ENVIRONMENTAL RISK ASSESSMENT OF HEAVY METALS IN URBAN STREET DUST

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I certify that this work has not been accepted in substance for any degree, and is not concurrently submitted for any other that of Doctor of Philosophy (PhD) of the University of Greenwich. I also declare that this work is the result of my own investigations except where otherwise stated.

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Abstract

Environment risk assessment of heavy metals has been widely used as a scientific method for evaluating possible environmental hazards presented in a product, a system and/or an industrial process. The results have been used for setting occupational standards and environmental regulations. However, in practice, environmental risk assessment generally does not take into account the bioavailability/mobility of chemicals in different environmental pathways and attention has rarely been paid to widely spread and un-regulated diffuse sources in the urban environment.

This thesis employs several practical approaches (chemical, biological, kinetics) together with a theoretical model to assess the potential risk of diffuse sources of cadmium, copper, lead and zinc in urban street dust in two pathways, namely, dust ingestion and the impact of heavy metals on soil adjacent to a road. Dust samples were collected from four sampling sites (two in Hong Kong and the other two in London) during a period of nineteen months.

Tessier's sequential extraction schemes were used to assess the geochemical phases/bioavailability of mobilisation potential of heavy metals in the dust. A series of single leaching methods were also used and time dependent metal release kinetics were carried out for evaluating the potential metal release under simulated different environmental pathways. These experiments showed that the partitioning and distribution of cadmium, copper, lead and zinc in urban street dust, regardless of locations, is relatively consistent. On the other hand, the different leaching methods gave rise to different results while pH was identified as a main factor influencing the metal release. Under acidic conditions, metal release generally followed a fast-slow release pattern.

Gastric conditions were also simulated in the laboratory to study the metal release mechanism of urban street dust to the risk of dust ingestion by human beings, especially children. High percentages of heavy metal release under simulated gastric conditions suggested the use of the total metal concentration in dust for risk assessment.

A theoretical model based on the assumption of a worst case scenario was developed and applied to evaluate the exposure between heavy metals in urban road dust and in soil adjacent to a road. The partition coefficient describing the tendency of heavy metals distributed between solid and liquid phases showed equal importance as physical factors such as rainfall intensity, traffic flow and road geometry in the risk model.

Root elongation, algal growth and light emission of luminescent bacteria were employed for assessing the toxic effect of heavy metals in urban dust. All test organisms showed suppressed response under different concentrations of dust elutriates, while no consistent correlation was found between the chemical speciation tests and the biological toxicity tests.

The results of the above operationally defined approaches to the risk assessment of heavy metal in urban street dust suggest that there is no simple and quick way for assessing their risk in different environmental pathways. An integrated approach based on the pH dependent chemical leaching method, sequential extraction, together with a modelling strategy in risk assessment may provide a more comprehensive view of the pathways between the source and receptor as well as an estimate of the most important factors.

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List of Symbols

k_{sw}	partition coefficient	C_{urban}	the concentration of dust particles in urban atmosphere
C_d	the concentration of metal in dust	R_r	the contamination entering the soil by runoff
C_s	the concentration of metal in solution	u	wind speed
k, k_1, k_2, k_3	reaction rate constants	$h(x)$	the depth of dust cloud
L	the volume of extraction liquid	x	the distance from the road
M	the mass of dust	w	rainfall velocity
f	the fraction of metal released from dust	θ	water content of soil
β	the fraction of metal in dust subject to the fast reversible reaction	ρ_s	the density of soil
		k_s	the rate of removal of metal from the soil
η	buffer capacity	$t_{1/2}$	the half life of the reaction
a, b	equilibrium constants	D_s	diffusion coefficient
P	accumulated dust on the road surface	S	the surface of the undissolved solid
k_d	the removal rate of dust in dry weather	h	the thickness of diffusion layer around the particle
k_w	the removal rate of dust in wet weather		
t_d	the mean duration of dry weather		
t_w	the mean duration of wet weather		
$P_d(t)$	the mean accumulated dust after time t in a dry period		
$P_w(t)$	the mean accumulated dust after time t in a wet period		
F_r	the fraction of dust runoff		
F_s	the fraction of dust resuspended		
E	emission factor		
N	the number of vehicles per second		
W	the width of the road		
v_g	the deposition velocity of urban dust		

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Chapter One

INTRODUCTION

1.1 Aim and objectives of the present study

The aim of the present study is to apply a number of different techniques, including chemical leaching methods, biological tests and theoretical models to assess the environmental effect of heavy metal (Cd, Cu, Pb and Zn) releases from diffuse sources using urban road dust as an example. The study considers two possible environmental pathways, the impact of heavy metal on the soil next to the road and ingestion of dust via hand to mouth behaviour by children, as examples of applications to risk assessments.

This chapter addresses some issues related to risk assessment of heavy metal in soil and ends with an overview of the thesis.

1.2 Problems of existing risk assessment techniques of heavy metals in soil

Although not wholly satisfactory from a chemical point of view, "heavy metals" is the most widely used term for elements considered to be metals (because of their electron properties) with atomic densities greater than 6 g cm^{-3} (Wild 1988; Alloway 1990) or atomic numbers between 21 (scandium) and 84 (polonium), such as Cd, Cu, Hg, Pb and Zn (Wild 1988; Schnoor, 1996). Heavy metals and other environmental pollutants which affect human health and cause a decline in environmental quality have caused much concern world-wide during the last few decades. High levels of heavy metal have been found in the terrestrial environment such as in urban areas, near metalliferous mines and next to major road systems. Of all the heavy metals, Cd, Cu, Pb and Zn are most often associated with toxicity from

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environmental exposures and their widespread occurrence in many natural processes as a result of release from human activities, such as combustion, smelting, metal plating and traffic emission (Reuther, 1986; Salbu and Steinnes,1994). Hence these heavy metals have been included in most of the toxicity studies undertaken to date.

The Integrated Pollution Control (IPC) approach in the UK and the Integrated Pollution, Prevention and Control (IPPC) regime shortly to be applied in Europe provide a systematic approach for assessing potentially harmful effects to the environment (UKDETR, 1999). They depend in their practical application on methods of assessing the transfer of pollutants through different environmental media such as air, water and land. Current applications are probably weakest when considering the transfer between different environmental phases such as between water and soil. Recently the Environmental Agency has attempted to produce standardised methods for environmental assessments (HMIP, 1997; van der Sloot *et al.*, 1997). The methods are necessarily rather complex and depend heavily on an accurate knowledge of the processes influencing the transfer of pollutants between different media.

Scientists and regulators carry out risk assessments and risk management exercises for toxic materials in order to determine the Best Practicable Environmental Option (BPEO) so that the objectives of IPC and IPPC can be achieved. Other effective legislative and administrative measures are implemented to reduce pollution levels and to safeguard human health and the natural environment from potentially harmful activities. The most important framework used to achieve this is the Environmental Risk Assessment (ERA) (Reuther, 1996).

In general, risk assessments rely on order-of-magnitude calculations, rather than exact estimates of risks in a given situation, since many uncertainties are involved in each case (Benson *et al.*, 1994). Chemical and biological measurements of toxic substances available to biota based on laboratory bioassays have served well for environmental risk assessments and the regulation of these substances in the past 15 to 20 years (Benson *et al.*, 1994). Although these approaches have allowed some important issues to be addressed and have facilitated the regulation of toxic materials in the environment, they are empirical and reflect the lack of detailed understanding of the physical, chemical and biological mechanisms underlying the measurements.

The problems of risk assessments and standardised environmental evaluations are illustrated by the following studies of the risk posed by heavy metals in the soil. The first study assessed the possible future impact of arsenic (As), nickel (Ni) and vanadium (V) release from a power station burning orimulsion on the surrounding soil (National Power Plc, 1994). No recommended standards or emission limits were available for these elements, so another method had to be found to determine whether the concentrations of these heavy metals in the soil were acceptable. The concentrations of As, Ni and V deposited in the soil by the power station over 30 years were calculated and then compared with their background concentrations using the total metals present in the soil. Since the calculated levels of As, Ni and V were much lower than those present in the background soil, it was concluded that they did not pose a risk to the environment and there was "no risk of concern".

In the second case, a risk assessment of building a new cement plant at Holborough, Kent (Blue Circle Cement Medway Works, 1997), involved consideration of the release of a large number of trace elements into the

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atmosphere where no standard emission limit applied. An operational approach to determining acceptable emission used the total metal concentration present in soil to compare with the typical metal concentrations found in the UK's soil from various previous research documents. It was concluded that the concentrations of metal detected were not above the average for the UK's soil.

However these studies analysed the total metal concentrations within the soil without considering the mobility and bioavailability of these metals in the environment. This may give a misleading assessment of the risk because although the calculated concentrations may be much lower, they may be more mobile than the higher concentration already present in the soil. Without a standardised method of chemical analysis for determining the availability of metal in soil, a comparison of the metal concentration of different samples is less meaningful. Furthermore, both these assessments were of metals associated with industrial chemical processes, so the metals are likely to be held in a form that will probably have quite a uniform structure. On the other hand, heavy metals in road dust are likely to be more complex mixtures of particles, which reflect the wide range of processes to which they are exposed.

1.3 Chemical speciation

It is accepted that analytical chemists normally test a soil sample for metal contamination in the laboratory using an aggressive acid digestion such as aqua regia (a mix of nitric and hydrochloric acid), and then measure the levels of any metals dissolved in solution. Government guidelines in Britain and the Netherlands give safe levels based on these so-called total metal concentrations, above which action is recommended. Although this is a simplistic approach, it has been generally recognised that the mobility, transfer pathways and bioavailability of heavy metals in the environment

depend on the physiochemical and specific binding forms of heavy metals in the contaminated media. Therefore, using total metal content as a criterion to assess the potential effects of environmental contaminated media (dusts, soil and sediment) may not be an appropriate method as it assumes that all forms of metals share the same impact (Tessier *et al.*, 1979). The chemical speciation approach such as sequential extraction (Tessier *et al.*, 1979) provides a more relevant measure to identify particular forms of metal binding — for instance, to distinguish the easily dissolved, the biologically reactive and the chemically stable forms.

The term "form" is used to indicate uncertainty or lack of knowledge about the exact nature of the species one expects to find in an environmental sample (Kersten and Forstner, 1989). The term "speciation" can be defined in various ways. According to Ure (1990) speciation is defined as follows:

> *...either (a) the process of identifying and quantifying the different, defined species, forms of phases present in a material; or (b) the description of the amounts and kinds of these species, forms or phases present. Whichever approach is taken, the species, forms or phases are defined (i) functionally, (ii) operationally, or (iii) as specific chemical compounds or oxidation states.*

Le Riche and Weir (1963) found various forms of chemical binding of metals in soil. Since then sophisticated chemical speciation and fractionation methods for analysis of heavy metals in soils and sediments have been and are still being developed and applied during the last two decades. In this thesis speciation will be defined largely operationally.

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1.4 Heavy metals in urban street dust

In future it is likely that acceptable limits of trace metal releases to the atmosphere from industrial processes will be widely applied through the enforcement of IPC and IPPC approvals. However, this will mean that various kinds of fugitive metal dust emissions from non-industrial processes are not so tightly controlled. This thesis is concerned with the most common type of fugitive metal release that is likely to come into contact with a large fraction of the population, namely, road dust. It is also a form of dust whose metal content arises from various sources that are either unknown or poorly defined. Moreover, the greatest risks are posed in this category when metal is transferred between different media. Therefore it is important to reassess road dust and to evaluate this risk in the urban environment.

Dust is often referred to as the particulate matter in the size range 1- 75 μm in diameter or according to a wider definition used in the mineral industry particulate matter under 2 mm in diameter (DoE Mineral Division, 1996). In the present study, the latter definition will be used. The amount of dust accumulation is likely to be a very variable quantity. Data is very limited on the amount of dust present on roads but QUARG (1996) quotes typical concentrations are of order 0.02 g m^{-2}.

The urban street environment provides a complex system for contaminants in terms of accumulation, transport pathways and removal processes (Revitt *et al.*, 1990). Urban street dust constitutes an important medium and reservoir of pollutants such as heavy metals (e.g. Davies *et al.* 1987; Fergusson and Kim, 1991). Heavy metal pollution in street dust has become a growing concern in recent years, partly due to poor control and regulation of traffic emissions and urban development as well as their potential impact on receiving waters via storm runoff (Tickell, 1997). Nevertheless,

international guidelines do not exist for the heavy metal content of street dust. Moreover, in the UK there are no regulations to control urban runoff, nor requirements to install the best available technology to reduce the pollution levels in storm runoff from a road, although surface water discharge criteria have recently been set by the USEPA (Sansalone and Buchberger, 1998).

Sources of street dust include particulate matter emitted from vehicle exhausts, particles disturbed from the road surface by passing traffic and erosion of road surfaces, together with all sorts of diffuse sources from the surrounding environment. In addition, construction and demolition activities, waste transfer stations, concrete batching plants and other urban industries such as incinerators, can contribute to more localised problems of street dust. Airborne dust and dirt are easily collected by paved surfaces in urban areas such as on roads.

Various sources contribute to the presence of heavy metals in urban street dust. These metals are present in various concentrations and are ubiquitous in the lower atmosphere, being mainly associated with particulate matter. Their widespread presence reflects their diverse sources (Alloway, 1995):

- Natural sources of heavy metals world wide are mainly generated from volcanic activities, wind-blown soil, sea salt aerosols, with local impact near surface mineralization and geological structures.

- Anthropogenic (human activities) sources of metals are mainly derived from fossil fuel combustion, metal refinery industries, agricultural practice, chemical industries and waste disposal.

Much attention has been focused on the lead (Pb) level in street dust, which frequently reaches the range of 1000 to 3000 mg kg^{-1} in the urban environment (e.g. Harrison, 1979 and 1981; Lau and Wong, 1982).

However, the levels of cadmium (Cd), copper (Cu) and zinc (Zn) in urban street dust have also caused concern as they may enter the food chain and may affect human well-being far into the future (Harrison, 1979; Lau and Wong, 1982; Gibson and Farmer, 1984; Hamilton *et al.*, 1984; Culbard *et al.*, 1988; Fergusson and Kim, 1991; Ahmed and Al-Swaidan, 1993; Ogunsola *et al.*, 1994; Stone and Marsalek, 1996). Studies have shown that some heavy metals have long residence times in the environment: for instance, Cd is estimated to have a 75 to 380 year residence period in soil whereas Cu, Pb and Zn have residence times of 1000 to 3000 years in soil (Bowen, 1979).

1.5 Environmental impact of urban street dust

Four major human and environmental impacts of pollutants in the urban street dust are addressed in the following subsections.

1.5.1 Direct impact on human health

The urban population may be exposed to toxicants in street dust via inhalation of re-suspended dust (USEPA, 1986), or through direct ingestion by urban paediatric groups (Fergusson and Kim, 1991). Although an attempt to assess the significance of street dust as a hazard to human health met with limited success, many studies in the UK and the USA (NRC, 1980) have suggested that contaminated street dust may represent an important source of Pb intake for humans. Young children are thought to be at higher risk due to the ingestion of non-food items (Angle *et al.*, 1974; Duggan and Williams, 1977; Duggan, 1983; Gallacher et al., 1984; Mushak, 1991; Fergusson and Kim, 1991).

Since Pb in street dust represents an important source of Pb exposure for young children, the need for standards for Pb in dust or dust fall-out has been repeatedly emphasised (Duggan, 1983; Brunekreef et al., 1983). It has

been proposed that 1000 μg g^{-1} may be an appropriate dust lead standard to prevent increased Pb exposure of children (Laxen et al., 1987; Ewers, 1988).

1.5.2 Impact on soil

The soil adjacent to highways are generally found to contain higher levels of Pb than soil distant from the highway (Smith, 1976; Nriagu, 1978; Paterson *et al.*, 1996). Traffic emissions as a result of using Pb additive fuel are one of the sources of such contamination. Page and Ganje (1970) found the accumulation of Pb in surface soil enhanced by a factor of two or three where traffic density increased from 80 vehicles to 580 vehicles per square mile. Urban soil showed significant increases in the concentration of Pb and Zn alongside arterial and city centre route (Paterson et al., 1996).

There are two possible pathways by which road dust can influence soil next to the road. One is direct deposition of dust onto soil from the atmosphere (in the same way as dust is deposited onto the road) which includes dust re-suspended from roads by moving vehicles. The other is the road surface runoff to the soil adjacent to the road. The concentrations of heavy metals in soil not exposed to pollution are expected to be lower than in dust because of the presence of organic materials mixed with metal in the soil. Although water is designed in most urban areas to run off to the gutter and then through a combined sewage and drainage system to sewage works for treatment, in exceptional conditions, such as after heavy rain or where there is no drainage system, runoff could drain to land and the soil particles in the runoff can tend to accumulate in the soil.

1.5.3 Impact of urban runoff on receiving waters

Urban street surfaces have been identified as potentially significant contributors of chemical contaminants and pathways for the transport of pollutants. In recent years heavy metals in urban runoff derived from urban

street surfaces have been given a lot of attention. For example, urban storm-water runoff appears to be the main problem in improving surface water quality in highly urbanised areas (Marsalek, 1991). It has been noted that the total Pb and Zn loads for surface water sewer discharge are 0.83 and 1.15 kg per impervious hectare per year, respectively, in Western Europe (Ellis, 1986). Heavy metals (e.g. Cd, Cu, Pb and Zn) originating from the urban environment via urban runoff may represent a large amount of the total metal entering local receiving waters (Ellis et al. 1987).

Wet precipitation provides a mechanism by which heavy metals in street dust and aerosol particles can be solubilised and washed off into the drainage system. The pH of rainwater is the major factor governing the metal solubility in precipitation (Losno *et al.*, 1988; Prospero *et al.*, 1987; Statham and Chester, 1988). Hence, the problem of acid rain in urban area can actually aggravate the pollution problem of heavy metals in street dust.

1.5.4 Ecological impact

The aggressive expansion of human development, industrialisation and urbanisation with its high volume of road vehicle traffic has resulted in disturbance to the structure of the natural environment and contamination of the terrestrial and aquatic environments, as well as high levels of heavy metal contributions. Since such contamination is not controlled, as compared to discharges from point sources, the possible impacts of diffuse sources have been somewhat neglected. While rainfall is essential for plant growth and living organism, the subsequent water flow is also a transport medium for pollutants between the terrestrial and aquatic environments.

Shutes (1984) used hydrobiological indices to evaluate the effects of urbanisation on the River Brent in London, England, and found a significant deterioration in aquatic life and water quality as the stream became more

urbanised. Portele *et al.* (1982) studied the effects of highway runoff on a stream and found that algae and zooplankton were adversely affected by the soluble fraction of the runoff, while the suspended solids caused high mortality of rainbow trout fry. Ehrenfeld and Schneider (1983) showed that typical plant species were lost and replaced by weeds and exotic plants in urban runoff-affected swamps. They also concluded that the presence of storm-water runoff in the clear swamps caused marked changes in community structure, vegetation dynamics and plant tissue element concentration.

1.6 The structure of the thesis

The study of heavy metals in road dust has been shown to be a good example with which to assess research that has formed the basis for current environmental regulations. The emphasis needs to be placed on adopting an operational procedure that can evaluate the risks posed at any location in the world.

