as cars are often street parked blocking off the path of the sweeper.

Table 7.13. Estimated metal mass removed from the Chilwell Gardens sub-catchment by street sweeping during the sample period (g).

Cd	Cu	Pb	Zn
0.007	0.442	2.430	2.540

7.11. A Predictive Model for Metal Concentrations in Stormwater Runoff.

The results of the mass balance studies described in preceding sections allow the construction of a simple model which relates heavy metal deposition rates on to the catchment surface at Chilwell Gardens, with the concentrations of metals in runoff from the catchment.

In considering metal inputs to the catchment over a dry period of time ,t (s), the metal mass deposited by dry deposition, I_d (µg), is given by:

$$I_d = D_d \; t \; (A_{rd} + A_{rf})$$

where D_d is the dry deposition rate ($\mu g \; m^{-2} \; s^{-1}$), and A_{rd} and A_{rf} are the areas (m^2) of the road surface and roof surface, respectively.

The dry deposition rate, D_d, is related to the airborne concentration of metal, C_a ($\mu g \; m^{-3}$), and the deposition velocity, V_d ($m \; s^{-1}$), by the relationship:

$$V_d = D_d/C_a$$

$$\text{so } I_d = C_a \; V_d \; t \; (A_{rd} + A_{rf})$$

The mass of metal deposited on the catchment by precipitation, I_w (μg), can be similarly described by the expression:

$$I_w = C_p \; P \; (A_{rd} + A_{rf})$$

where C_p is the concentration of metal in precipitation ($\mu g \; m^{-3}$), and P is the depth of precipitation (m) falling on the catchment.

The mass of metal removed in runoff is the combined metal input by wet and dry deposition to the road and roof surfaces less that mass of metal which is:

a) adsorbed onto surface sediments;
b) retained by the gully pots;
c) retained in the roof guttering;
d) deposited in the underground drainage system;
e) lost through resuspension and dispersion;
f) removed by street sweeping.

The mass of metal in runoff, R (μg), is thus:

$$R = A_{rd} \; f_{rd} \; (C_a \; V_d \; t + C_p \; P) + A_{rf} \; f_{rf} \; (C_a \; V_d \; t + C_p \; P)$$

where f_{rd} is the fractional removal efficiency of the road surface and f_{rf} is the fractional removal efficiency of the roof surfaces.

For highway surface runoff to occur certain water storage thresholds must be exceeded. These result from surface ponding, evaporation/wind losses and infiltration capacity. A volume P $(A_{rd} + A_{rf})$, of precipitation will therefore produce a lower volume, S (m^3), of stormwater runoff.

The concentration of metal in stormwater runoff, C_r ($\mu g\ m^{-3}$), can be obtained from the expression:

$$C_r = R/S$$

7.11.1. Comparison with experimental values.

The mean values of C_a and V_d for Cd, Cu, Pb and Zn obtained from an eight week sampling period are given in Table 7.1. The concentration of these metals in precipitation (C_p) can be derived from the data in Table 7.1 and the total volume of rainfall presented in Table 7.5. The total runoff volume (S) can be obtained from Table 7.5. The fractional removal efficiencies for the road and roof surfaces derived from data in Tables 7.7 and 7.11 are given below in Table 7.14.

Table 7.14. The fractional removal efficiencies of Cd, Cu, Pb and Zn for the road and roof surfaces at Chilwell Gardens.

	Cd	Cu	Pb	Zn
Road surface removal efficiency (f_{rd})	0.19	0.22	0.07	0.30
Roof surface removal efficiency (f_{rf})	0.21	0.56	0.14	0.08