The framework of this thesis starts with an introduction to this project. A review of the studies of Cd, Cu, Pb and Zn in urban dust and the possible sources and toxicity effect of Cd, Cu, Pb and Zn in the urban environment together with the profile of the study sites is presented in Chapter 2. In Chapter 3, the sequential extraction scheme (Tessier *et al.*, 1979) is used to analyse the different geochemical phases of metal binding in urban street dust and the results of applying sequential extraction are discussed. This is intended to provide a more refined set of criteria for risk assessment of urban street dust in different operationally defined conditions. A wide range of chemical methods, including single leaching approaches, a pH dependent leaching method and a time dependent method are used to evaluate the metal release mechanisms and within the context of a risk assessment to see if there is an operational way to apply the results of a sequential extraction (Chapter

4). Modelling is an alternative approach to risk assessment. In Chapter 5, a simple risk model is constructed to assess the impact of Cd, Cu, Pb and Zn on soil via runoff from the road to the soil next to the road. As the emphasis in Chapter 3 to 5 has been on a single pathway of exposure to heavy metal in road dust, an alternative pathway is considered. Cadmium, Cu, Pb and Zn release under simulated gastric conditions were studied and results are discussed in Chapter 6. In order to obtain further information on the risk of Cd, Cu, Pb and Zn in dust a completely different approach is adopted using the biological toxicity tests as a surrogate of the chemical approach. Three different biological toxicity tests were used to evaluate the possible toxic effect caused by toxic matters in street dust (Chapter 7). The findings of these investigation are summarised in each chapter and in a general discussion (Chapter 8).

C h a p t e r   T w o

BACKGROUND REVIEW AND STUDY SITES

2.1 Introduction

This chapter reviews some previous studies and background information on Cd, Cu, Pb, and Zn in urban street dust, followed by a profile of the study sites of this research.

2.2 Background review

Street dust has been widely used as a tool for investigating environmental metallic contamination in urban area and for baseline studies (e.g. Culbard *et al.*, 1988). Elevated levels of heavy metals have been found in urban dust on national and regional scales (Gibson and Farmer, 1984; Fergusson, 1984; Davies *et al.* 1987; Yim and Nau, 1987; Culbard *et al.* 1988; Chan *et al.* 1989; Leharne *et al.* 1992; Wang *et al.* 1997), particularly near motorways and city streets (Harrison *et al.* 1981; Lau and Wong, 1983; Hamilton *et al.* 1984; Fergusson *et al.* 1986; Stone and Marsalek, 1996). Numerous studies have contributed various findings including the significant correlation between Pb and traffic density (Lau and Wong, 1983; Chan *et al.* 1989), the possible relationship between Pb in dust and Pb levels in children's blood (Gibson and Farmer, 1984; Wang *et al.* 1997) and the distribution of metals in dust with different land use (Yim and Nau, 1987; Leharne *et al.* 1992). Cadmium, Cu, Pb and Zn are the four heavy metals which have most frequently been studied in urban street dust. Tables 2.1 to 2.3 summarise the literature data on Cd, Cu, Pb and Zn in urban street dust since the 1970s. Note that these studies employed various techniques for sampling, collection, preparation, analysis and interpretation of data.

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Table 2.1 Concentrations ($\mu g\ g^{-1}$) of Cd, Cu, Pb and Zn in urban dust in Hong Kong from the 1970s to the 1990s.

Year	Type	Cd		Cu		Pb		Zn		particle size (µm)	extractant	lead in petrol ($g\ l^{-1}$)	Reference
		mean	range	mean	range	mean	range	mean	range				
1979	road dust -city -urban			465 223		2924 1039				<750	HNO_3	0.8	Ho, 1979
1981	road dust soil	15.6 27	6-28 12-54	92 42	16-271 3-205	1556 88	132-3876 29-259	2449 88	220-8160 21-229	<106 <2000	$HNO_3/$ $H_2SO_4/$ $HClO_4$	0.6	Lau & Wong, 1982
1983	urban dust	7.6	0-58	635	2-5606	1287	134-16800	2902	170-63500	<170	$HNO3/$ $HClO_4$	0.4	Yim & Nau, 1983
1986	road dust	2	0-30	300	10-1770	550	70-1630	1210	90-3060	<850	HNO_3	0.25	Chan et al. 1989
1987	road dust soil			297 142	50-741 13-553	347 268	107-915 42-1034	2582 1281	534-6584 173-11316	<750 <2000	$HNO_3/$ $H_2SO_4/$ $HClO_4$	0.15	Tam et al. 1987
1987/ 1988	playground pavement					284 283	138-1723 178-1212			<180	$HNO_3/$ $H_2SO_4/$ $HClO_4$	0.15	Friends of Earth, 1987

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Table 2.1 Concentrations (μg g⁻¹) of Cd, Cu, Pb and Zn in urban dust in Hong Kong from the 1970s to the 1990s.(Cont.)

Year	Type	Cd mean	range	Cu mean	range	Pb mean	range	Zn mean	range	particle size (μm)	extractant	lead in petrol (g l⁻¹)	Reference
1996	playground dust	2.6	1.6-3.2	201	20-417	302	100-574	1517	480-2400	<1000	HNO_3/ $HClO_4$	0.15	Wong & Mak, 1996
	soil	2.3	1.7-3.0	28	3-67	195	70-420	237	50-550				
1996	soil												Chen et al. 1997
	-industrial	1.3		26		88		63		<2000	HF/ $HClO_4$		
	-commercial/ residential	1.0		14		73		51			HNO3/ H_2SO_4	0.15	
	-rural	0.7		9		41		51					

Table 2.2 Concentrations (μg g^{-1}) of Cd, Cu, Pb and Zn in urban dust in London from the 1970s to the 1990s.

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (µm)	extractant	lead in petrol (g l^{-1})	Reference
1978	road dust					3060				<125	HNO3/ HCl	0.5	Biggins & Harrison, 1980
						2015				125-250			
						1100				250-500			
1979	motorway dust	3.9	3.8-4.2	186	161-212	1230	895-1690	909	1010-1760	>250	HNO$_3$		Ellis & Revitt, 1982
		6.4	6-6.8	479	386-640	2000	1604-2296	1703	1212-2020	<250			
	road dust	1.7		110		723		245		>250			
		5.3		280		1826		695		<250			
	country lane dust	0.7		27		40		92		>250			
		1.3		43		111		119		<250			
--	road dust	2.8		112		19		571		<600	sequential extraction		Harrison et al. 1981
1981/ 1982	playground dust	2.4^G	<1-12	9^G	16-712	430^G	93-6860	620^G	134-3740	<1000	HNO$_3$/ HClO$_4$		Culbard et al. 1988
	road dust	4.2^G	<1-280	115^G	18-2400	1354^G	172-9660	424^G	58-13100				
	garden soil	1.0^G	<1-2	73^G	13-2320	654^G	60-13700	183^G	34-482				

G: geometric mean; if not mentioned explicitly mean is arithmetic mean.

Table 2.2 Concentrations ($\mu g\,g^{-1}$) of Cd, Cu, Pb and Zn in urban dust in London from the 1970s to the 1990s.(Cont.)

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (µm)	extractant	lead in petrol (g l⁻¹)	Reference
1982	road dust												
	-trunk road	3.1	1.5-4.3	237	100-324	2346	1128-3276	527	336-623	<500	$HNO_3/HClO_4$		Hamilton et al. 1984
	-resident -street	2.2	1.8-2.4	181	60-260	1045	765-1250	401	389-435				
1982/ 1983	street dust	3.3/ 2.7ᴳ	<1.2- 20	131/ 80ᴳ	4-2050	660/ 370ᴳ	30-17900	510/ 372ᴳ	61-3200	<180	$HNO_3/HClO_4$	0.34	Schwar et al. 1988
1983	street dust	6.6	5.2-7.9	198	191-204	3031	2008-4053	1171	1176-1171	<963	HNO_3	0.34	Fergusson, 1984
1985	urban dust	3.5/ 3.3ᴳ	<1.2- 8.7	155/ 102ᴳ	24-2050	1030/ 574ᴳ	84-15300	680/ 508ᴳ	97-6800	<500	$HNO_3/HClO_4$		Schwar et al. 1988
1987	road dust	3.8	3.3-4.3	514	445-628	3496	3010-4420	950	825-1206	<500	$HNO_3/HClO_4$	0.143	Warren & Birch, 1987
	roadside soil	6		346		1769		972					
1987	road dust												
	-scrap yard	13	1.9- 64.7	2114	121-34200	4380	562-32700	3192	238-10700	<1000	HNO_3		Blake et al. 1987
1989	road dust												
	-residential			140		656				<1000	HNO_3		Leharne et al. 1992
	-industrial			151		713							
	-main road			143		978							
	-garage			140		2241							

G: geometric mean; if not mentioned explicitly mean is arithmetic mean.

Table 2.2 Concentrations ($\mu g\,g^{-1}$) of Cd, Cu, Pb and Zn in urban dust in London from the 1970s to the 1990s. (*Cont.*)

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (μm)	extractant	lead in petrol (g l⁻¹)	Reference
1990	road dust	1.3	0.4-5.3	60	24-207	357	135-1538	332	115-728		$HNO_3/$ $HClO_4$		Revitt *et al.* 1990

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Table 2.3. Concentrations (μg g^{-1}) of Cd, Cu, Pb and Zn in urban dust world wide from the 1970s to the 1990s.

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (μm)	extractant	lead in petrol (g l^{-1})	Reference
1977	urban dust												
	street	1.7	0-4.0	238	164-275	427	142-780	610	396-910	62-2000	HNO$_3$/HCl		Dong et al., 1984
		11.6	6.2-17	317	166-478	1350	370-2570	1068	810-1320	2-62			
		21.3	15-29	371	319-433	2602	120-5080	2250	1720-2890	≤2			
	river	0.3	0-1.9	18	3-102	63	14-277	46	23-127	62-2000			
	sediment	1.2	0.3-5.0	58	12-219	244	32-770	220	50-469	2-62			
		6.2	0-33.0	156	0-475	813	0-1439	960	0-2160	≤2			
	soil			2	0-4	4	0-10	9	0-7	62-2000			
		0.2	0-0.5	14	5-27	9	10-14	38	20-71	2-62			
		0.6	0-1.2	59	15-106	40	36-58	157	31-345	≤2			

(U.S.A.) Wisconsin

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (μm)	extractant	lead in petrol (g l^{-1})	Reference
1977	street dust												
	-car parks	7.0	1-14.6	206	104-375	6630	2200-15000	1600	1010-3725	<600	HNO$_3$/HCl		Harrison, 1979
	-urban	4.6	1.3-10.1	143	57-312	1880	920-3560	534	200-940				
	-rural	2.1	1-2.9	79	53-150	550	150-870	297	160-710				

(UK) Lancaster

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Table 2.3. Concentrations (μg g⁻¹) of Cd, Cu, Pb and Zn in urban dust world wide from the 1970s to the 1990s. *(Cont.)*

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (μm)	extractant	lead in petrol (g l⁻¹)	Reference
						Lancaster							
1981	road dust	3.2		175		1465		397		<600	HNO_3		Harrison *et al.* 1981
	car park dust	4.9		71		939		440					
1985	road dust					1406	480-2600			<2000	HNO_3		Sturges and Harrison, 1985
						Leeds							
	road dust					775							
						New York (U.S.A.)							
1983	street dust	8	4.6-11.6	356	171-540	2583	2213-2952	1319	984-2638	<963	HNO_3		Fergusson, 1984
						Halifax (Canada)							
		1	1.4-0.6	87	54-119	1297	674-1919	468	315-620				
						Christchurch (New Zealand)							
		1	1.1-0.8	75	48-258	1090	887-1294	548	365-850				
						Kingston(Jamaica)							
		0.8	0.8-0.8	66	59-72	863	817-909	765	533-996				

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Table 2.3. Concentrations ($\mu g\ g^{-1}$) of Cd, Cu, Pb and Zn in urban dust world wide from the 1970s to the 1990s. (Cont.)

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (µm)	extractant	lead in petrol (g l⁻¹)	Reference
1991	Lagos (Nigeria)												
	street dust												
	-residential	0.7	0.4-1.1	42	27-68	172	51-297	90	30-168	<100	HNO_3/ $H_2O_{2\text{-Cd/Cu}}$		Ogunsola et al. 1994
	-industrial	≤0.6		≤53		308	193-417	169	72-273		HNO_3/ $HF_{\text{-Pb/Zn}}$		
	-highway	0.7	0.6-0.8	60	41-80	641	25-1180	151	50-431				
	-marine area	0.6	0.5-0.6	43	39-47	218	78-413	138	53-372				
	-bus stop	0.8	0.4-1.2	28	17-39	189	44-1025	141	34-201				
1991	Bahrain												
	road dust												
	-rural	62	10-200			444	189-1037	153	27-812	<600	HNO_3		Akhter & Madany, 1993
	-high traffic	45	5.8-117			895	485-1325	266	173-343				
	Carpark dust												
	-rural	48	14-140			555	223-913	125	25-317				
	-high traffic	47	7.3-125			918	259-1385	187	73-407				
1991	street dust			87	27-802	91	33-261	227	52-2782	<2000	$HF/HClO_4$ HNO_3/ HCl		Stone and Marsalek, 1996

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Table 2.3. Concentrations ($\mu g\ g^{-1}$) of Cd, Cu, Pb and Zn in urban dust world wide from the 1970s to the 1990s. (Cont.)

Year	Type	Cd mean	Cd range	Cu mean	Cu range	Pb mean	Pb range	Zn mean	Zn range	particle size (μm)	extractant	lead in petrol (g l⁻¹)	Reference
1993	dust												
						Riyadh (Saudi Arabia)							
	-street dust	1.7		257						<500	HNO_3		Ahmed and Al-swaidan, 1993
	-car park	2.0		336									
	-industrial	2.8		208									
	-rural	1.6		106									
						Cape Town (South Africa)							
	street dust					2258	410-3620				HNO_3	0.84	Von Schirnding, Fuggle, 1996

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In Hong Kong, studies of metal contamination in street dust began in the late 1970s (Table 2.1). The levels of Pb content of road dust have gradually been reduced since 1981. That reduction seems to have been in line with the progressive reductions of Pb in petrol (0.84, 0.6, 0.4, 0.25, 0.15 g l^{-1} in 1980, 1981, 1983, 1985 and 1987, respectively) as well as the introduction of unleaded petrol in 1991. These reductions have eased Pb pollution in the urban environment of Hong Kong (Chan *et al.* 1989). On the other hand, the Zn content of street dust seems to have remained stable (1814-2611 μg g^{-1}) since 1982. The wear of Zn-containing car tyres, the wearing away of road surfaces by traffic and the increased use of galvanised and corrosion resistant automobile parts containing Zn plating may be a major source of Zn in street dust (Sansalone and Bucherger, 1998), although it is not clear what the increase in the number of cars and hence the volume of traffic in Hong Kong has done to Zn pollution.

In London, all new vehicles were required to operate on unleaded petrol starting from 1990. Higher Pb levels have been observed near trunk roads, garages and metal scrap yards in London. Harrison (1979) confirmed that elevated Pb levels were often associated with garages using vehicles running on leaded fuels.

The Cd, Cu, Pb and Zn contents in urban dusts from other cities world-wide vary, probably due to different weather conditions, city types, geological differences (e.g. soil types), and the level of Pb in petrol. High levels of Cd found in urban dust from Bahrain (42- 62 μg g^{-1}) and in Cape Town where the Pb levels in street dust reached 2258 μg g^{-1} were ascribed to the high Pb content (0.84 g l^{-1}) in petrol (Table 2.3). The use of unleaded petrol in Canada has been cited as a possible reason for low levels of Pb in Sault Ste. Marie (Stone and Marsalek, 1996). Low levels of metal were also found in Lagos (Nigeria) and Riyadh.

2.2.1   Cd, Cu, Pb and Zn in urban street dust

Lead has been in use by mankind since the earliest recorded time. It has been smelted, ingested as a homeopathic medicine, applied as a cosmetic, used in painted within buildings and as glaze on the ceramic pots since ancient times (Ellenhorn and Varceloux, 1988). The sources of lead that contaminate urban surfaces include petrol additives, car exhaust particulates, car corroded body-work, motor oils, car tyres, car brake linings, traffic paint, anti-corrosion paint, road pavement and pesticides (Morrison *et al*. 1985). For example, the Pb content of car tyres is of order 60 µg g^{-1} (National Power Plc, 1994).

Cadmium is a toxic element and has no biological function. The use of Cd is mainly found in solder and alkaline storage batteries; it is also used as an amalgam in dentistry, a stabiliser for polyvinyl chloride, and in engravings and pigments in industry. Fumes and particulate matter from Zn and Pb smelting (Taylor *et al*. 1984) and municipal waste incineration (Hutton *et al*. 1988) also contribute to Cd in the urban environment. On the street surface Cd could be the result of car tyre wear, motor oil, car corroded bodywork, car brake linings, car battery, car exhaust particulates, road pavement, alloys and electroplating and wood preservatives, water treatment chemicals and pesticides (Morrison *et al*. 1985). The Cd content of car tyres is about 1 ppm (National Power Plc, 1994).

The source of copper on urban street surface could derive from petrol additives, motor oils and car exhaust particulates, car brake linings, corroded body-work, tyres, road pavement, building materials, anti-algal paints, algicides and wood preservatives, and water treatment chemicals (Morrison *et al*. 1985). Cu is also found in car tyres at a concentration of the order 60 µg g^{-1} (National Power Plc, 1994).

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Zinc is a good indicator of man-made environmental contamination and may also be traced to local vehicle sources (Harrison and Williams, 1982). It is geochemically associated with Pb. The use of Zn and its compounds is found in or associated with soldering flux, dry battery cells, oil refining, dentists' cement, pharmaceutical manufacturing, rubber formulation, vulcanising, polymer stabiliser and white pigment. In the urban street environment, the wear of Zn-containing car tyres, the road surface and the use of Zn-containing motor oils and lubricating grease are the major sources of Zn. The Zn content of car tyres is of order 10,000 μg g^{-1}. (National Power Plc, 1994). In addition, the corrosion of galvanized structures and atmospheric deposition contribute to Zn at the urban surface.

2.2.2 Urban runoff

Rain is the natural process that supplies water for plant growth in the natural environment. At the same time, rain also coveys materials from the terrestrial towards the aquatic environment. There are two processes involved in the mobilisation of metals in urban street dust by rain. Firstly, rainfall provides a removal mechanism that washes off dust from the street surface to the drainage system or to the neighbouring environment. Secondly, the acidity of rain could be a crucial factor dominating the transport of Cd, Cu, Pb and Zn in urban dust to the dissolved phase during rain events.

Urban runoff from the urban surface has long been recognized as a source of a wide variety of pollutants. Among a wide range of materials found in urban runoff, particular concern has been expressed at the significant amounts of solids and heavy metals (Ellis and Revitt, 1982). In particular, runoff from motorway surfaces has been found to be a potential source of pollutants such as Cd, Pb and Zn (Colwill et al., 1985). It has been

suggested that between 35 to 75% of the total receiving stream metal budget might be derived from such highway runoff (Colwill et al., 1984; Hoffman et al., 1985). Ellis et al. (1987) predicted a 46%, 78%, 47% and 13% contribution to the total Cd, Cu, Pb and Zn loading, respectively, from road runoff using a mass balance model when studying a 0.05 ha asphalted highway surface located within a 243 ha residential housing estate at the north west fringe of the Greater London. A survey of a section of motorway (M1) with a traffic density of 25,000 to 40,000 vehicles per 24 h, between London and Birmingham in a rural area about 56 km north west of London found that Pb and Zn were the two principal elements (representing up to 90 % of the total non-ferrous metal concentration in untreated runoff) in motorway runoff, followed by Cu, Cr, Ni and Cd (together accounting for about 10 %) (Colwill et al., 1985).

Runoff from urban road surfaces or highway surfaces can present a serious water quality problem to receiving waters, particularly if the waters are subsequently utilised as sources of potable water supply. Particulate in urban runoff is the most important mechanism of sediment accumulation downstream of runoff discharge locations. Particulate with the highest heavy metals is usually associated with street surfaces and parking lots, and the heavy metal contents are almost all contributed by urban runoff except for areas with heavy industrial activities (Pitt, 1995). Most of the heavy metals entering urban receiving waters via urban runoff settle by precipitation and gravity or are rapidly absorbed by sediment (Van Hassel et al., 1979). In USA, Field and Cibik (1980) reported on a study conducted in an area exposed to wastewater effluent and urban runoff in Virginia where water, sediment, detritus, caddisflies, snails, and crayfish were analysed for iron (Fe), manganese (Mn), nickel (Ni), Pb, Cd, Zn, chromium (Cr), and Cu. Their results showed that metal concentrations increased immediately below storm-water discharge locations. Morrison et

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al. (1990) found that ionic Pb and Cu released from road dirt by acid rain was subsequently scavenged by dissolved organic material and suspended solids when pH was naturally increased in the drainage system. However Cd and Zn remained in dissolved forms according to research conducted in Sweden.

2.2.3 *Potential human exposure pathways of heavy metals in street dust*

There are several human exposure pathways for Cd, Cu, Pb and Zn present in urban street dust.

2.2.3.1 *Dust/soil ingestion*

A possible exposure pathway is direct ingestion of contaminated dust, particularly for young children with a mouthing and pica habit. This route has been identified as a source of Pb exposure (Duggan *et al.* 1985). Lepow *et al.* (1974) suggested that about 100 mg dust daily is consumed by young children via hand to mouth activities. A level of 193 mg kg^{-1} of Pb in household dust in the vicinity of a small lead refinery in UK has been reported (Muskett *et al.* 1979). Daily ingestion of 100 mg of such dust would result in the intake of a high amount of Pb.

Urban street dust and soil can be brought into the indoor environment via clothing and shoes. The concentrations of contaminants in indoor dust are generally correlated with their concentrations in soil, but other factors influence the relationship e.g. paint and the age of the house.

2.2.3.2 *Inhalation*

Inhalation of suspended particulate is also a potentially important route for metals to enter the human body. Much higher Cd and Pb concentrations are found in areas close to major atmospheric metal sources, and the concentrations can fluctuate widely as a result of weather conditions or changes in the emission characteristics (Muskett *et al*, 1979). Long term

inhalation studies of rats exposed to aerosols of cadmium chloride, sulphate and oxide fumes and dust at low concentrations showed a high incidence of primary lung cancer with evidence of a dose-response relationship (Friberg *et al*, 1992). Traffic wardens in Nigeria (Ogunsloa *et al*. 1994) and in Cairo (Kamal *et al*. 1991) who are occupationally exposure to traffic fumes had higher blood Pb levels than the non-exposure group. This indicates the greater risk of Pb poisoning for the traffic wardens than the general non-exposed population. Hence, traffic exhaust fumes and the dispersion of street dust by heavy traffic flow especially are possible routes of human exposure via inhalation for the urban population.

The World Health Organisation (WHO, 1987) Regional Office for Europe published "Air Quality Guidelines" for Europe (Ewers, 1991) which included recommended guideline values of Cd and Pb in air as follows:

Cd : 1-5 ng m^{-3} (one year average for rural areas),

Cd: 10-20 ng m^{-3} (one year average for urban areas),

Pb : 0.5-1 μg m^{-3} (one year average).

2.2.3.3 Water

The daily drinking water supply is a potential route of human exposure to heavy metals. The water supplies throughout the world mostly have relatively low concentrations of Pb. For instance, Pb in drinking water in USA range from 10 to 30 μg l^{-1} (WHO, 1977; USEPA, 1989). An extensive survey carried out in 1975 to 1976 showed that the majority of households in the UK had a lead concentration in daytime samples of tap water of less than 10 μg l^{-1} (DoE, 1977). However, several studies showed that Pb concentration can rise dramatically when soft acid water is conveyed by Pb plumbing (Weston, 1920; Moore, 1973). In addition, the high concentrations of Pb in water and the actual accumulation of Pb by food

from cooking water during the culinary process will increase the total quantity ingested in a more than additive manner (Berlin *et al.*, 1977; Moore *et al.*, 1979; Smart *et al.*, 1981).

The threat to the human health as a result of exposure to high intakes of heavy metals from drinking water provided in Pb and Cu plumbing (such as acidic water was conveyed by Cu pipes in Sweden; naturally acidic water is conveyed in lead pipe in Glasgow and Manchester, UK) is well known. The exposure to a higher heavy metal intake, particularly of mercury (Hg) and Cd from the bioaccumulation process in the aquatic food chain, has been considered (Environmental Resource Limited, 1983). A study showed diarrhoea in infants in Sweden, suspected to have been caused or prolonged by the presence of copper in water (Environmental Resource Limited, 1983).

2.2.3.4 Food

Cadmium, Cu, Pb and Zn are normal constitutes of most food crops (see Table 2.4). Metals in crops may be derived from aerosol deposition on the surface of crops or by the uptake from soil with a high metal content.

It has also been noted that canned food preserved in soldered cans is contaminated by Pb, and there is evidence showing that processed food absorbs metals from cooking media and from cooking utensils (MAFF, 1972; DHSS, 1980). Canned food presents two main sources of Pb in food. One is from the solder joining the sides of the can since this may flow into the can interior. The other is the tin plate itself although a standard Pb content of no more than 0.08% has been set (British Standard). However, some acidic foodstuffs such as fruit can facilitate leaching of the Pb from tin plate (Lansdown and Yule, 1986).

Table 2.4. Metal contents in agricultural crops (Wolnik *et al.*, 1985).

crops	metal content (mg kg^{-1})			
	Cd	Cu	Pb	Zn
carrot	0.028	0.58	0.009	2.6
field corn	0.012	1.50	0.022	18.5
potato	0.028	0.96	0.027	3.1
rice	0.012	1.90	0.007	13.5
tomato	0.017	0.65	0.002	1.4
spinach	0.065	0.66	0.045	4.5

In England, canned food has been calculated to contribute about 15% of the total dietary intake of Pb for adults (MAFF, 1983). Following the Food Regulation of 1979 in the UK, manufacturers do not use Pb in cans for infant food.

2.2.4 Human toxic effects of Cd, Cu, Pb and Zn

2.2.4.1 Cadmium

Cadmium is a toxic metal and a nonessential element in human biological functions with a low rate of excretion from the human body. It is predominantly accumulated in kidneys and livers. Exposure to Cd dust could cause emphysema and proteinuria of lung tumours (Friberg, 1948). In the 1960s, the itai-itai disease caused severe arthalgias and osteomalacis in middle-aged Japanese women who consumed Cd contaminated rice and water. In England, the average soil Cd level can reach 87 µg g^{-1} (range 2-520 µg g^{-1}) in Cd mining areas but no diagnosis of adverse health effects has been reported (Gloag, 1981 and Philipp *et al*, 1985). Buchet and co-workers (1983) observed a correlation between Cd intake from dust and

the level of blood and urinary Cd in children from an area of Belgium subjected to air contamination. The toxic effects of heavy exposure to Cd in humans (Perry *et al*, 1976) are listed as follows:

- acute gastro-enteritis
- acute pulmonary edema and interstitial pneumonitis
- decreased pulmonary function
    emphysema
    bronchitis
- renal dysfunction(proteinuria, glucosuria, aminoaciduria)
- moderate anaemia
- itai-itai disease
- increased mortality
- possible carcinogenesis

Due to the potentially adverse effects of Cd to human and animals, the WHO recommends that the daily intake of Cd should not exceed 1 μg kg^{-1}. The US EPA set the allowable daily oral intake to be 5×10^{-4} mg kg^{-1} day^{-1} (EPA, 1986) and established a primary drinking water standard of 10 μg l^{-1} for Cd. The EPA's Carcinogen Assessment Group adapted epidemiological data (Tunn *et al*. 1985) to calculate a unit cancer risk of 1.8×10^{-3} μg m^{-3} for Cd (EPA, 1985).

2.2.4.2 Copper

Copper is an essential element and plays an important role in human metabolism (Harris, 1991). Humans take Cu as a trace element from their daily diet, e.g. an adult requires approximately 1.5 to 3.0 mg per day of Cu for normal health (NAS, 1989). Copper may exist as oxides, sulphate or carbonate (ATSDR, 1990). Copper(II) also forms a number of stable complexes with ligands (inorganic or organic), or is bound to particulate matter in water (Stiff, 1971). Human beings can be exposed to Cu by

inhalation, ingestion and dermal contact because Cu is widely distributed in various environmental media. Ingestion of copper-contaminated food and beverages could cause acute gastrointestinal illness.

2.2.4.3 *Lead*

The Pb dose absorbed by adults and children can be approximately 5-10% and 40%, respectively, via gastrointestinal tract ingestion; between 50% and 70% of an inhaled dose can be absorbed if the particle size is less than $1\mu m$; organic Pb could have toxic effect on skin via heavy exposure (Ellenhorn and Varceloux, 1988). The global average daily intake of lead, estimated by the United Nations Environment Program (UNEP) (1991), was 80 μg d^{-1} from food and 40 μg d^{-1} from drinking water. The adverse human health effects caused by Pb (ATSDR, 1991 and 1993) are listed as follows:

- anaemia
- kidney diseases
- brain damage
- impaired function in peripheral nerve system
- high blood pressure(in middle-aged man)
- reproductive abnormalities
- development defects
- abnormal vitamin D metabolism
- death under certain circumstances.

For young children, low Pb level exposure may reduce intelligence, impair the function of learning, attention and classroom performance and reduce the growth rate of young children (Ellenhorn and Varceloux, 1988; Marecek *et al*, 1983). The relationships between Pb in dust/soil and the blood Pb level in children have been examined at different geological and mining areas, (Barltrop, 1975; Heyworth *et al.*, 1981; Bomschein *et al.*,

1989; ATSDR, 1990), traffic flows (Brunekreef *et al.*, 1983; Brunekreef, 1984; Rabinowitz *et al.*, 1984) and home environments (Stark *et al.*, 1982; Charney *et al.*, 1983; Bornschein *et al.*, 1987). The relationships among Pb in blood, dust and soil examined by different researchers according to the results of regression analysis are shown in Table 2.5. The geometric mean of the blood Pb level seemed to be higher in populations from the urban environment than those from smelter and mining areas (see Table 2.5). It has been suggested that Pb bioavailability is lower at mining sites as compared to urban environments due to the existence of relatively insoluble forms of Pb associated with mining waste (Cotter-Howells and Thornton, 1991; Davies *et al.*, 1992). This is an example showing the relevance of applying chemical speciation in environmental risk assessment.

Table 2.5 Best estimates of the linear response of lead in blood to changes in the lead level in soil and dust (cited by Burgoon et al., 1995).

study site	sources	period	population age (years old)	geometric mean PbB concentration ($\mu g\ dl^{-1}$)	slope estimate of blood to soil ($\mu g\ dl^{-1}$ per 1000 $\mu g\ g^{-1}$)	slope estimate of blood to dust ($\mu g\ dl^{-1}$ per 1000 $\mu g\ g^{-1}$)	reference
Omaha, Nevraska, USA	U/B	1970-1977	1- 18	21.47	14.4	10.6	Angle and McIntire, 1979
New Haven, CT, USA	U	1977	1- 6	26.94	2.2	2.9	Stark et al., 1982
Boston, USA	U	4/1979-4/1981	2	6[a]	2.2	nd	Rabinowitz et al., 1985
Cincinnati, USA	I	1980-1987	birth- 5	16.91	6.2	3.4	Bornschein et al., 1985; Bornschein et al., 1987
Edinburgh, UK	U	1983-1985	class 3/4	10.1[m]	nd	1.8	Laxen et al., 1987
Helena Valley, Montana, USA	S	1983	1- 5	9.76	nd	5.0	LCCHD, 1986
Kellogg, Idoho, USA	S	1983	1-9	15.8	0.6	1.9	PDHD, 1986
Telluride	M	1986	child/adult	6.1	nd	8.1	Bornschein et al., 1989
Leadville, Colorado, USA	C	1988	6- 7 months	8.7	2.8	nd	CDH and ATSDR, 1990
Midvale, Utah,USA	S	1989	6-72 months	4.93	1.9	nd	UC, 1990
Butte-Silver Bow, Montana, USA	M	8/1990-9/1990	<6	3.56	1.8	nd	UC, 1991

B: battery plant; C: city; I: inner city; M: mining; S: smelter; U: urban; [a]: arithmetic mean; [m]: median; nd: not detectable

2.2.4.4 Zinc

Zinc is an essential trace metal in human beings, and is a component or cofactor of more than two hundred enzymes (e.g. oxido-reductases, transferases, hydrolases, isomerases, and ligases) with a role in the metabolism of carbohydrates, proteins and lipids (Cleven *et al*, 1993). King and Turnlund (1989) summarised the adequate Zn levels required by the human body from ten countries to be 8-16,9-21, 15-25 and 2-6 mg per day for adults, pregnant women, lactating women and children, respectively. Studies of zinc toxicity to humans exposed by natural routes is limited. Some *in vitro* tests have shown that Zn is potentially genotoxic but there is no indications that Zn is carcinogenic (Cleven *et al*, 1993). The symptoms of Zn toxicity in human organs include caustic and irritant gastrointestinal tracts, elevated glucose and amylase levels and depressed calcium levels in pancreas, acute tubular necrosis and interstitial nephritis in kidneys (Ellenhorn and Varceloux, 1988).

2.3   Partitioning techniques

Partitioning techniques have been developed and widely used to study the chemical species of metals during last two decades. These approaches, such as X-ray diffraction (XRD) and the SEM/EDX based technique (Hunt *et al*., 1993; Davis *et al*, 1993), have proved to be very effective in determining the micro-mineralogy of heavy metal. However such techniques are limited as metals may spread evenly into the light solid matrix such as clay minerals and organic matter. In addition, some metal concentrations, such as Cd, Cu, Pb and Zn, in soils and dusts in the urban environment are usually not high enough to be detected by SEM. Chemical equilibrium models, such as GEOCHEM, DIASTB, and MINTEQ, are also used to calculate the speciation of metal in soil solution and in the gastrointestinal

tract (Sposito and Coves, 1988; Hemphill *et al.*, 1991). However, these models are subject to uncertainties in the assumptions and data available.

Due to the difficulties involved in physical determination and chemical equilibrium modelling, selective chemical extraction techniques have been developed to characterise particular physicochemical form of metals in sediment and soils (Tessier and Campbell, 1988; Li *et al.*, 1995). The sequential extraction techniques, particularly the procedure initiated by Tessier *et al.* (1979) and adapted by Li *et al.* (1995) for multi-element analysis using ICP-AES, have proved successful in partitioning the geochemical phases of heavy metal. The sequential extraction procedure focuses mainly on the hierarchical ranking of the strength of metal bindings according to the five operationally defined geochemical forms representing: (1) exchangeable, (2) carbonate, (3) reducible, (4) iron/manganese oxide, and (5) residual fractions with respect to their labile abilities (Tessier *et al.* 1979). Sequential extraction is recognised as a useful method for gaining information about the origin, manner of occurrence, bioavailability, mobilisation and transport of heavy metals.
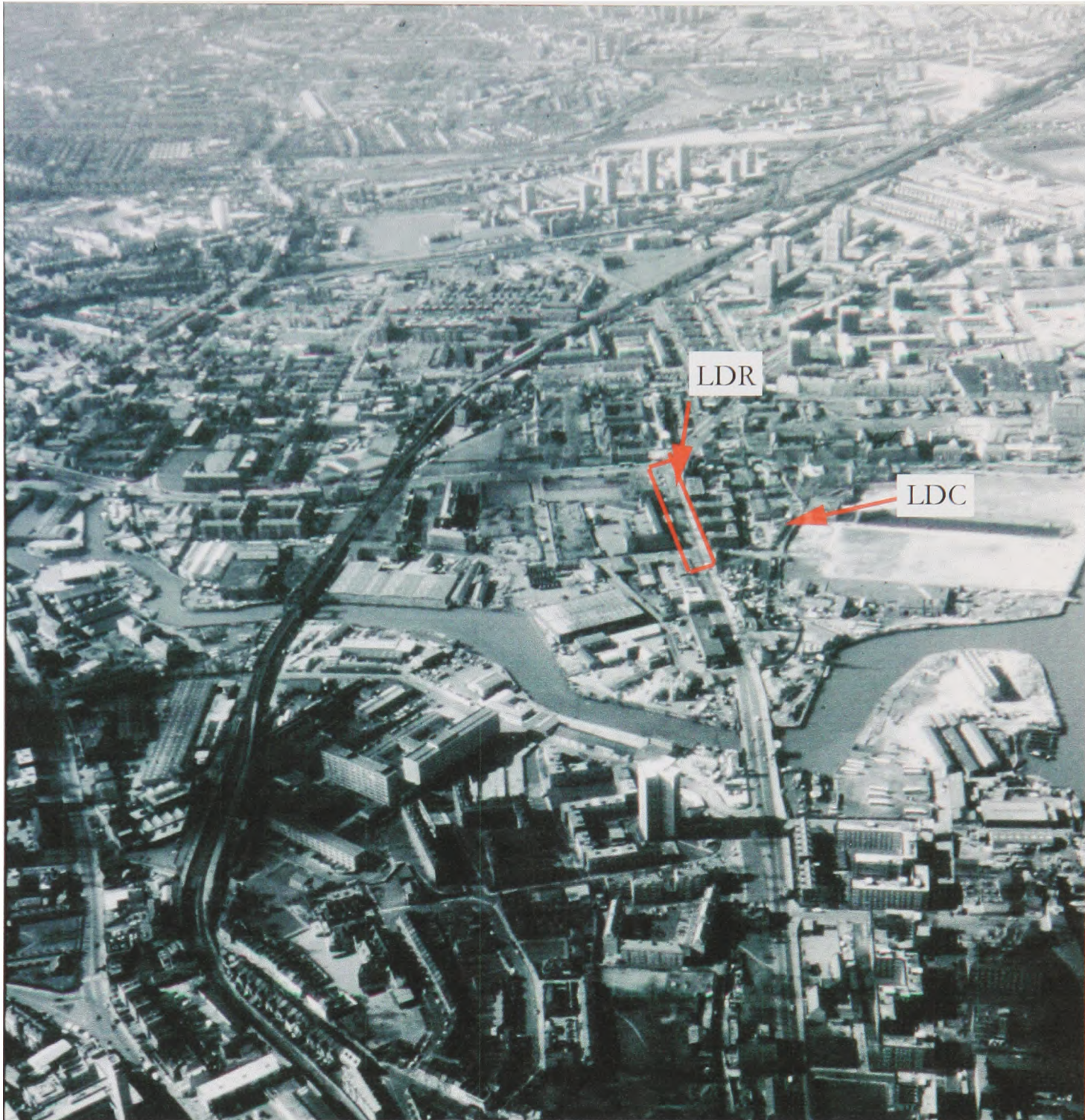
Figure 2.1 London road site (LDR) and car park site (LDC).