To check the accuracy of the computation, substitution of these values into the predictive model described above produces the total mass of each metal removed in stormwater over the eight week sampling period:

$$R_{Cd} = 533.09*0.19\ (1.05\text{x}10^{-3}*0.01*4752\text{x}10^{3} + 2431.0*0.0253)$$
$$+$$
$$393.53*0.21\ (1.05\text{x}10^{-3}*0.01*4752\text{x}10^{3} + 2431.0*0.0253)$$

$$= 20476.0\ \mu g$$

$$R_{Cu} = 533.09*0.22\ (0.01*0.006*4752x10^3 + 7792.28*0.0253)$$
$$+$$
$$393.53*0.56\ (0.01*0.006*4752x10^3 + 7792.28*0.0253)$$

$$= 162801 \quad \mu g$$

$$R_{Pb} = 533.09*0.07\ (0.22*0.001*4752x10^3 + 152047.09*0.0253)$$
$$+$$
$$393.53*0.14\ (0.22*0.001*4752x10^3 + 152047.09*0.0253)$$

$$= 452150 \quad \mu g$$

$$R_{Zn} = 533.09*0.30\ (0.086*0.002*4752x10^3 + 176140.2*0.0253)$$
$$+$$
$$393.53*0.08\ (0.086*0.002*4752x10^3 + 176140.2*0.0253)$$

$$= 1009366 \quad \mu g$$

The total volume of runoff recorded over the eight week period was 16783.61 l, and the overall metal concentrations in stormwater are given in Table 7.15.

Table 7.15. The calculated and actual overall stormwater concentrations of heavy metals ($\mu g\ l^{-1}$).

	Cd	Cu	Pb	Zn
Predicted	1.22	9.70	26.94	60.14
Determined	1.26	8.75	27.03	56.44

It can be seen from Table 7.15 that the predicted stormwater concentrations are similar to those actually determined for all metals over the eight week sampling period. The metal data for the three storms sampled for which total deposition values are known have been used to further test the predictions of the model further. The input data for each storm are given in Table 7.16, and the results of the calculations are given in Table 7.17.

Table 7.16. Predictive model input data for individual storms.

Storm date	Dry period t (s)	Atmospheric concentration (μg m^{-3})				Rainfall depth (m)	Rainfall concentration (μg l^{-1})			
		Cd	Cu	Pb	Zn		Cd	Cu	Pb	Zn
B 8-8-84	261×10^4	0.3×10^{-3}	5.15×10^{-3}	0.086	0.093	0.0034	4.85	25.16	189.81	234.12
C 23-8-84	129.6×10^4	2.3×10^{-3}	6.0×10^{-3}	0.314	0.096	0.0020	9.65	52.48	1080.66	930.14
D 6-9-84	121×10^4	0.8×10^{-3}	6.5×10^{-3}	0.141	0.053	0.0066	2.88	4.97	155.95	211.00

Table 7.17. The predicted and actual average stormwater metal concentrations for individual storms.

	Metal concentration ($\mu g\ l^{-1}$)		
	Storm B 8-8-84	Storm C 23-8-84	Storm D 6-9-84
Cd predicted	1.66	7.61	1.03
determined	1.18	0.84	1.17
Cu predicted	20.25	65.22	5.25
determined	7.09	6.74	7.58
Pb predicted	30.21	199.84	21.55
determined	5.43	21.90	16.72
Zn predicted	90.30	339.96	56.60
determined	40.96	61.47	80.11

The predicted average stormwater metal concentrations for storm D shown in Table 7.17 are close to and except for Pb slightly lower than the actual stormwater concentrations. For storm B the observed average Cd concentration was close to that predicted, but for Zn, Cu and Pb the predicted concentrations were elevated by factors of x2, x3 and x5, respectively. The predicted stormwater metal concentrations for storm C are approximately 9 times higher for Cd, Cu and Pb, and 5 times higher for Zn than the average observed concentrations of these metals. The amount of metal washed off the catchment surface will depend on the hydrological characteristics of each storm event. Ellis et al. (1986) have used a stepwise linear regression analysis of pollutant loadings against five selected hydrological parameters to develop predictive equations for metal loadings in runoff. The results indicate that total runoff volume and storm duration explain over 90% of the observed variance in Pb and Cd loadings. For Zn, 79% of the observed variance could be explained. Both storm duration and total surface runoff are indicators of storm flow conditions and would be expected to influence washoff loadings. A significant surface flow volume is required to overcome critical sediment storage and retention thresholds on the road surface. Storm C was markedly different in character than the others sampled being of much shorter duration (Table 7.5) and consequently the total storm runoff volume was much lower than for the other storms. In addition the concentrations of metals in rainfall, particularly Pb and Zn, are considerably higher in storm C than in the two other storms (Table 7.16). Although in the predictive model outlined above, consideration of antecedent dry period forms an integral part of the calculations, Ellis et al. (1986) observed that antecedent dry period length is an insignificant factor in explaining variations in pollutant loadings (see also Section 2.5.4). Rainfall intensity was also found not to exert a significant influence on runoff pollutant loadings, which would confirm the observations of Randall et al. (1982) outlined in Sections 2.5.4 and 7.9.1.

The predictive model was based on the average fractional removal efficiency over an eight week sample period including one storm for which the antecedent dry period was not accurately known and hence the total dry deposition could not be calculated. A more accurate predictive model could have been produced had the fractional removal efficiencies been calculated for the time period between the end of storm A and the end of storm B. Nevertheless, the model produced predictions of stormwater metal concentrations with variable accuracy. It must be noted that such models are site specific and may not be suitable for universal application.

7.12. Conclusions.

The following conclusions can be drawn from the mass balance study of heavy metals at the Chilwell Gardens sub-catchment:-

a) Vehicle derived sources which deposited directly into the catchment appear to represent a significant source of Zn in street sediments even for a lightly trafficked roadway such as Chilwell Gardens. For Cd, Cu and Pb deposition from general urban background sources dominate over local automotive sources.

b) Stormwater runoff from the sub-catchment removed only a minor fraction of the metal deposited in the catchment during the sampling period. Copper showed the largest proportion of deposited metal discharged in runoff (36%), and Pb the least (10%), Cd and Zn occupied an intermediate position (20%). This trend was also exhibited by individual storm events, but the mass of metal discharged by each storm event varied considerably.

c) The sub-catchment comprises of two distinct areas, the road surface plus adjacent pavement areas, and the roof surfaces. Roof surfaces were found to contribute the greater proportion of Cu and Pb to the total runoff, whilst for Zn the roof surfaces contributed a minor fraction (17%).

d) Resuspension of road surface sediments either by vehicles using the road or the action of wind was estimated not to contribute significantly to the removal of road surface sediments from the sub-catchment.

e) Street sweeping appears to be effective at removing sediment associated metals from the catchment, if carried out regularly.

f) A predictive model has been developed which allows the determination of stormwater metal concentrations. Average stormwater metal concentrations for the eight week sampling period could be predicted with reasonable accuracy. However, for individual storm events predictions of metal concentrations in runoff were less accurate. Total surface and storm duration were observed to be important factors controlling stormwater pollutant loadings.

CHAPTER 8. CONCLUSIONS.

8.1. Summary of Major Findings.

a) A review of the relevant literature, in conjunction with experimental trials conducted as part of this research project, has allowed the design of a suitable procedure for the sampling and analysis of total heavy metal levels in road surface sediments. The technique adopted involved the sampling of a large area (typically 10 m^2) of street surface using vacuum techniques. The collected dusts were analysed for their heavy metal content by extraction with concentrated HNO_3-$HClO_4$ followed by atomic absorption spectrometry.

b) Detailed variations in heavy metal levels across urban road surfaces of varying traffic characteristics, and surface composition and condition have been established. The concentrations and loadings of Cd, Cu, Pb and Zn were found to decrease with decreasing traffic density, but not proportionally. Metal loadings were observed to follow the closest relationship to traffic density. Intra-site variations in metal concentrations were not uniform for all metals. The nature of the road surface was found to be an important controlling parameter. Coarse surfaces were observed to trap fine particles of sediment, in particular Pb bearing exhaust emissions. Metal loadings were observed to show the most consistent spatial distribution trends.

c) Vehicle induced resuspension has been shown to be an important factor influencing heavy metal loadings across the highway and adjacent surfaces. Road surface sediments were found to be dispersed laterally on roads where traffic was heavy and fast moving. Resuspension will dominate on such roads after only a few days of consecutive dry weather. On other roads resuspension will seldom dominate due to low traffic flows.