HDR
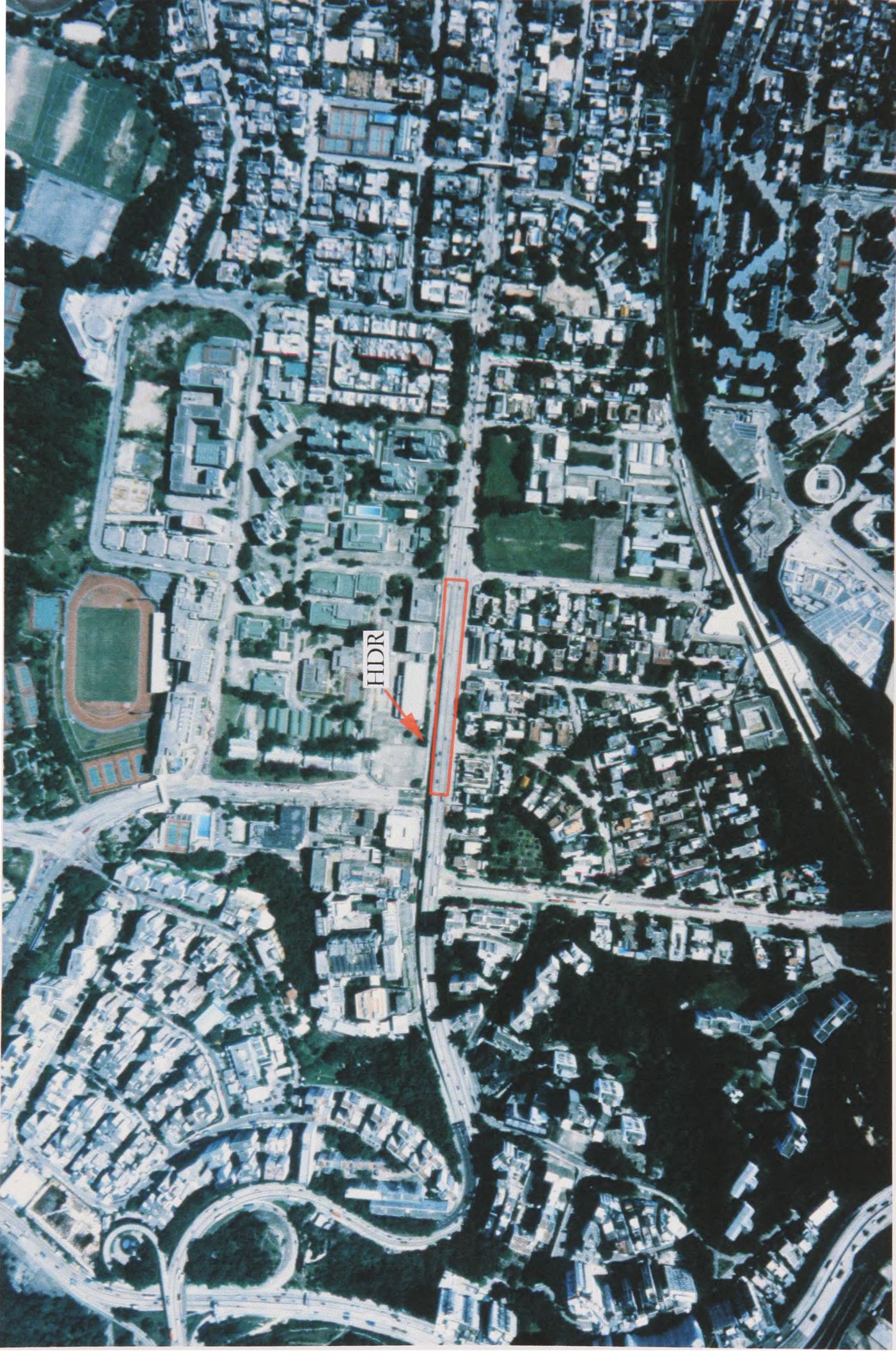
Figure 2.2 Hong Kong road site (HDR).

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Figure 2.3 Hong Kong car park site (HDC).

2.4 The study sites

Street dust samples were collected at four sampling sites (Table 2.6) chosen for this study: two from Hong Kong and two from London. Background soil samples were collected at another two sites, one from Hong Kong and one from London. A labeling system for samples was adopted (see Table 2.6) and used throughout this thesis.

One reason for choosing the sample sites in London and Hong Kong was that they had similar road systems, traffic flows (about 20,000 vehicles per day), and populations. However, these two places have different climates and different industrial histories. London, with an area of 1,579 km^2, is located in the temperate zone of Europe with an average temperature of

Table 2.6. Sampling sites.

Site	Site details	Surface
Site 1: LDR	The busy road junction between Creek Road (23,300 vehicles/day) and Deptford Church Street (16,700 vehicles/day), London.	Asphalt -stone
Site 2: LDC	A 40 year old school car park (used as Deptford Power Station's car park since the 1950's), Deptford Campus, University of Greenwich, Gonson Street, Deptford, London.	cement -stone
Site 3: HDR	A section of Waterloo Road (25,000 vehicles/day) between Junction Road and Suffolk Road, Kowloon, Hong Kong.	Cement -stone
Site 4: HDC	A 20 year old car park at the Chinese University of Hong Kong, Shatin, Hong Kong.	Cement -stone
Site 5: LSB	soil sample Beckham Place Park, Lewisham, London	Soil
Site 6: HSB	soil sample Ma On Shan, Shatin, HK	Soil

11°C and an annual average rainfall of 579 mm in 1995. Hong Kong is located within the sub-tropical zone of Asia with an area of 1078 km², an average temperature of 23.3 °C, and 2243 mm of annual rainfall (Census and Statistics Department, HK, 1996). The pH of rainwater is between 3.67 and 7.14 in London in 1995 (Clark, 1996). In Hong Kong, the weighted mean (different climatic rainfall) pH of rainwater is equal to 4.8 in 1996 (EPAHK, Air Quality in Hong Kong, result from the EPA Air Quality Monitoring Network).

High levels of dust, combined with other air pollutants (e.g. sulphur dioxide, nitrogen oxides and carbon monoxide) have made Hong Kong one of the most polluted areas in the region in terms of air pollution, threatening the health of the urban population and city aesthetics. In fact, dust has been reported to be Hong Kong's main air pollution problem (Environmental Protection Department, HK, 1995).

Both sites LDR (Figure 2.1) and HDR (Figure 2.2)are located near busy road junctions in commercial/residential areas with nursery schools and colleges nearby. Sampling sites LDC (Figure 2.1) and HDC (Figure 2.3) are both inside university car parks. However, the sampling site LDC that used to be a car park of the Deptford Power Station, is close to an industrial area and has been affected by industrial activities of the past whereas HDC in Hong Kong is a twenty year old university car park and has not been subject to any influence of industrial activities.

2.4.1 *Background of London sites*

London has a history of industrial activities for over 200 years whereas Hong Kong has only been industrialised in the last few decades. Table 2.7 shows the period and types of industrial activities and their possible

contribution to metal contamination in Deptford, London (LDR and LDC sites, see Table 2.6). The lower temperature in London, especially in winter, may increase the use of chokes on car engines and therefore increased fuel consumption - hence, more traffic pollution. In Hong Kong, the heavy and frequent rain episodes in summer may wash off the aerosol and remove particles (or soluble phases thereof) from the street surface and therefore diminish heavy metal accumulation on the urban dusts.

The London car park (LDC) has been used by the Deptford Power Station staff since 1950's but is now the car park of the University of Greenwich Deptford campus, where the demolished power station is only across the street. A metal scrap yard is also present only a few yards away. This shows the post and present industries may still have high influence of high level of metal in dust around the site. In addition, the car park is confined in an area surrounded by brick walls. Dust and pollutants are not easily blown away and are therefore prone to accumulate inside the car park. In contrast to LDC, the road site, LDR, is more like an open space and the dust on the road surface may easily blow away or mix with the soil from the roadside.

Although traffic is the major contribution to Pb in the urban environment, the Cd, Cu, Pb and Zn contents of dust samples in LDR and LDC are possibly due to earlier industrial activities in the Deptford region. LDR is located at a junction between Creek Road and Deptford Church Street in Deptford, London. Creek Road runs westwards towards Central London whereas Deptford Church Street connects to the A2 which is one of the busiest two lane roads in south-east London. LDC is located at Gonson Street, a street behind the Creek Road towards the River Thames.

Table 2.7 The period and types of industrial activities and its possible contaminated sources in Deptford, London (Paterson, 1990).

Period	Industrial activities near the study sites	Possible metal contaminating sources
Prior 1897	General Steam Navigation Company works	Cu, Pb, Zn
	Gas work	As, Cd, Cu, Mn, Pb and Fe oxides
	Coal storage	
1897	General Steam Navigation Work	Cu, Pb, Zn
	Gas work	As, Cd, Cu, Mn, Pb and Fe oxides
	Coal storage	
	Stone work	
	Iron shipyard	As, Cu, Hg, Zn, Pb
		As, Cu, Hg, Pb, Cr, Zn
1916	Gas work	As, Cd, Cu, Mn, Pb and Fe oxides
	Sawing and desiccating works	
	Engineering works	metal dust
	Iron work	Cu, Pb
		Pb
1920	Gas work	As, Cd, Cu, Mn, Pb and Fe oxides
	Engineering work	
	Coal storage	Cu, Pb
1950	Deptford Power Station (coal fire)	Heavy metals
	Marine engineering works	As, Cd, Cr, Cu, Hg, Pb, Zn
	Electrical welding	Cr, Mn, molybdenum
	Dreadnought yard	As, Cu, Hg, Pb, Zn
1970/ 77/ 83	Egg processing and cold store for meat	Heavy metals
	Power station (demolished in 1980)	
	Coal store	Cd, Cr, Cu, Ni, Mn, Pb, V, W, Zn
	Scrap metal recovery (east of Gonson Street)	Cd, Cr, Cu, Ni, Mn, Pb, V, W, Zn
	scrap metal recovery and processing	Cd, Pb, Zn
	Vehicle/barge repairs	Pb
	Graphics company	Pb

The industrial activities in Deptford commenced in the 17th century with an iron shipbuilding yard. From that time onwards, there have been a myriad of industries in this area including gas works, shipyards, stoneworks, metal scrap yards and a power station (see Table 2.7). Lead scrap yards contribute significantly to environmental contamination albeit in localised areas (Blake *et al.* 1987).

In a previous study carried out for the Greater London area (Schwar *et al.* 1988), Cd, Cu, Pb and Zn contents in street dust were found to be lower in rural and residential areas, and distinctly higher in industrial regions. The effects of industry are now seen in remote areas; for example, the Pb level in Greenland has increased 20 times within a period of two hundred years, since the beginning of the Industrial Revolution in 1780 (Sawyer *et al*, 1985) and Pb concentrations have increased dramatically since 1940s; coinciding with the introduction of lead-additive in petrol since 1923.

2.4.2 Background of Hong Kong sites

The Hong Kong car park site (HDC) is located on the top of a hill with its three sides surrounded by trees and the remaining side facing the campus of the Chinese University of Hong Kong. The car park is used by school buses and privates cars and there is no additional traffic or industrial activities nearby. The Waterloo Road site (HDR) is located at one of major routes between the New Territories and Kowloon. Yim and Nau (1987) analysed 287 urban dust samples in Hong Kong. They reported that Waterloo Road in the Kowloon area had the highest Cd, Cu, Pb and Zn contents in road dust and concluded that the main contribution to Pb in road dusts was derived from vehicle exhausts. The area is densely populated and includes a university, a hospital, a military station, a nursing

home for the elderly, schools and residential estates. This site is subject to a complex mix of sources of pollutants.

Although Hong Kong does not have heavy metal industries (such as mines and smelters), the metal products industry is the fifth largest manufacturing industry. There are in total 3511 metal products establishments in 1995 in Hong Kong (CSDHK, 1996). These industries mainly comprise of fabricated metal products, aluminium utensils, buffing, polishing, electroplating, metal cutting, welding, badges and galvanising (CSDHK, 1996). Industrial discharges are therefore likely to be an important contributor of Cd, Cu, Pb and Zn in Hong Kong.

Chapter Three

CHARACTERISATION OF HEAVY METALS IN URBAN DUST USING SEQUENTIAL EXTRACTION

3.1 Introduction

This chapter discusses the use of Tessier's chemical speciation method (Tessier *et al.*, 1979) in: (1) providing information on operationally defined geochemical forms of street dust and their distribution; (2) evaluating the levels of heavy metals in urban street dust samples collected in London and Hong Kong and; (3) finding possible explanations for the different levels of metal content in street dust as criteria for the risk assessment of different environmental pathways.

3.1.1 Sequential Extraction

The procedures of sequential extraction have been widely used to examine the chemical associations of metals in many kinds of environmental particles. For instance, Schnoor (1996) lists various kinds of particles with which metal ions can form surface complexes in natural waters. These include clays, carbonate, complexes, iron and manganese hydroxides, algae and bacteria and organic detritus. Schnoor (1996) remarks that quartz particles do not bind trace metals to the extent of FeOOH and MnO_2 particle but quartz grains can be coated by iron oxides or organic coatings. The binding of metals varies according to the type of the particles. There is clearly an advantage in being able to categorise the metal content of mixed groups of particles which arise in natural systems, such as in river sediments, soils and street dust in a systematic way.

The lack of standardised procedures of sequential extraction had previously made it difficult to compare experimental data from different studies. However, during recent years investigators have tended to use the same or similar schemes, such as Tessier and co-workers' scheme (Tessier *et al.* 1979). Tessier and co-workers' sequential extraction procedure has been widely applied to assess different metal contaminated environmental media including river sediment (Tessier *et al.*, 1979; Hickey and Kittrick, 1984), sewage sludge (Calvet and Bourgeois, 1990), soil (Harrison *et al.*, 1981; Hickey and Kittrick, 1984; Gibson and Farmer, 1986; Calvet *et al.*, 1990), street dusts (Harrison *et al.*, 1981; Gibson and Farmer, 1984; Hamilton *et al.*, 1984; Fergusson and Kim, 1991; Stone and Marsalek, 1996) and house dust (Fergusson and Kim, 1991).

3.1.2 Size spectrum

The size spectrum of dust particles is another important factor affecting the mobilisation and transport pathways of heavy metals in dust. In general, fine dust particles are more likely to be blown by wind and disturbed by passing traffic, increasing their chances of being inhaled directly or ingested through adherence to fingers, nails, and contaminated food. Fine dust particles are also easily washed away by storm-water.

Lau and Wong (1983) suggested that street dust particles with sizes smaller than 125 μm in diameter should be used to indicate levels of Pb contamination because dust particles of this size range belong to a more homogeneous group and has no significant difference in metal content. In addition, having studied the efficiency of street sweepers, it was found that dust particles in size ranges of 0-125μm, 125-250μm and 250-500μm were subject to removal rates of about 20%, 50%, and 60% respectively (Sartor and Boyd, 1972). Sartor and Boyd (1974) also found that a great portion (more than 50%) of contaminants including Pb and Zn are associated with

Table 3.1: The sampling period.

Sites		sampling months					
LDR & LDC	1995	Jan	Mar	May	Jul	Sep	Nov
HDR & HDC	1996	Jan	Mar	May	Jul		
LSB	1995		Mar				
HSB	1996				Jul		

the fine solid fraction of street surface particulate, typically, 250 μm or less. Ellis and Revitt (1982) indicated that about 50% of Cd, Cu, Pb, and Zn by mass in road sediment were found in particles of sizes less than 500 μm. Therefore, in order to ensure representative metal content in dust samples and to facilitate comparison, the following size ranges are used in the present study: (1) less than 125 μm, (2) between 125 and 250 μm, and (3) between 250 and 500 μm.

3.2 Materials and methods

3.2.1 Sampling and sample collection

Dust samples were collected in London (LDR and LDC) once every two months from January 1995 until November 1995 (Table 3.1), resulting in six batches of dust samples. In Hong Kong (HDR and HDC), dust samples were collected once every two months from January 1996 until July 1996. (For a profile of the sampling sites, see Chapter 2 Section 2.3).

Street dust samples were collected by gently sweeping the ground surfaces (as this is the most widely used sampling techniques for collecting dust from street surface) of the random sites from a selected street with a plastic brush into a dustpan taking care not to disturb some of the smaller particles that might be lost by suspension into the atmosphere.

The samples were oven-dried at 40°C for seven days and then sieved to three different particle size ranges: 0-125 μm, 125-250 μm and 250-500 μm using British Standard sieves. Code numbers are designated to the samples as in Table 3.2.

3.2.1 Sequential extraction

The sequential extraction scheme developed by Tessier and co-workers (1979) is summarised in Flowchart 3.1. 0.5 g of dust/ soil was used for each extraction. Extraction was performed in 50 ml polypropylene centrifuge tubes with an orbital shaker to mix well as required. All extraction was performed in triplicate for each sample. During each extraction, the solution was centrifuged at 4000-4500 rpm for 30 min. The supernatant was filtered using 5C filter paper into a 25 ml volume metric flask and made up to 25 ml using ultra-pure water then decanted into polythene bottles. Samples were stored in a 4 °C cool room until further analysis. The same matrix of standard was prepared for each extraction for atomic absorption (AAS) measurement. All chemicals used in the experiment were Analytical Reagent (A.R.) grade.

Table 3.2: Code numbers for dust samples.

| particle size | London | | Hong Kong | |
	Road dust (LDR)	Car park dust (LDC)	Road dust (HDR)	Car park dust (HDC)
< 125μm	LDR1	LDC1	HDR1	HDC1
125-250μm	LDR2	LDC2	HDR2	HDC2
250-500μm	LDR3	LDC3	HDR3	HDC3

3.2.3 Physio-chemical analysis

The following measurements were made:

pH and electrical conductivity of dust and soil were analysed using an Orion pH/ISE Meter Model 920A and a PW 9418 pH meter, following the method of Rump and Krist (1988). Carbonate contents were determined by the volumetric method (Rump and Krist, 1988). Organic contents were measured by loss-on-ignition (Allen, 1989). Concentrations of Cd, Cu, Pb and Zn in the solution were determined by using a flame atomic absorption spectrophotometer (Instrumentation Laboratories Inc. Mass, USA) and an anodic stripping voltameter (TraceLab™ Radiometer, Copenhagen).

3.2.3.1 AAS

Flame atomic absorption spectrometry (AAS) still remains a frequently used method for element analysis in environmental media. In principle, the techniques is a measure of atomic vapour and to pass through it radiation of the right wavelength to excite atom from the ground state to an excited electronic level (Skoog and Leary, 1992). A hollow cathode lamp is used as excitation source and a atomiser is combustion flame. The absorption of radiation of excited atoms from ground state to high energy level is a quantitative measure for the ground state atom in the vapour and is proportional to the concentration of absorbing (Skoog and Leary, 1992). In this study, detection limits of Cu, Cd, Pb and Zn using AAS (Instrument Lab.) were 0.01, 0.035, 0.1 and 0.01 mg l^{-1} respectively.

Flowchart 3.1. Procedure of Sequential Extraction (modified from Tessier et al., 1979)

↓ 0.5 g dust/ soil sample

1 M $MgCl_2$ (8ml)
T = 20°C
pH = 7
1 hour
.... Exchangeable

↓ Residue

1M Sodium acetate (8ml)
T = 20°C
pH = 5
5 hours
.... Carbonate

↓ Residue

0.04M NH_4OHHCl in 25% acetic acid (20ml)
T = 96 ± 3°C
pH = 4
6 hours
.... Fe - Mn Hydrous Oxides

↓ Residue

(1) 0.02 M HNO_3 (3ml)
   30% H_2O_2 (5ml)
   T = 85°C ; pH = 2
   2 hours
(2) 30% H_2O_2 (3ml)
   T = 85°C ; pH = 2
   3 hours
(3) 3.2 M Ammonium acetate
   in 20% HNO_3 (5ml)
   T = 20°C ; pH = 2
   0.5 hour
.... Organic matter

↓ Residue

(1) 70 % HNO_3 (5ml)
(2) Aqua regia
.... Residual

T: temperature

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3.2.3.2 Anodic stripping voltametery

Anodic stripping voltametery (ASV) is a high sensitivity technique to determined the concentration of the metals in solution. ASV is operated in two steps. The electrolysis step which is a pre-concentration step where the metal ions of interested are reduce to free metal and deposited on a working electrode as a thin film or a drop of mercury. This is followed by the stripping step in which the metals are removed from the electrode to the solution by oxidation into ionic form solution (Skoog and Leary, 1992). The measurements are made in the stripping step. The detection limits of this techniques can be as low as 1 ppm to 1 ppb of the solution (Skoog and Leary, 1992).

3.3 Results

3.3.1 Total Cd, Cu, Pb and Zn concentrations in the dust and background soil

samples

Table 3.3 summarises the arithmetic mean and standard deviation of concentrations of Cd, Cu, Pb and Zn, pH, calcium carbonate and organic contents of dust and soil samples. The total Cd, Cu, Pb and Zn concentrations in the dust and soil were the summation of exchangeable, carbonate, Fe-Mn oxides, organic and residual fraction of sequential extraction. It is noted that the enrichment factors for Cd, Cu, Pb and Zn in the dust samples relative to the background soil samples were approximately 3, 20, 10 and 10 respectively. The urban dust samples from London were slightly alkaline with pH ranging between 7.01 and 8.49 whereas the pH of dust samples from Hong Kong was between 6.48 to 7.86. Background soil samples collected from both London and Hong Kong were acidic (LSB: pH 5.48; HSB: pH 4.65).