d) A seasonal pattern in the heavy metal loadings and concentrations was observed. Reduced levels of metals were recorded during the winter months. This may be due to the increased frequency of street cleaning, and the increased and more intense rainfall occurring during these months.

e) The speciation of the trace metals under study confirmed the distribution patterns observed by previous workers. Cadmium was the only metal to show significant levels in the exchangeable phase, which is considered the most available fraction in terms of environmental mobility and bioavailability. Lead and Zn were distributed mainly in the carbonate and Fe-Mn oxide phases. These are considered to be moderately available. Copper was predominantly bound to organic matter, but also showed the highest affinity for the residual phase of the metals.

f) Metal concentrations in each of the five chemical fractions were observed to increase with decreasing particle size. This has been related to the increased surface area and consequent increase in exchange sites with decreasing particle size.

g) The physico-chemical associations of Pb in dust produced by five techniques of paint stripping have been investigated. Belt sanding was found to produce considerably higher airborne Pb levels, which could be more easily dispersed away from the area being. The other techniques tested produced dust of much larger particle size and fallout was confined mainly to the work area.

h) The measurement of metal levels in playground dust following the external redecoration of a school has shown levels of Pb in dust to be greatly increased during paint stripping. The highest levels of Pb in dust were recorded close to the school building during redecoration when Pb concentrations exceeded the G.L.C. 'interim action limit' by twenty three times. Clean up operations performed by the contractors on completion of their work were found to be ineffective in reducing Pb in dust concentrations to acceptable levels.

i) Studies of the chemical associations of metals in playground dust have shown that considerable quantities of Pb occur in the combined exchangeable and carbonate phases. This represents metal which is readily available for uptake via ingestion. The levels of Pb available for uptake have been estimated for playground dusts and road surface dusts to be 422-1172 $\mu g\ g^{-1}$ and 74-183 $\mu g\ g^{-1}$ respectively.

j) Stormwater runoff from the catchment removed only a minor fraction of the metal deposited in the catchment during the sampling period. Copper showed the largest proportion of deposited metal discharged in runoff (36%) and Pb the least (10%). Cadmium and Zn occupied an intermediate position (20%).

k) Roof runoff was found to contribute significant quantities of Cu and Pb to the total runoff from the catchment, whilst for Zn the roof surfaces contributed only a minor fraction.

l) Control practices have been assessed, in particular the efficiency of street cleaning using mechanical sweeper. Metal concentrations were found to be enhanced, possibly due to the preferential removal of larger particles. However, loadings of all metals decreased markedly after road sweeping had taken place.

m) A predictive model has been developed which allows the determination of stormwater metal concentrations. Average stormwater metal concentrations for the eight week sampling period studied could be predicted with reasonable precision.

8.2. Implications for Control of Metal Pollution of Road Surface Sediments.

The investigations carried out during this research project have provided useful indications of the effectiveness of municipal cleaning practices for the control of urban surface sediments and related metal pollution. The work also suggests alternative practices for the reduction of potentially harmful metal pollutants in the urban environment.

In the long term, alterations in highway construction could be adopted which would lessen the build up of sediments on road surfaces. One such modification could be the removal of kerbstones and other barriers to the lateral dispersion of sediments. Alternative means could be devised to separate traffic and pedestrians. Also further efforts could be made to use smoother surface materials, as coarse surfaces such as asphalt/chippings have been shown to retain fine highly polluted sediment.

Kerbs do have the advantage of concentrating the sediment build up in the street gutter, and hence making street sweeping more effective. The kerbstones by acting as barrier to surface flow also help channel stormwater into gully pots. Optimisation of street sweeping and gully pot emptying would improve the quality of stormwater by reducing the loadings of source sediments on road surfaces and gully pot chambers. Similarly the introduction of dry weather flushing would reduce pollutant loadings. These measures would not only reduce solids and metal loadings in stormwater, but would also reduce the levels of other stormwater pollutants such as BOD, hydrocarbons and nutrients.

In addition to the already well established municipal cleaning practises discussed above greater thought could be given to highway management practises. For example, control of street parking could be used to reduce metal pollutant loadings in particularly sensitive areas. Street parking also makes street sweeping difficult in some areas by preventing access to the gutters.

Where painted surfaces are undergoing reparation there is a greater need for improved control over stripping and clean up operations. Analytical techniques are available which allow rapid screening of painted surfaces with a high Pb content. Decorators could then be warned about potential hazards involved in stripping and appropriate techniques such as chemical stripping could be employed. Sweeping has been shown to be ineffective in removing dusts contaminated by paint, and therefore where high Pb paint has been detected, clean up using vacuum techniques should be employed. Heavy duty vacuum cleaners similar to that used for sample collection in this project are now widely available. The contaminated waste could then be safely disposed along with other hazardous wastes.

8.3. Suggestions for Further Work.

a) The temporal variations of heavy metal levels in street surface sediments have not been studied as extensively as was originally hoped. The statistical analysis carried out in Chapter 4 has indicated possible relationships between certain hydrometeorological parameters and metal levels in urban surface sediments. The analysis was limited by the relatively small number of sample visits made. An increased sampling frequency at a wider number of sites would allow a more precise statistical determination of these relationships.

b) The studies described in Chapters 5 and 6 have indicated that the quantities of metal available for uptake by children through ingestion of contaminated urban surface sediments may have been underestimated. Further work should be undertaken to broaden the scope of these investigations, and direct attention should be given to the relationship between street sediment metal levels, the chemical associations of the metals in street dust and uptake via hand to mouth activity.

c) The results of this study suggest that roof runoff can contribute significant quantities of metal pollutants to stormwater, and so to receiving waters. The effect of factors such as roof slope, construction material and drainage system condition need to be investigated in order to quantify more precisely this source of metal input to urban stormwater.

d) A major part of this work has concentrated on Pb levels in urban street sediments for which the major source is exhaust emissions.

The sources of the other metals studied are less easily quantified and further work needs to be carried out in this area. In addition to the metals studied here, recent work has suggested that corrosion of metals from motor vehicles may be a significant source of a range of trace elements. These include the rare earth metals; cerium, samarium, lanthanum, which have been detected at concentrations of 2-10 $\mu g\ g^{-1}$ in motorway soils (Bird 1987), and also platinum and palladium derived from exhaust catalysts. Modern analytical techniques such as ICP-MS are now available which can rapidly determine trace concentrations of large numbers of different metals in environmental samples and further work should be carried out in this area.

e) The introduction of lead free petrol has produced a significant fall in environmental lead levels, particularly in urban areas (see Section 2.2.1). Changes in fuel composition necessary to maintain the octane rating of petrol may result in an increase in the ambient atmospheric concentrations of polycyclic aromatic hydrocarbons. The carcinogenic and mutagenic potential of polycyclic aromatic hydrocarbons is well documented and therefore it is important that the pathways of these pollutants in the atmosphere are understood. Atmospheric levels of polycyclic aromatic hydrocarbons have been determined but no attempts have been made to model the dispersion, deposition and resuspension processes responsible for the transport of these pollutants and further work should be carried out in this direction.

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APPENDIX A.

The following co-authored papers were published during the course of the research project:

A2-A17. Levels and physico-chemical associations of Cd, Cu, Pb and Zn in road sediments. The Science of the Total Environment, Vol. 33, 1984, pp. 59-74.

A18. SEM studies on heavy metals in urban dust particles. The Science of the Total Environment, Vol. 33, 1984, pp. 283.

A19-A21. Resuspension of heavy metals from road surface dust. In: Proc. 5th Int. Conf. Heavy Metals in the Environment, Athens, 1985. CEP Consultants, Edinburgh, 1985, pp. 85-87.

A22-A24. Environmental contamination caused by lead based paint. In: Proc. 2nd Int. Conf. Environmental Contamination, Amsterdam, 1986. CEP Consultants, Edinburgh, 1986, pp. 297-299.

A25-A28. Metal mass balance studies within a small highway dominated catchment. The Science of the Total Environment, Vol. 59, 1987, pp. 365-368.