Table 3.3: Total concentrations (arithmetic mean ± sd µg g⁻¹) of Cd, Cu, Pb and Zn, pH, calcium carbonate content (%) and organic content (%) in dust and soil samples.

	n	Cd	Cu	Pb	Zn	pH	Calcium carbonate content (%)	Organic content (%)
Dust samples								
Site 1: LDR1	18	5.7 ± 2.2	273.2 ± 56.6	1283.9 ± 345.5	1876.1 ± 614.5	7.98 ± 0.43	4.08 ± 0.82	10.7 ± 2.8
LDR2	18	3.6 ± 0.4	223.3 ± 69.5	818.6 ± 245.9	1167.8 ± 529.6	8.22 ± 0.39	2.35 ± 0.61	7.22 ± 1.6
LDR3	18	3.4 ± 0.4	267.1 ± 111.5	560.0 ± 285.7	1100.0 ± 546.4	8.49 ± 0.31	1.50 ± 0.24	4.22 ± 0.8
Site 2: LDC1	18	6.9 ± 1.6	358.9 ± 154.2	1936.5 ± 534.0	2807.7 ± 413.4	7.03 ± 0.29	3.73 ± 0.41	11.0 ± 2.5
LDC2	18	5.9 ± 0.8	255.3 ± 90.3	995.9 ± 194.6	1735.6 ± 153.5	7.01 ± 0.26	4.63 ± 0.56	5.27 ± 1.3
LDC3	18	5.5 ± 0.7	302.0 ± 212.4	795.7 ± 151.3	1391.4 ± 250.2	7.03 ± 0.31	16.40 ± 2.75	8.01 ± 1.6
Site 3: HDR1	12	4.8 ± 0.4	330.1 ± 52.6	896.6 ± 208.4	2444.3 ± 186.6	7.86 ± 0.60	1.67 ± 0.46	17.5 ± 2.8
HDR2	12	4.2 ± 0.3	242.1 ± 9.6	659.4 ± 97.6	2194.2 ± 223.7	7.57 ± 0.61	2.46 ± 0.60	15.0 ± 2.0
HDR3	12	3.3 ± 0.2	231.9 ± 108.2	533.2 ± 120.0	1608.9 ± 310.0	7.53 ± 0.53	3.92 ± 1.54	13.9 ± 0.9
Site 4: HDC1	12	3.2 ± 0.1	115.7 ± 38.8	260.3 ± 22.6	704.6 ± 119.7	6.68 ± 0.27	4.53 ± 0.78	12.9 ± 2.2
HDC2	12	2.7 ± 0.2	118.6 ± 29.6	244.4 ± 36.8	709.6 ± 60.6	6.52 ± 0.32	4.41 ± 0.99	14.3 ± 1.5
HDC3	12	2.7 ± 0.3	123.5 ± 39.8	229.1 ± 65.3	646.9 ± 120.6	6.48 ± 0.35	12.01 ± 2.11	13.8 ± 2.7
Soil samples								
Site 5: LSB	6	1.4 ± 0.3	16.4 ± 2.7	149.4 ± 10.2	228.2 ± 12.6	5.48 ± 0.25	8.01 ± 0.45	15.8 ± 0.6
Site 6: HSB	6	1.2 ± 0.1	11.5 ± 2.0	69.5 ± 3.2	126.4 ± 10.3	4.65 ± 0.21	4.96 ± 0.56	17.6 ± 1.0
dust:/soil ratio	≈ 3	≈ 20	≈ 10	≈ 10				

n: number of samples
LDR1, LDR2, LDR3/ LDC1, LDC2, LDC3: London road dust/ London car park dust 0-125 µm, 125-250 µm, 250-500 µm, respectively.
HDR1, HDR2, HDR3/ HDC1, HDC2, HDC3 : Hong Kong road dust/ Hong Kong car park dust 0-125 µm, 125-250 µm, 250-500 µm, respectively.
LSB and HSB are the London soil and Hong Kong soil, respectively.

Table 3.4 Correlation between Cd, Cu, Pb and Zn contents in dust samples form LDC, LDR, HDC and HDR sites.

	Pb	Cu	Zn
	LDR		
Cu	0.15		
Zn	0.71***	0.24	
Cd	0.65**	0.07	0.72***
	LDC		
Cu	0.44		
Zn	0.78**	0.31	
Cd	0.31*	0.14	0.34
	HDR		
Cu	0.25		
Zn	0.49	0.52	
Cd	0.57*	0.54	0.73**
	HDC		
Cu	0.62*		
Zn	0.24	0.25	
Cd	0.38	0.04	0.01

Note: significant correlation at the p level of significance is show as:
*: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$. The remaining correlation coefficients were not found to be significant.

Table 3.4 shows the correlation among the Cd, Cu, Pb and Zn contents of all dust samples. Note that significant correlation can be found between the levels of Pb and Cd and between the levels of Zn and Cd in dust samples, both from LDR and HDR sites.

Table 3.5: The results of a Student t-test for differences in mean concentration of each metal between pairs of sites.

	LDR vs. HDR		LDC vs. HDC		LDR vs. LDC		HDR vs. HDC	
	t	p	t	p	t	p	t	p
Cd	0.008	0.994	1.877	0.070	-3.959	<0.001	2.466	0.023
Cu	-0.563	0.579	2.064	0.055	-1.004	0.323	2.297	0.033
Pb	1.123	0.270	3.108	0.005	-2.672	0.012	2.422	0.026
Zn	-3.881	0.001	1.005	0.328	-3.044	0.004	3.728	0.002

t: t statistic; p: level of significance.
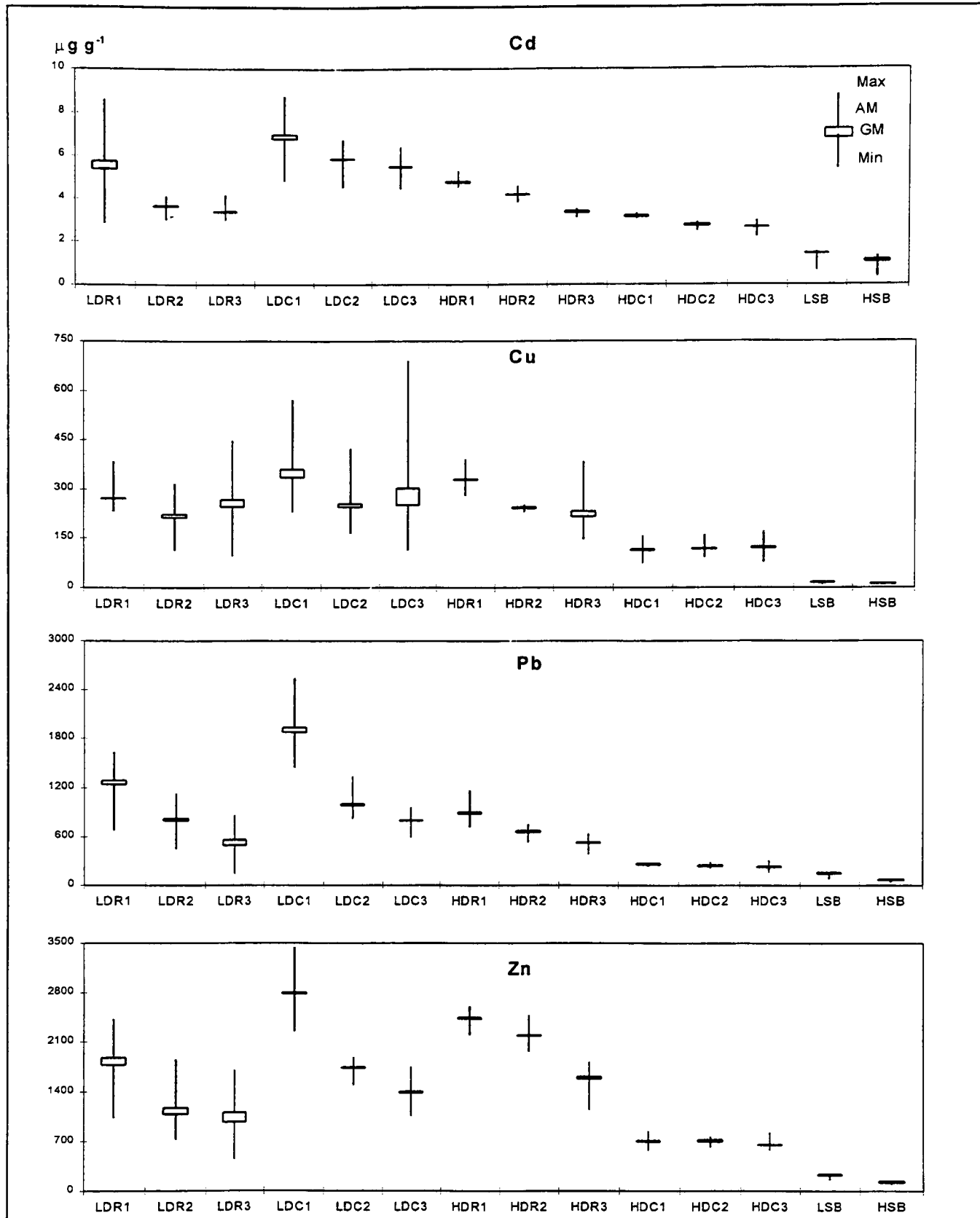
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LDR1, LDR2, LDR3 : London road dust 0-125 µm, 125-250 µm, 250-500 µm, respectively.
LDC1, LDC2, LDC3 : London car park dust 0-125 µm, 125-250 µm, 250-500 µm, respectively.
HDR1, HDR2, HDR3: Hong Kong road dust 0-125 µm, 125-250 µm, 250-500 µm, respectively
HDC1, HDC2, HDC3: Hong Kong car park dust 0-125 µm, 125-250 µm, 250-500 µm, respectively.

Figure 3.1: Box plots showing comparison of the maximum (Max), minimum (Min), arithmetic (AM) and geometric (GM) means of Cd, Cu, Pb and Zn levels in different dust soil samples.

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A Student t-test has been applied to see if there are any significant differences among dust samples from the different sampling sites in terms of their metal concentrations. The results are given in Table 3.5. When comparing the road dust samples from London with those from Hong Kong, only the Zn concentrations show a significant difference ($p < 0.05$). For car park dust, only the Pb concentrations show a significant difference ($p < 0.05$). On the other hand, when comparing road dust samples with car park dust samples, almost all the metal concentrations (except Cu) show significant differences ($p < 0.05$), whether the samples are from London or Hong Kong.

Figure 3.1 shows the distribution of maximum, minimum, arithmetic mean and geometric mean of Cd, Cu, Pb and Zn contents in different size ranges of dust samples as well as in the background soil samples. The higher Cd, Cu, Pb and Zn contents tend to be associated with the finest particles for dust samples from the LDR, LDC and HDR sites. For the HDC site, heavy metal contents tend to be evenly distributed among all three different size ranges of dust samples.

The heavy metal contents of dust samples from London (LDR and LDC) show greater ranges of concentrations than from Hong Kong (HDR and HDC). On the whole, there is not much difference between the arithmetic mean and the geometric mean in all dust samples.
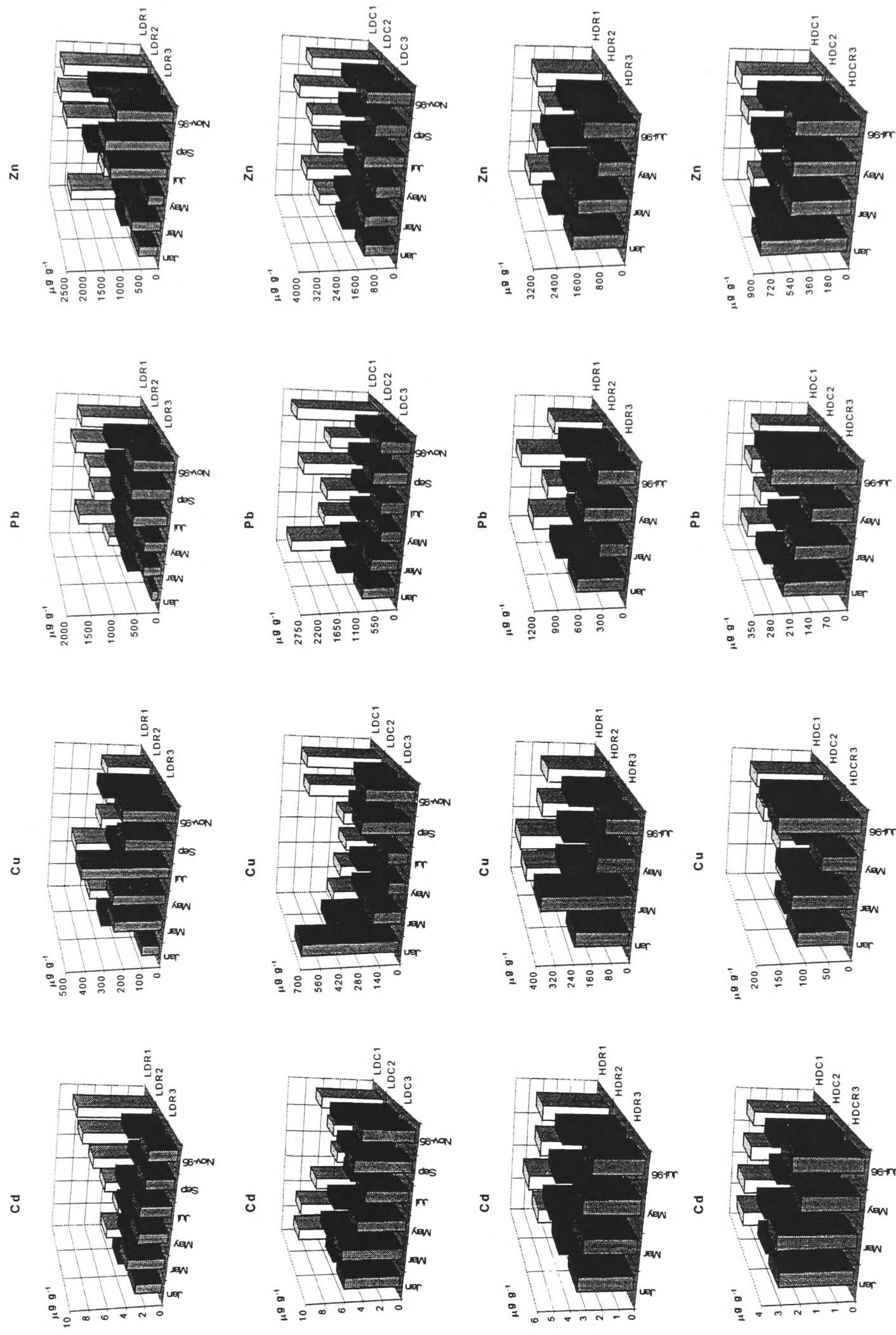
LDR1, LDR2, LDR3/ LDC1, LDC2, LDC3: London road/ London car park dust 0-125 mm, 125-250 mm, 250-500 mm, respectively.
HDR1, HDR2, HDR3/ HDC1, HDC2, HDCR3:Hong Kong road/ Hong Kong car park dust 0-125 mm, 125-250 mm, 250-500 mm, respectively.
Figure 3.2 Total Cd, Cu, Pb and Zn contents of dust sample over the sampling period.

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The temporal variation of total Cd, Cu, Pb and Zn contents of dust samples over the sampling period is shown in Figure 3.2. The data indicates that concentrations of Cd, Cu, Pb and Zn in dust samples from the HDR and HDC sites had less fluctuation temporally than from the LDR and LDC sites. For the LDR dust samples, the levels of Cd and Zn in particles of size less than 125 μm increased gradually from January to November 1995 while the lowest levels of Cu and Pb appeared in January and September 1996, respectively. In general, metal concentrations in the finest dust particles exhibited stronger fluctuations.

3.1.2 Chemical speciation of Cd, Cu, Pb and Zn

The chemical partitioning (%) of Cd, Cu, Pb and Zn in the dust and soil samples based on the Tessier's sequential extraction are presented in Table 3.6. Figure 3.3 shows a graphical representation of the chemical partitioning of metals in the finest dust particles.

Among the four metals, Cd appears to exist with the highest percentages (20.8-30.9%) in the exchangeable phase in the dust samples. Copper is predominately associated with the organic fraction in the dust samples (55 to 75 %), followed by the Fe-Mn oxides fraction, and then the residual fraction; together these three fractions account for more than 85% of total Cu content in the dust samples.

Lead is primarily associated with Fe-Mn oxides fraction (46 to 60%), followed by the carbonate and organic fractions, and with less than 2% of Pb associated with the exchangeable fraction. The Fe-Mn oxides fraction is by far the most important faction for Zn, with the carbonate fraction being the second important one, followed by the organic and residual fractions.

Table 3.6 Mean chemical partitioning (percent of total) of Cd, Cu, Pb and Zn in the dust and soil samples from the study sites.

	Site1			Site 2			Site 3			Site 4			Site 5	Site 6
	LDR1	LDR2	LDR3	LDC1	LDC2	LDC3	HDR1	HDR2	HDR3	HDC1	HDC2	HDC3	LSB	HSB
Cadmium														
Exchangeable	25.0	22.4	26.1	23.6	25.9	23.3	20.8	21.3	25.0	30.9	29.6	31.6	15.0	27.1
Carbonate	17.4	17.9	22.9	13.7	16.2	16.7	21.8	24.0	29.7	27.9	29.0	29.4	24.3	26.5
Fe-Mn oxide	39.9	36.4	26.2	43.5	37.2	36.3	37.0	37.4	29.1	20.9	18.7	18.7	32.4	20.5
Organic	11.4	14.1	13.7	10.9	12.9	16.5	11.6	10.3	9.2	13.1	12.6	8.7	13.3	13.3
Residual	6.4	9.3	11.0	8.3	7.8	7.2	8.8	6.9	7.1	7.1	10.1	11.5	15.0	12.7
Copper														
Exchangeable	3.2	2.3	2.1	2.6	3.5	3.2	2.7	2.6	3.1	6.5	6.0	6.0	2.2	2.8
Carbonate	10.9	6.1	6.3	5.5	4.9	6.0	2.3	2.2	2.1	4.2	3.2	3.4	14.6	14.5
Fe-Mn oxide	19.2	22.3	10.6	13.2	19.2	17.8	14.0	8.0	9.9	20.4	13.3	15.2	6.1	8.5
Organic	59.3	56.3	67.2	63.9	55.7	58.1	72.2	75.6	78.3	59.6	71.3	69.9	48.7	43.6
Residual	8.2	13.0	13.8	14.9	16.7	14.9	8.8	11.6	6.7	9.2	6.2	5.5	28.4	23.3
Lead														
Exchangeable	1.0	1.1	1.9	1.2	1.9	2.1	1.9	1.9	3.1	7.2	6.4	6.8	8.9	5.0
Carbonate	26.1	25.7	22.1	16.1	18.5	15.3	11.8	12.3	12.6	14.4	14.4	6.8	29.8	24.7
Fe-Mn oxide	51.1	49.7	46.3	60.3	58.9	56.3	59.4	59.4	57.0	50.1	51.2	59.6	24.3	34.0
Organic	14.5	18.1	22.4	14.6	13.2	18.2	20.3	20.3	20.4	19.4	20.5	17.2	19.7	11.2
Residual	7.3	5.5	7.3	7.7	7.5	8.1	6.6	6.1	6.9	9.0	7.5	9.5	17.3	23.9
Zinc														
Exchangeable	3.8	3.5	3.1	3.7	5.8	4.4	0.9	1.1	1.2	8.3	6.9	6.2	4.1	4.2
Carbonate	41.4	38.4	31.4	25.3	28.5	26.2	35.3	35.4	35.1	29.1	29.3	29.4	14.4	16.5
Fe-Mn oxide	40.9	47.5	46.8	58.4	49.7	50.0	52.4	52.3	51.8	43.0	47.0	46.6	64.1	53.1
Organic	6.1	7.2	11.7	6.3	8.5	10.2	7.9	8.3	8.5	11.7	11.8	11.6	5.3	7.1
Residual	7.9	3.5	7.0	6.2	7.5	9.2	3.5	2.9	3.2	7.9	5.0	6.1	12.0	19.1

LDR1, LDR2, LDR3/ LDC1, LDC2, LDC3: site 1 (London road)/ site 2 (London car park) dust 0-125 μm, 125-250 μm, 250-500 μm, respectively.
HDR1, HDR2, HDR3/ HDC1, HDC2, HDC3: site 3 (Hong Kong road)/ site 4 (Hong Kong car park) dust 0-125 μm, 125-250 μm, 250-500 μm, respectively.
LSB and HSB are site 5 (London soil) and site 6 (Hong Kong soil), respectively.

Figure 3.4 shows how the Cd, Cu, Pb and Zn contents of dust samples are distributed among geochemical phases and among particles of different size ranges. The first thing to notice from Figure 3.4 is that dust particles of different size ranges from the Hong Kong car park site are remarkably homogeneous in term of their heavy metal contents among all geochemical phases. For the other three sites, the finest particles tend to possess higher heavy metal concentrations in certain geochemical phases: for Zn and Pb, it tends to be the carbonate and Fe-Mn oxides fractions; for Cu, it tends to be the organic fraction; for Cd, it tends to be the exchangeable and oxides fractions.

Figures 3.5-3.9 compare the road dust samples against the car park dust samples for their heavy metal contents in each of the five geochemical phases. On the whole, the Hong Kong road dust samples have higher heavy metal contents than the Hong Kong car park dust samples in all geochemical phases *except* the exchangeable phase. On the contrary, the London car park dust samples have generally higher concentrations of Zn, Pb, and Cd (but not Cu) than the London road dust samples.
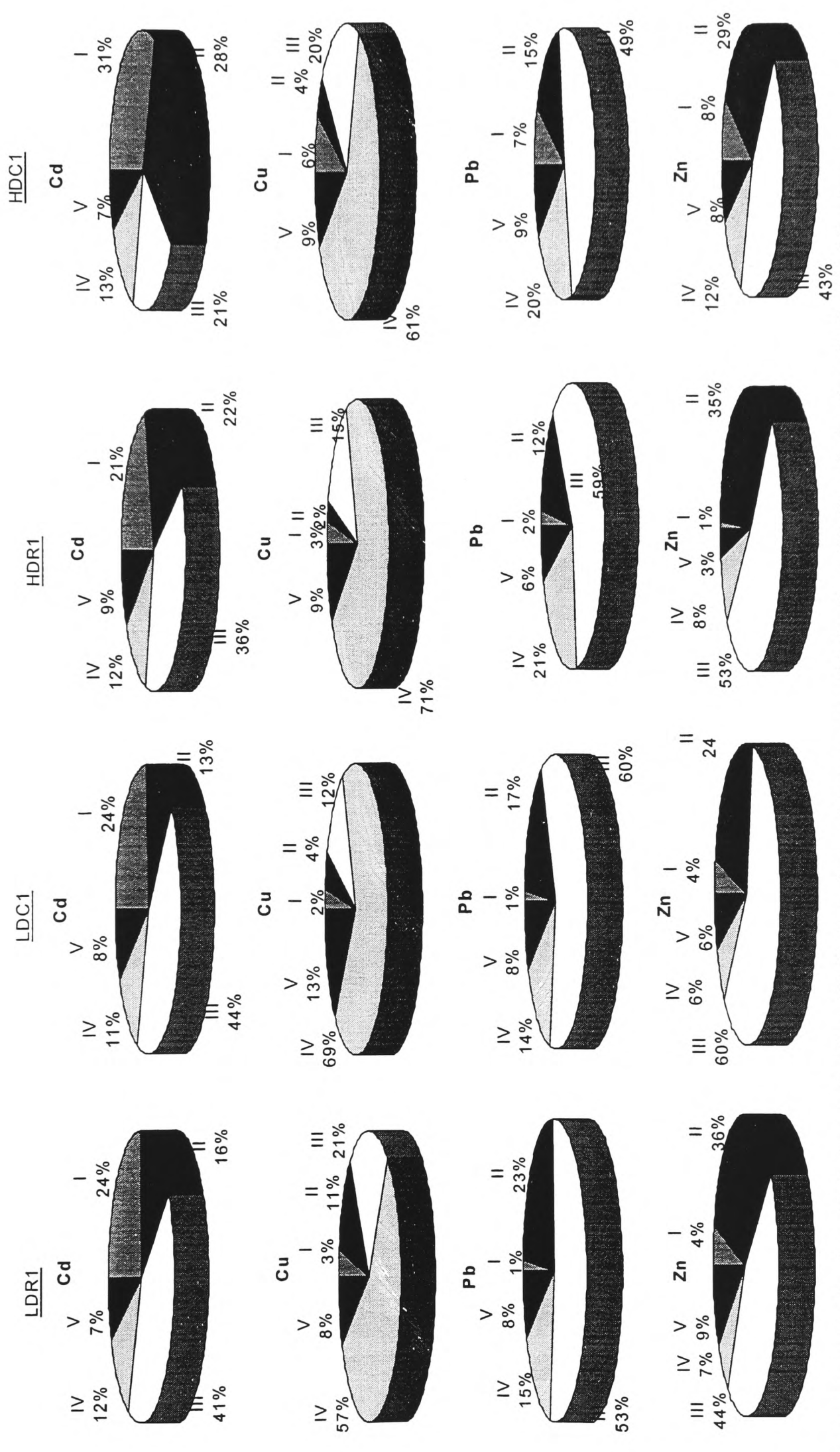
I: Exchangeable fraction; II: Carbonate fraction; III: Hydrous iron and manganese oxide fraction; IV: Organic fraction; V: Residual fraction

Figure 3.3 Chemical fractionation (%) of Cd, Cu, Pb and Zn in urban dust (particle size < 125 μm).

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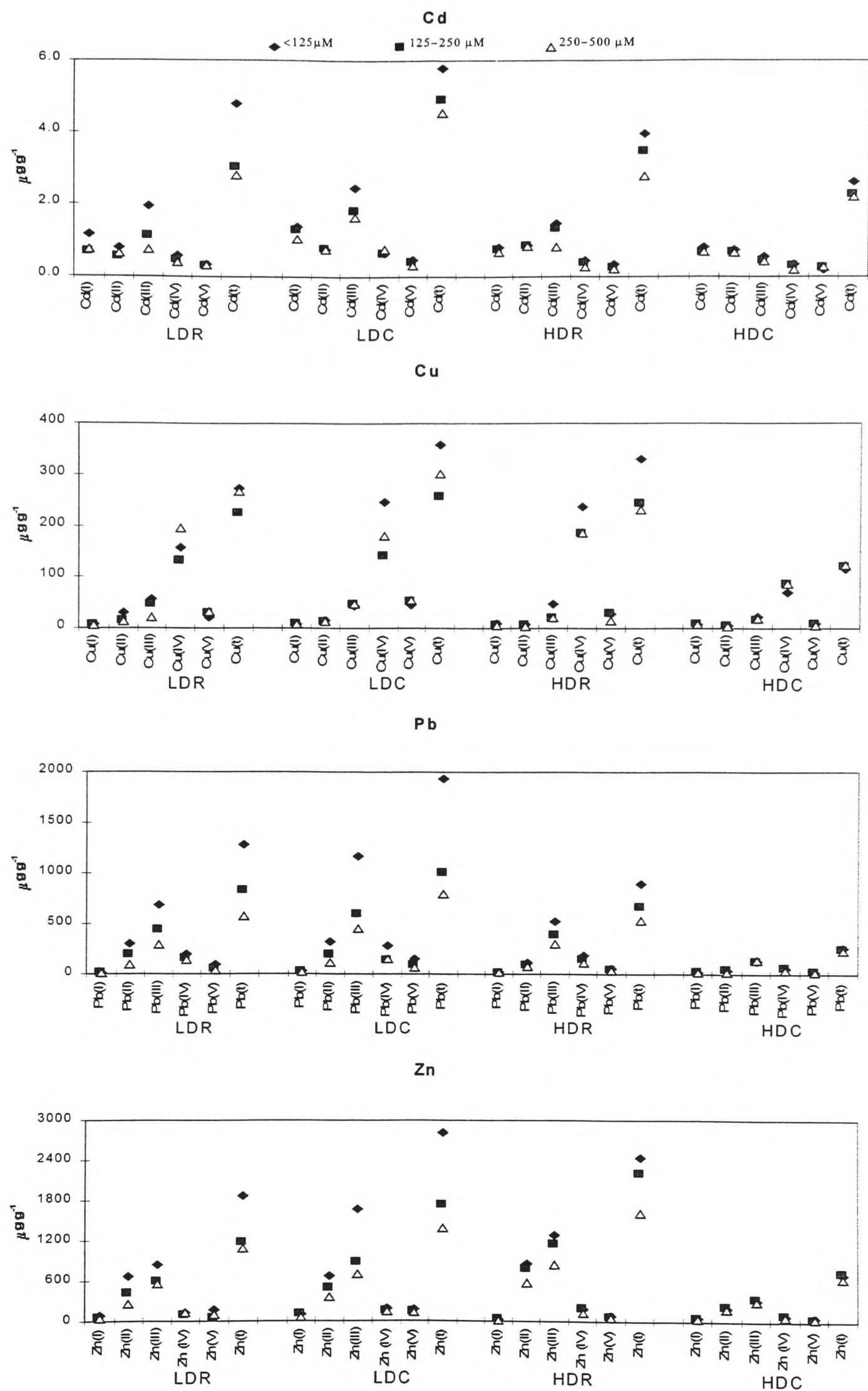
(I): exchangeable fraction;(II): carbonate fraction; (III) Fe-Mn oxides fractions;
(IV): organic fraction; (V): residual; (t): total metal content

Figure 3.4 The distribution of Cd, Cu, Pb and Zn content of different size range of dust sample in different geochemical phases.
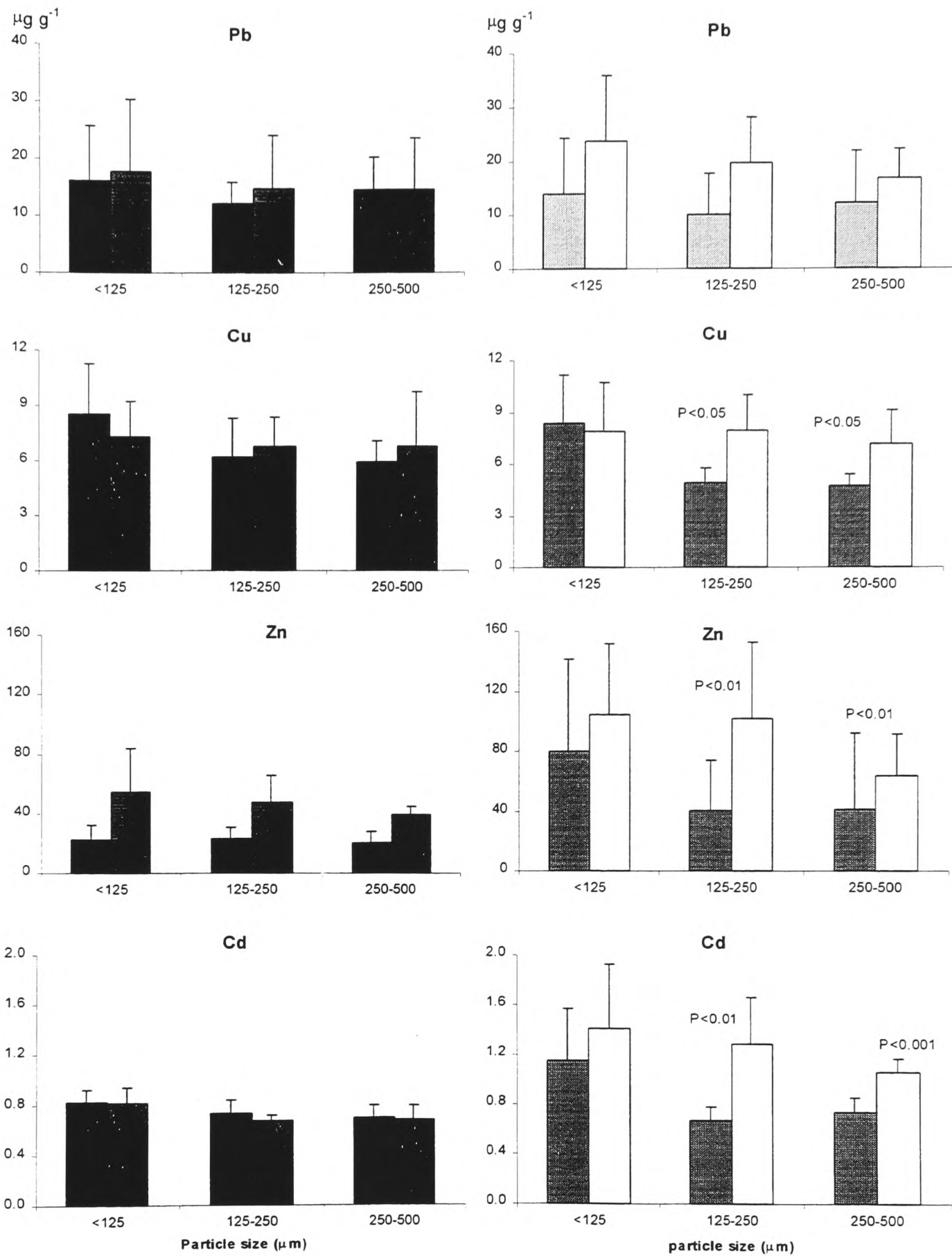
: Hong Kong road dust; : Hong Kong car park dust : London road dust; : London car park dust

Figure 3.5 Comparison of the exchangeable fraction of Pb, Cu, Cd and Zn contents between car park dust and road dust.

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μg g⁻¹

Pb

Cu

P<0.001   P<0.001   P<0.01

Zn

Cd

Particle size (μm)

■: Hong Kong road dust ; ▦: Hong Kong car park dust

μg g⁻¹

Pb

Cu

Zn

Cd

P<0.01

particle size (μm)

▦: London road dust ; □: London car park dust
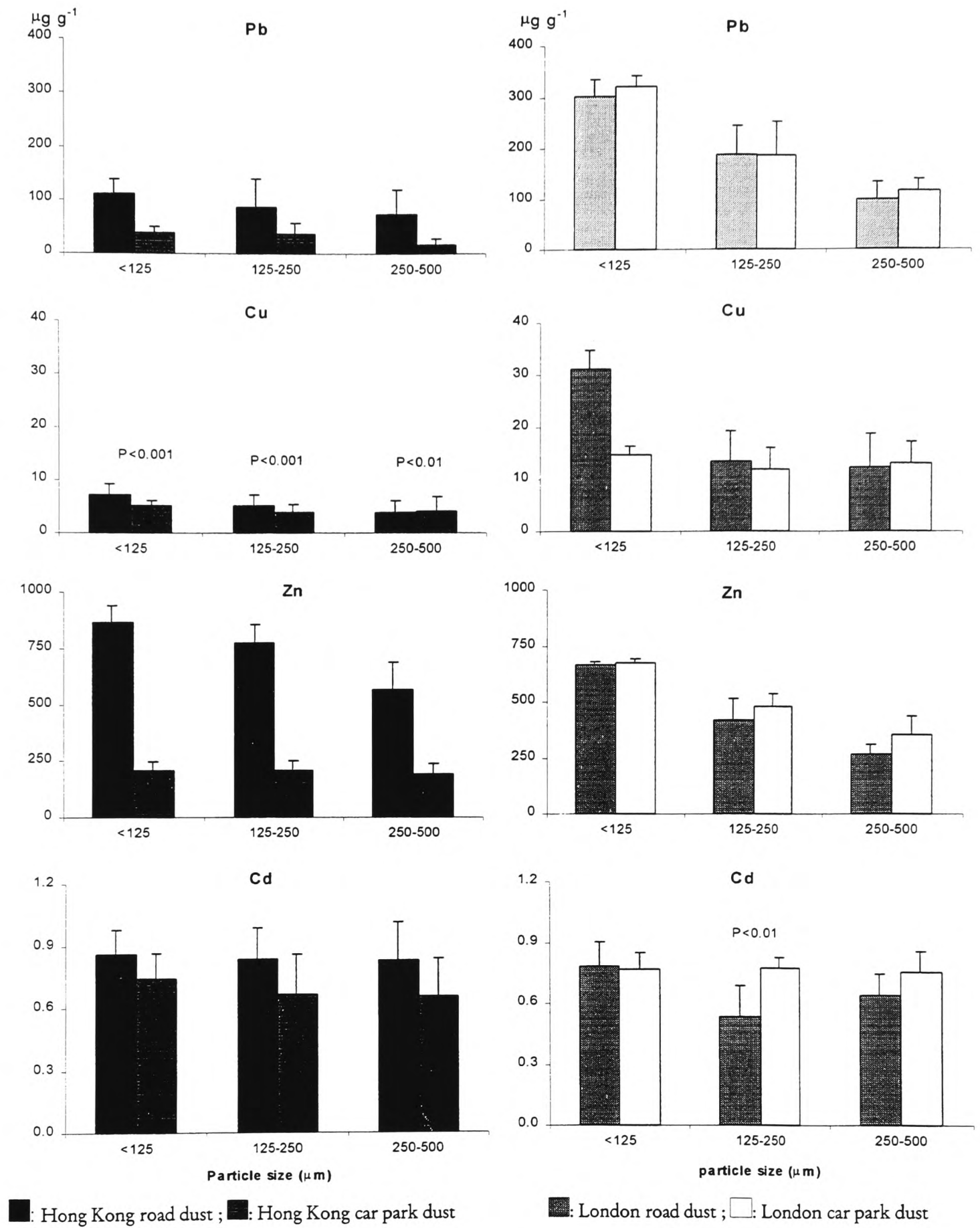
Figure 3.6 Comparison of the carbonate fraction of Pb, Cu, Cd and Zn
contents between car park dust and road dust.

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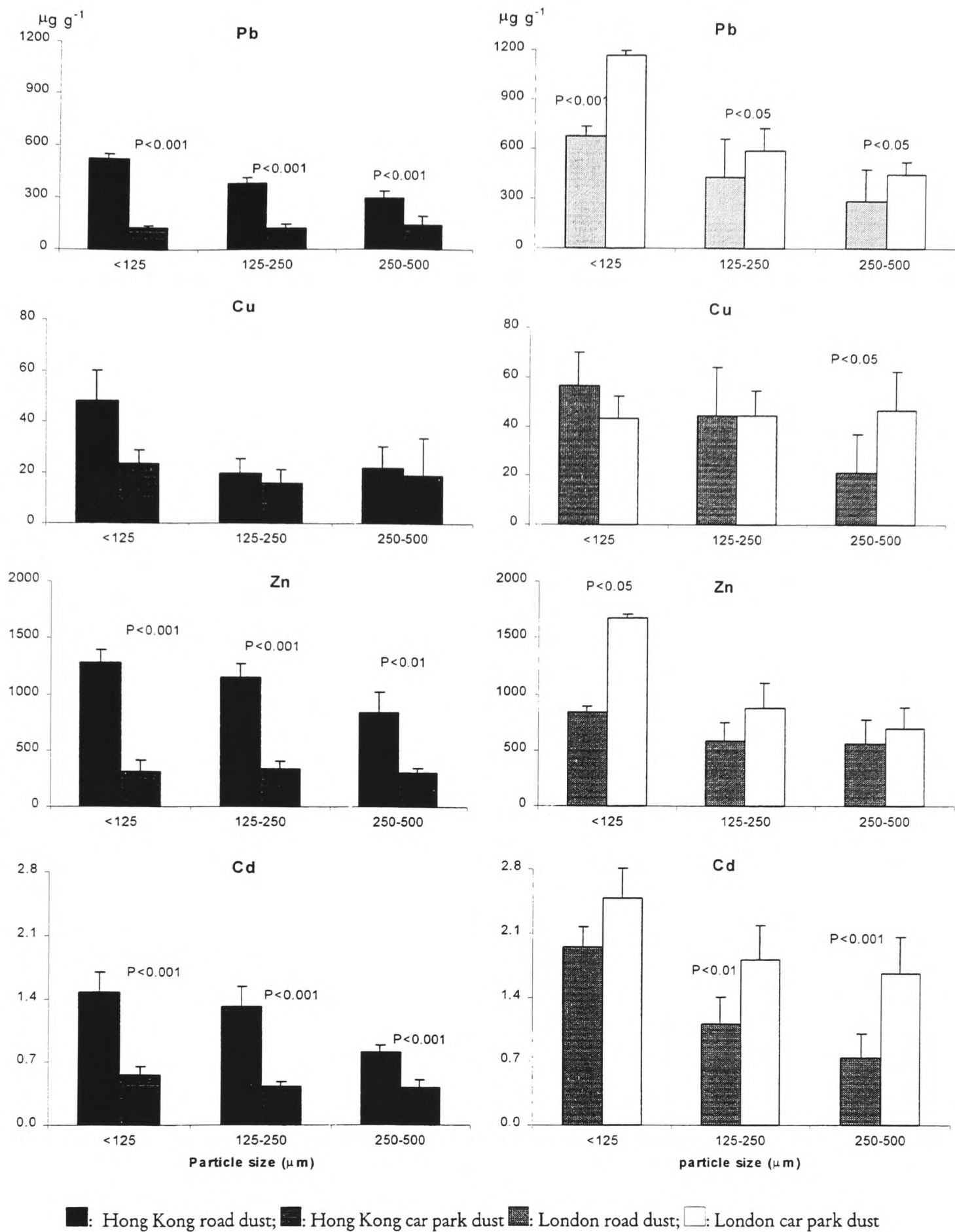
Figure 3.7 Comparison of the hydrous Fe-Mn oxides fraction of Pb, Cu, Cd and Zn contents between car park dust and road dust.

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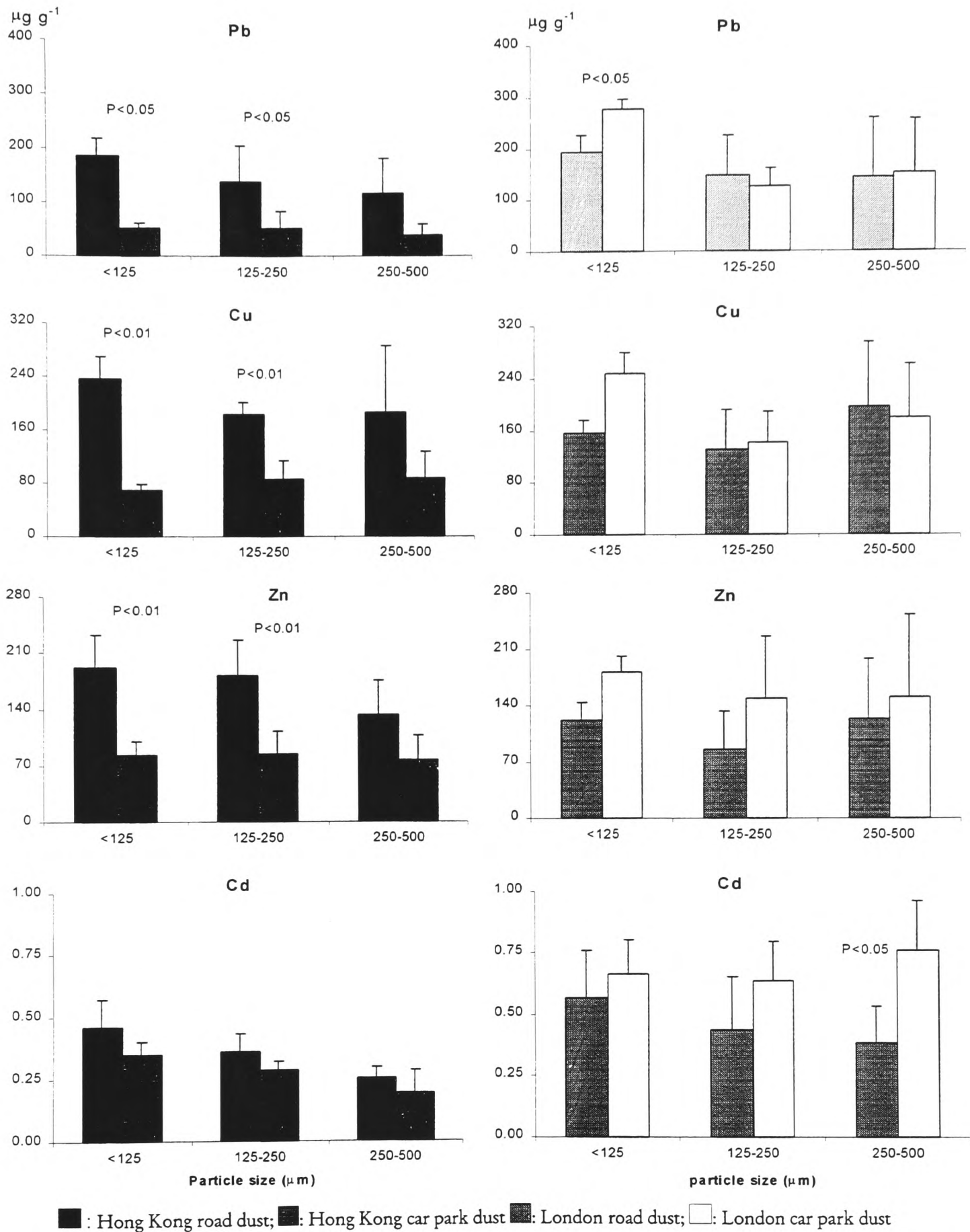
Figure 3.8 Comparison of the organic fraction of Pb, Cu, Cd and Zn contents between car park dust and road dust.

Figure 3.9 Comparison of the residual fraction of Pb, Cu, Cd and Zn contents between car park dust and road dust.

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3.4 Discussion

3.4.1 Total heavy metal contents of dust samples

3.4.1.1 Variations among sampling sites

Among the dust samples collected from four different sites in different months during 1995 and 1996, significant differences ($p < 0.05$) in heavy metal contents can be observed between:

a) road dust samples and car park dust samples from both London and Hong Kong (see Table 3.5),

b) the finest ($< 125\mu m$) and coarser particles of the dust samples from London sites (see Figure 3.1), and

c) to a lesser extent, the finest and coarser particles of the *road* dust samples from Hong Kong sites (see Figure 3.1).

For the difference in (a), the local factors and location discussed in Chapter 2 Section 2.4 may offer the best explanation for the difference between Hong Kong road site (HDR) and car park site(HDC). In London, the car park site (LDC) is confined in an area surrounded by brick wall hence dust and pollutants are not easily blown away and are prone to accumulate inside the car park. In contrast to LDC, the road site, LDR is more like an open space and the dust on the road surface may easily blow away or mixes with the soil from the roadside. Although LDR and LDC sites are in very close distance, their heavy metal may derive from different sources. However the differences between two pairs of sites cannot be explained in terms of any known large fixed source.

For the differences in (b) and (c), similar results were obtained for street dust from the Menomonee River watershed, Wisconsin, USA (Dong *et al.* 1984). According to that study there are two likely factors. First in geochemistry

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higher surface sorption is usually associated with the finer particles. The other factor is that much of the Cd, Pb and Zn from the combustion of leaded petrol, oil lubricants, or aerosol emission may pass through a vapour phase prior to sorption on particle surfaces and tend to be concentrated on particles of larger surface area. There was no obvious trend noticeable for Hong Kong sites (HDC & HDR). Higher levels of metal were associated with smaller particles particularly, in carbonate and hydrous Fe-Mn oxides fractions (Figures 3.6 and 3.7). On the other hand, the Cu contents of street dusts were more evenly distributed among the particle size ranges. Similar results were reported by Dong et al (1984). It was suggested this might be due to the abrasion of metal surfaces with varying degrees of corrosion and pulverisation.

As seen in Figure 3.2, no particular trend of seasonal variations during the sampling period can be found in metal content in this study. This may be due to urban dust being subject to the meteorological factors such as wind speed and intensity of rainfall and prolonged periods of dust accumulation. These factors may relocate dust from the urban street surfaces. Duggan (1984) who measured the airborne Pb level for a period of 12 months at two monitoring sites in London found no evidence of seasonal variation in the concentration of Pb in dust. However, there are also findings which show that the highest metal content are found in winter and these are explained by the increasing occurrences of urban smog, vertical poor diffusion and also increased fuel combustion of coal and oil in winter (Peirson et al. 1973; Salmon et al. 1976: Miller, et al. 1987).

Despite all the above observations on variations among dust samples, the aim of the thesis is to investigate the availability of metals in dust, not the variation of metal concentration in dust in time and space. Hence effort has not been spent on taking more samples. In fact the later analyses show that

Table 3.7 Greater London Council classification for contaminated soil: suggested range of vales mg kg^{-1} air dried soils. (Kelly, 1980).

	Cd	Cu	Pb	Zn
Typical values for uncontaminated soils	0-1	0-100	0-200	0-250
Slight contamination	1-3	100-200	200-500	250-500
Contamination	3-10	200-500	500-1000	500-1000
Heavy contamination	10-50	500-2500	1000-5000	1000-5000
Unusually heavy contamination	50	2500	5000	5000

the forms in which metals are held in dust are more important than variations in concentration.

3.1.1.2 International guidelines for soils

International guidelines do *not* exist for the heavy metal content of dust accumulated on road surfaces. In soils that are not exposed to other polluting sources one expects the concentrations of heavy metals to be lower than in dust because of the presence of organic material mixed with the soil. Not surprisingly measured concentrations in soil are found to be lower than in road dust (Table 3.3).

Table 3.7 shows the Greater London Council (GLC)'s suggested ranges of classification for metal contaminated soil. It is noted that the GLC classification does not depend on the availability of the metal. Table 3.8 shows the Dutch Criteria Index (DCI), the Ontario Provincial Sediment Quality (OMOE) guideline for metal, the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) guidance for assessment of contaminated land, together with the Swiss guidelines for soil.

Although there is no regulation or standard limit for metals in dust in UK at present, the Great London Council (GLC) has proposed a guideline value of 500 μg g^{-1} for Pb (in the 0.5 mm size fraction of dust in external air) as justifying additional investigation and 5000 μg g^{-1} as a level subject to remedial actions or control (Duggan, 1981). Among the study sites, the average Pb levels in road dust at the LDR, LDC and HDR sites were 1.1-4 times higher than the GLC guideline for additional investigation.

According to the GLC classification for contaminated soil (Table 3.7), Cd and Cu contents fell into "slight contamination" or "contamination" ranges in all dust samples. The Pb content in the finest dust particles was within the "heavy contamination" range for LDR and LDC and in the "contamination" range for the other sites. The Zn level was in the "heavy contamination" range for dust at LDR, LDC and HDR, and in the "contamination" range for dust at HDC. None of the soil samples (LSB and HSB) exceeded the "slight contamination" range.

According to the Dutch Criteria Index (DCI) guidelines (Table 3.8), the Cd content of the dust samples in the present study fell into the "further investigation" category for LDR and LDC. Cu and Zn contents fell into in the "further investigation" category for all dust samples. "Clean-up investigation" would be needed for LDR, LDC and HDR as far as Pb was concerned. The levels of Cu, Pb and Zn also fell into the "severe effect" category for LDR, LDC and HKR according to Ontario Provincial Sediment Quality (OMOE) guidelines (Stone and Marsalek, 1996).

Table 3.8 The international guidance of Cd, Cu, Pb and Zn in soil and sediment.

	Cd	Cu	Pb	Zn	References
		(mg kg^{-1})			
DCI guidelevels					Tiller, 1992
A (background value)	1	50	50	200	
B (further investigation)	5	50	150	500	
C(clean-up investigation)	20	100	600	3000	
OMOE guidelines		500			Stone and Marsalek, 1996
Lowest effect level	0.6	16	31	120	
Severe effect level	10	110	250	820	
ICRCL "Trigger concentration" guidance					ICRCL, 1987
[a]Group A:	3[a1]		500[a1]		
	15[a2]		2000[a2]		
[b]Group B:		130[b1]		300[b1]	
Swiss guide value for soil					FOEFL, 1986
Total content (pseudo): 2M HNO$_3$-extract	0.8	50	50	200	
Soluble content: 0.1M NaNO$_3$ -extract	0.03	0.7	1	0.5	

Explanation:

*DCI guide levels: Dutch Criteria Index for assessing soil contamination guide levels.

*OMOE guidelines: Ontario Provincial Sediment Quality Guidelines for Metals.

*ICRCL guidance: Interdepartmental Committee on the Redevelopment of Contaminated Land Guidance on the assessment of contaminated land.

[a]Group A: contaminants which may pose hazards to health.

[b]Group B: contaminants which are phytotoxic but not normally hazards to health.

[a1] : planned used for domestic garden, allotments.

[a2] : planned used for parks, playing fields, open space.

[b1] : soil pH should be maintained at about 6.5; total concentration (extractable by HNO$_3$/ HClO$_4$); the phytotoxic effects of Cu, Ni and Zn may be additive; the value are applicable as the 'worst-case'; the concentration might not have an adverse effect on grass.

Under the Interdepartmental Committee on the Redevelopment of Contamination Land (ICRCL) tentative "trigger concentration" guidelines (see Table 3.7), Cu and Zn levels in most dust samples might cause

Table 3.9 Comparison between the level of metal in dust samples and different aerosol particulate and urban soil.

	Cd	Cu	Pb	Zn	Reference
London		$\mu g\ g^{-1}$			
dust collected in Nov. 95					
LDR:dust < 125 µm	8.7	240	1532	2393	present study
125-250 µm	4.0	316	1125	1822	
250-500 µm	3.2	273	860	1491	
LDR: roadside aerosol PM_{10}	19.1	315	2219		Rosch, 1996
indoor aerosol PM_{10}	26.3	304	1431		
London Boroughs					
Garden soil	2.4^G	9^G	654^G	424^G	Culbard et al., 1988
Incineration fly ash (Edmonton)	476		9118		Wadge et al., 1986
Hong Kong					present study
HDR:dust < 125 µm	4.8	330.1	897	2444	
125-250 µm	4.2	242.1	659	2194	
250-500 µm	3.3	231.9	533	1609	
HDC:dust < 125 µm	3.2	115.7	260	705	
125-250 µm	2.7	118.6	244	710.	
250-500 µm	2.7	123.5	229	647	
Hong Kong coal fly ash	35	40	115	44	Wong and Wong, 1986
Incineration fly ash	206	1630	7315	120801	Liu et al., 1987
Hong Kong urban soil	0.9	16	90	59	Chen et al., 1997

G : geometric mean.

phytotoxic effect to plants; Cd and Pb levels might pose health hazards at the LDR, LDC and HDR sites. The ratios of dust to soil for Cd, Cu, Pb and Zn at the study sites were 2-5, 10-22, 3-13 and 5-12.

The evidence shows that the levels of Cd, Cu, Pb and Zn in the dust samples have reached noticeably high levels, but urban soil does not contain levels of metal concentration, which exceed guidelines. In other words, the issue of metals in urban dust deserves further separate attention.

3.1.1.3 Aerosol particulate as a source of metal contamination in urban dusts

Aerosol particulates can be deposited on the street surface, amid high humidity or intermittent episodes of rain. Hence aerosol particulates could also be an important source of metal in street dust. A previous study (Rosch, 1996) which measured metal concentrations of PM_{10} particulates during the period 29th November 1995 to 27th February 1996 was carried out at the LDR site. Samples of PM_{10} were collected from the kerbside of Creek Road and inside the Rachel McMillian Building adjacent to Creek Road. PM_{10} is defined as particulate matter which is less than 10 μm in aerodynamic diameter (QUARG, 1993). Table 3.9 shows the metal content of the PM_{10} particulates collected at the LDR site in comparison with the results on urban dust obtained by the present study.

For London, the concentrations of Cd, Cu and Pb in aerosol particulate, PM_{10}, from LDR were somewhat higher than in dust samples. Pb concentration in roadside PM_{10} was somewhat 1.4-2.6 times higher than dust from the road surface. Cd content was much greater (2-8 times) in PM_{10} particulates (particularly the indoor PM_{10}) than in roadside dust. To put these difference in context it may be seen that incineration fly ash from the Edmonton Waste Incinerator has 6-10 times higher Pb concentrations and 50-150 times higher Cd concentrations than road dust. In Hong Kong, the

Cd, Cu, Pb and Zn contents of incineration fly ashes are 45-100, 5-14, 8-32 and 49-187 times higher, respectively, considerably higher than those of urban dust. The Cd content of coal fly ash Hong Kong is also 7-13 times higher than that of urban road dust. In Hong Kong, Pb concentration in roadside dust was approximately equal to that in dust samples collected from window frames on the 2nd to 24th floors of a high rise building (Chui and Chan, 1986). This may suggest the association of roadside dust with the aerosol and suspended particles in Hong Kong, because the high rising buildings and subtropical climate in Hong Kong provide an environment for good vertical mixing of air.

Incineration fly ash from both London and Hong Kong contains higher metal levels than soil, PM_{10} and urban dust (Table 3.9). Wage and Hutton (1987) suggest that the municipal waste incineration was the single largest source of airborne Cd in UK. Owing to the stringent emission standards (effected on 1 December 1996), incinerators in UK built in the late 1960's and early 1970's have all been shutdown or modernised, including the Edmonton Waste Incinerator in London to meet the new standards (RCEP, 1993). In Hong Kong, there were three incinerators that were used to deal with solid municipal waste. However, these three municipal incinerators have been closed down since December 1990, March 1993 and May 1997, respectively, due to emission problems (EPDHK, 1997). Although the incinerators in the study region of Hong Kong and London have been shutdown, particulate matters that were produced during previous period of operation may still be present in the environment because of long residence time of metals, though in a highly diluted form.

The long-term trend of annual average of Cd, Cu, Pb and Zn levels in air in Greater London between 1985 and 1992 are shown in Figure 3.10. Concentrations of Pb declined sharply between 1985 and 1986 and then

gradually reduced from 1986 to 1992 while Zn remained relatively stable except in the years 1990 and 1991. The level of Cd and Cu in air peaked in 1989 after which Cd levels declined sharply from 1989 to 1992.

Petrol combustion is the most important source of Pb emission from traffic (Dinman, 1972; Ter Haar *et al.*, 1972; Cantwell *et al.*, 1972; Huntzicker *et al.* 1975; Lau and Wong, 1983). In England, the permitted Pb content of petrol was reduced from 0.40 to 0.15 g l^{-1} in January 1986 and there has been a subsequent and progressive introduction unleaded petrol (Pb content less than 0.012 g l^{-1}). As a result Pb emission in air has been reduced substantially. It was estimated that between year 1984 and 1990 annual vehicle emissions of Pb in the UK decreased 70 % from 7.2 kT to 2.2 kT (Coleman *et al*, 1991; McInnes, 1987). A summary of the results (Figure 3.10) showing atmosphere levels of Cd, Cu, Pb and Zn in London between 1984/1985 and 1991/1992 illustrates that in general the trends in Cd, Cu, Pb and Zn, display a reduction. Lead shows a considerable reduction resulting initially from the reductions in the Pb additives of petrol (years 1986-1987) and subsequent increase in use of unleaded petrol (years 1988-1990). Although the decline in use of leaded petrol suggests that the importance of this source is declining, Pb has a long residence time in soil, so vehicle emissions are still present as an important source of lead in the surface environment. According to recent research, road transport is still the largest contributor (about 74%, in 1994) of Pb in UK (AEA, 1996).

According to the information on the Cd, Cu, Pb and Zn content in PM_{10}, urban soil, and fly ash from literature and in urban road dust from the present study, the levels of metal content show the following trend:

Incineration fly ash > PM_{10} > urban road dust > urban soil.

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Aerosol particulate might be one of the major metal contributors in urban background whereas urban soil does not much influence the high levels of metal in urban road dust. The above discussion suggests a strong relationship between aerosol particulate and urban dust regarding their metal content. However, this is beyond the scope of the present study and is not pursued any further in this thesis.
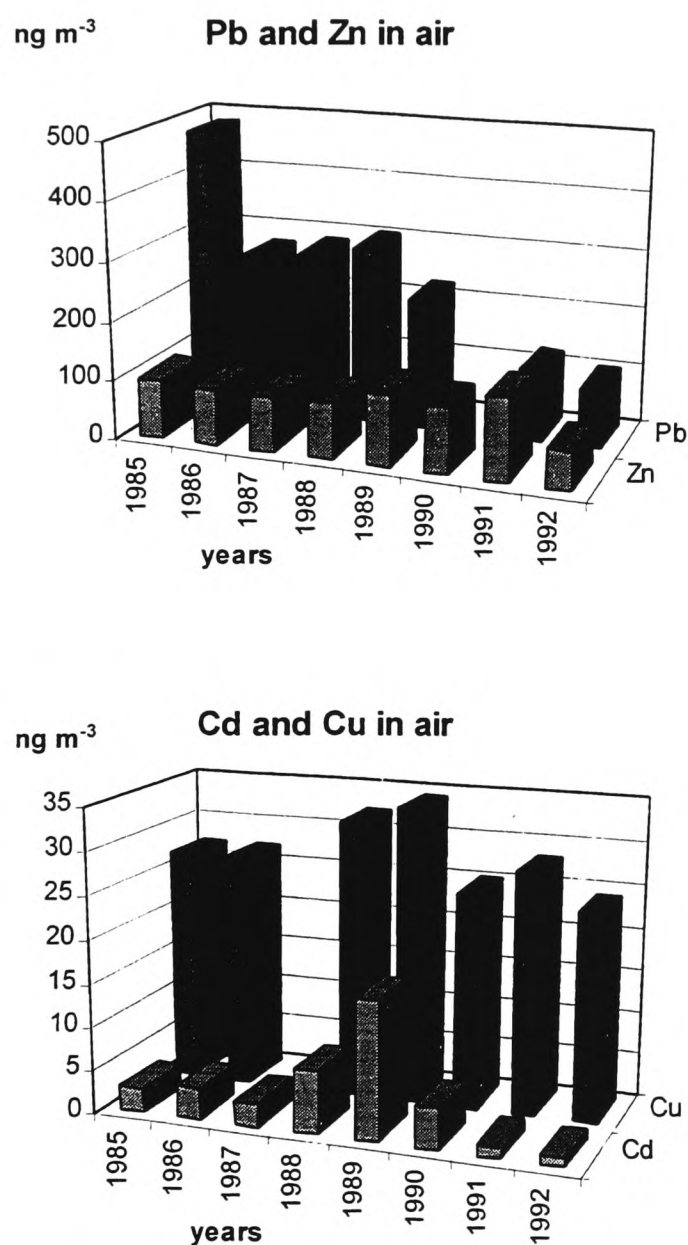
Figure 3.10 Annual average concentration of Cd, Cu, Pb and Zn in air at Greater London from 1985 to 1992 (DoE, 1994).

3.1.2 Chemical speciation of Cd, Cu, Pb and Zn in dust samples

The sequential extraction procedure fractionates the metal present in dust samples into different geochemical phases, including exchangeable, carbonate, organic, hydrous iron and manganese oxide and residual phases (Tessier *et al.* 1979). Each phase represents a different form of association and different mechanism of availability. Harrison *et al.* (1981) suggested that mobility and bioavailability of the metals decrease approximately in the order of the extraction sequence. According to the data obtained from the chemical partitioning of Cd, Cu, Pb and Zn in dust samples (Table 3.7 and Figure 3.3), the different fractions obtained in different dust samples are further discussed below. A summary of similar studies conducted in different cities is shown in Table 3.10

3.1.2.1 Exchangeable cation

This fraction is the most mobilised and will be immediately available in the natural aquatic environment. Cadmium in the urban dust was concentrated in the first three fractions (ca. 80-85%) with the highest amount in the exchangeable fraction (ca. 20-30%) (see Table 3.7). In contrast to Cd, Cu (2.1-6.5%), Pb (1.0-7.2%) and Zn (0.9-8.3) showed less affinity to the exchangeable fraction. Similar observations were made by Harrison and co-workers (1981) when they analysed six samples of street dust from Lancaster and London, and by Fergusson and Ryan (1984) in assessing dust samples from various city's streets (Table 3.10). Considerable levels of metal in the exchangeable fraction of Cd (31.6 %), Cu (6.5%), Pb (7.2 %) and Zn (8.3 %) were found in HDC and some in LSB and HSB (Table 3.7). These may be due to the lower pH associated with these dust and soil samples, as lower pH will promote the leaching of metals (Maclean *et al.* 1969; Jack and Laerhoven, 1972). The exchangeable fractions will become immediately available to the environment during exposure to highly acid rain.

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Table 3.10 Mean chemical partitioning (%) of heavy metal in street dust and soil.

	Geochemical fractions				
	f(I)	f(II)	f(III)	f(IV)	f(V)
Cadmium					
(1) London (street dust), UK	24.4	17.5	36.6	13.3	8.3
Hong Kong (street dust)	26.5	27.0	27.0	10.9	8.6
London (soil), UK	15.0	24.3	32.4	13.3	15.0
Hong Kong (soil)	27.1	26.5	20.5	13.3	12.7
(2) London (street dust), UK	20.1	50.0	21.5	2.5	6.0
Lancaster (street dust), UK	19.9	31.8	31.3	10.5	6.5
Lancaster (soil), UK	24.9	23.2	23.7	12.3	15.9
(3) Street dust from world wide cities	17.7	31.4	38.3	7.8	4.7
(4) Glasgow (street dust), UK	27.0	19.0	16.0	22.0	16.0
Glasgow (soil)	19.0	13.0	19.0	7.0	42.0
(5) Sault Ste Marie (street dust), Canada	14.8	19.3	20.3	33.6	11.7
Copper					
(1) London (street dust), UK	2.8	6.6	17.0	60.1	13.6
Hong Kong (street dust)	4.5	2.9	13.5	71.2	8.0
London (soil), UK	2.2	14.6	6.1	48.7	28.4
Hong Kong (soil)	2.8	14.5	8.5	43.6	23.3
(2) London (street dust), UK	3.2	4.9	2.5	60.1	29.2
Lancaster (street dust), UK	5.5	23.9	4.4	53.3	12.9
Lancaster (soil), UK	1.4	11.4	48.3	36.7	3.2
(3) Street dust from world wide cities	1.3	8.6	11.3	53.2	25.6
(4) Glasgow (street dust), UK	11.0	4.0	11.0	43.0	31.0
Glasgow (soil)	2.0	2.0	9.0	41.0	46.0
(5) Sault Ste Marie (street dust), Canada	0.6	10.0	4.8	65.3	19.3
Lead					
(1) London (street dust), UK	1.5	20.6	53.8	16.8	7.2
Hong Kong (street dust)	4.5	12.1	56.1	19.7	7.6
London (soil), UK	8.9	29.8	24.3	19.7	17.3
Hong Kong (soil)	5.0	24.7	34.0	11.2	23.9
(2) London (street dust), UK	1.1	62.7	23.8	5.6	6.7
Lancaster (street dust), UK	1.3	41.1	38.5	8.1	11.0
Lancaster (soil), UK	1.4	27.3	43.9	10.5	16.9
(3) Street dust from world wide cities	1.9	34.1	44.2	7.1	11.2
(4) Glasgow (street dust), UK	13.0	28.0	32.0	14.0	13.0
Glasgow (soil)	2.0	11.0	51.0	19.0	17.0
(5) Sault Ste Marie (street dust), Canada	1.5	21.1	34.5	27.5	15.4
Zinc					
(1) London (street dust), UK	4.1	31.9	48.9	8.3	6.9
Hong Kong (street dust)	4.1	32.3	48.9	10.0	4.8
London (soil), UK	4.1	14.4	64.1	5.3	12.0
Hong Kong (soil)	4.2	16.5	53.1	7.1	19.1
(2) London (street dust), UK	1.5	59.6	20.1	5.2	13.5
Lancaster (street dust), UK	1.9	39.0	47.1	7.0	5.0
Lancaster (soil), UK	3.2	30.3	43.4	7.7	15.5
(3) Street dust from world wide cities	3.4	30.2	50.8	9.1	6.6
(4) Glasgow (street dust), UK	10.0	23.0	25.0	16.0	26.0
Glasgow (soil)	3.0	7.0	17.0	29.0	43.0
(5) Sault Ste Marie (street dust), Canada	0.7	21.4	15.6	46.5	15.8

(1) Present study, 1995/1996; (2) Harrison, et al. 1981; (3) Fergusson and Ryan, 1984; (4) Gibson and Farmer, 1984; (5) Stone and Marsalek, 1996; f(I): Exchangeable fraction; f(II): Carbonate fraction; f(III): Fe-Mn oxides; f(IV): Organic fraction; f(V): Residual fraction.

In terms of mobility, Cd is the most mobile cation in the exchangeable phase and is also considered more mobile than other metals in the aquatic environment (Salomons and Forstner, 1984). In road dust, this fraction is subject to sorption-desorption processes through ion exchange and is available primarily and immediately for biological uptake (Stover *et al.*, 1976). Hamilton *et al.* (1984) found higher levels of Cd and Zn obtained from rainwater leachate experiments on road sediment. The mobility of metals in the exchangeable fraction from road dust found in the present study follows a similar order, i.e. Cd > Zn > Pb > Cu.

In London, the heavy metal contents of car park dust were higher than those in road dust (Figure 3.5). Cd, Cu, Pb and Zn contents in the exchangeable fraction in Hong Kong car park dust were similar or slightly higher than those in road sites, despite much higher total metal contents in road dust (Figure 3.5). In general, the concentration (μg g^{-1}) of Pb and Cu in exchangeable fraction were similar both in London and Hong Kong except Cu, Pb and Zn in coarser particles in LDR and LDC sites. Higher total Pb levels were found in London dust than those in Hong Kong site while both have similar Pb contents (μg g^{-1}) in the exchangeable fraction, this suggests that Pb was more mobile in the Hong Kong dust.

In Hong Kong, high and intensive rainfall may promote the transfer of the highly exchangeable fraction of metals in dust into the drainage system and consequently to receiving water. In contrast, although heavy metals in urban dust from London were also subject to rainfall and other meteorological factors, they seemed to remain at high levels on the street surface and may be more hazardous to people in the urban environment.

The metal levels in the exchangeable fractions of Hong Kong and London dusts in the present study were within the range of the results from other

studies (see Table 3.10) in Lancaster (Harrison, *et al.* 1981), various cities (Fergusson and Ryan, 1984) and Sault Ste Marie, Ontario (Stone and Marsalek, 1996) and in Glasgow (Gibson and Farmer, 1984).

3.1.1.2 Carbonate bound

Heavy metal concentration can be significantly associated with sedimentary carbonates (Gentry *et al.*, 1987). The present study results show that Zn (27-41%), Pb (12-26%), Cd (14-30%) and Cu (2-11%) were preferentially bound to carbonates (Table 3.7). Gibson and Farmer (1986) proposed that the high level of Pb associated with the carbonate phase were probably a consequence of the more alkaline nature of the samples and this may explain the high percentage of carbonate fraction at LDR. The carbonate contents of Cu and Pb in Hong Kong dust were much less than those in London dust. The percentages of carbonate fraction of Cd, Cu, Pb and Zn in the present study were similar to the studies of Gibson and Farmer (1984) and Stone and Marslek (1996) (Table 3.10).

The carbonate fraction presents the quantity of metals that are associated and co-precipitated with carbonates. This may be an important scavenger mechanism for metals when the hydrous Fe-Mn oxides and organic substance are less abundant (Tessier *et al.* 1979). This fraction was further analysed by Harrison *et al.* (1981) through X-ray diffraction and identified as calcite ($CaCO_3$) and various mica. In the carbonate fraction, the metals are considered to be moderately available for release. This depends strongly on the pH; a lowering of pH due to acid rain would be likely to dissolve carbonates and encourage associated trace metal release. The pH of rainwater is between 3.67 and 7.14 (average 5.5) in London (AEA, 1996) and between 4.1 and 6.5 (average 4.6) in Hong Kong. Therefore, metals in the carbonate fraction might become available during wet acidic precipitation both in Hong Kong and London dusts.

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3.1.1.3 Sorption and co-precipitation on hydrous Fe/Mn oxides

The hydrous iron and manganese oxide fractions are very similar to the carbonate phase and are moderately available in the environment. The oxides exist in dust possibly as concretions, cement between particles or the surface coating on the particles and this fraction has been found a good co-precipitation for the trace metals in aquatic system (Tessier *et al.* 1979). The adsorption of metals in this fraction depends on the pH; the higher pH, the higher adsorbance. Under reducing conditions the oxides decompose and release their heavy metal load. Trace metals associated with this fraction might be released in soluble forms under anoxic condition e.g. gully pot sediment (Hamilton *et al.*, 1984). In the low pH and reducing conditions of a gastric system, this fraction of metal becomes relatively mobile within biological systems and become bio-available.

For the Hong Kong dust samples, the Cd, Pb and Zn contents of this fraction are significantly higher in road dust than in car park dust (Figure 3.7). In the case of London, the Fe-Mn oxides fractions of the road dust and the car park dust are significantly different across all three particle size ranges only in their Pb content. As far as this particular fraction is concerned, the results of the present study bear similarity with the results of some previous studies (Table 3.10), particularly those obtained by Fergusson and Ryan's world-wide studies (1984).

3.1.1.4 Organic matter

Copper was strongly associated with the organic fraction (55-78%). This contrasted with Cd (8-14%) and Zn (6.7-12%) and to some extent Pb (14-22%). These results were similar to those observed in other investigations (Harrison *et al*, 1981; Hamilton *et al*, 1984). It has been indicated that soil organic matter is able to form more stable complexes with Cu (Cheam and

Gamble, 1974). Stumm and Morgan (1981) also reported that Cu could form stable Cu-organic complexes in aquatic environments. In aquatic system, organic matter exhibits a high degree of selectivity for divalent ions and the probable order of binding strength for metal ions to organic matter was $Hg^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ (Jonasson, 1977). The association of metal with organic matter in surface dust in the present study is $Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$ and this result suggests that the preferential binding of these elements to organic matter may also apply to urban street dust.

The metals bound to the organic fraction are most likely to be coating particles from various forms of plant derived organic materials (Tessier *et al.* 1979). Under strong oxidising conditions in natural water, organic matter is likely to be degraded, leading to release of soluble trace metal from urban runoff e.g. high COD or high bacterial activities (Stone and Marsalek, 1996). This fraction is generally immobile and unavailable in the environment because in general, the organic strongly chelates metals. Few significant differences were found between car park dust and road dust at the LDC and LDR sites (Figure 3.8). In the organic fraction, metal levels in the present study were similar to the study in Lancaster, Glasgow and various cities (Table 3.10). This may further indicate that the organic fraction is quite stable and not subject to strong fluctuations.

3.1.1.5 Residual

Moderate amounts of Cd (6-11%), Cu (8-17%), Pb (5-9%) and Zn (3-9%) were found in the residual phase of the dust samples. Compared with road dusts higher residual fractions (12-28%) were found in background soils (LSB and HSB). This suggests that the Cd, Cu, Pb and Zn in soil is subject to weathering and also associated with the geological/geomorphological factors influencing soil formation. The residual fraction is only available by

digestion with strong acid since this fraction of metals is strongly bound to the crystal lattice of minerals (Tessier *et al.* 1979) and can be considered as environmentally immobile. This fraction is likely to reflect the geological characteristics of the study sites. The differences of residual metal content between road site and car park, in London and Hong Kong showed similar trends to the Fe-Mn oxides fraction. It can be seen from Table 3.10 that the residual fraction is generally within the ranges which are found from other literature data. The small percentages ($\cong$ 10 %) of metal appearing in the residual fraction suggest that the metal sources in the present study are mainly anthropogenic sources and are less from the minerals.

3.1.3 Chemical speciation for risk assessment of metals in dust.

In most European countries, a myriad of regulatory guidelines is commonly employed to assess and manage heavy metal risk in soil and sediment. Most standards are based on total metal content. These values can provide excellent criteria to define the metal build up in soil and to estimate the total cation exchange capacity saturated by metals. However for the prediction of biological impact, the total metal content does not necessarily show a specific effect. For the risk assessment of ingestion by children (hand to mouth behaviour) of metals from metal rich soil/dust, total metal content might be a good criterion because of the low pH in the gastric tract. However, for assessing the metal release through wet deposition into urban runoff towards the receiving water system or plant uptake, the total metal content might overestimate the loading of the metal in the receiving water system or ecosystem. Furthermore, the relationship between soil and plant is complicated and needs more sophisticated surveys. This is difficult to predict simply using the total metal content to evaluate the risk via the food chain.

Tessier's chemical speciation scheme is used to address the possible geochemical phases of metal binding in the dusts under this operationally defined approach. The results of the chemical speciation approach may be used as criteria in risk assessments for different environmental pathways. Firstly, metal in the exchangeable phase could be referred to as the metal that will dissolve and become immediately available to plants. Secondly, the first two phases: the exchangeable phase and the carbonate phase could be categorised as metal which will be potentially released during acid rain. Then the total metal concentration may be used as a criterion for dust directly ingested by children. These consideration will be presented in more detail in the following chapters.

3.1.4 Limitations of the sequential extraction method

As with the other chemical extraction approaches to metal in solid, the sequential extraction procedure suffers from some shortcoming. Two major experimental problems of sequential extraction have be recognised: the incomplete selectivity of the reagents used to attach the metal in a given phase, and the metal redistribution amongst the phases during the extraction process (Tessier and Campbell, 1990; Nirel and Morel, 1990; Calvet and Bourgeois, 1990; Kheboian and Fauer, 1987). There are several chemical mechanisms, including cation exchange, specific adsorption, organic complexations and co-precipitation, involved in metal cation absorption in heterogeneous natural material such as dust, soil and sediment (Alloway, 1990). In general, for metal cations with different retention energies, sequential extraction has provided valuable information in the field of geochemistry, although the fractionation of metal in solid matrices remains operationally defined (Tack and Verloo, 1995; Tessier *et al.*, 1989). In order to establish the accuracy and better quality control for sequential extraction procedures, it is important to develop certified reference materials in this scheme. The limitation to current understanding is primarily that there is

no wholly objective way of interpreting the partitioning of metal species between dissolved and particulate form in particles collected in road dust.

Modelling using thermodynamic database or a chemical equilibrium model cannot be used as the particles are of many different types. The real situation represents a complex mixture of particles in contact in the natural world with complicated solutions. The metal ions in solution may form varied complexes with inorganic and organic ligands. Any attempt to calculate the partitioning would be impossible unless very detailed information about the particles was available. Examples of theoretical work undertaken to understand the chemistry of metal complexes associated with the surface of particles are presented by Schnoor (1996). The basic criticism of the sequential extraction procedure is that it assumes that metal released during each phase of the metal is independent. During extraction metals may be redistributed into different phases.

One possible future approach not applied here would be to use a scanning electron microscope to investigate in detail of the particles left after each stage of the sequential extraction. This may be able to resolve some of the problems with sequential extraction discussed above. One might be able to associate certain explicit particle types with each extraction procedure.

3.5 Summary and conclusion

Over a sampling period in 1995 and 1996, dust samples collected from London have showed levels of Cd, Cu, Pb and Zn being 5 μg g^{-1} (range 3 to 9), 280 μg g^{-1} (range 97 to 691), 1030 μg g^{-1} (range 141 to 2537) and 1676 μg g^{-1} (range 446 to 3443), respectively, while the metal levels in dust samples from Hong Kong are 4 μg g^{-1} (range 3 to 6), 194 μg g^{-1} (range 75 to 392), 471 μg g^{-1} (range 157 to 1170) and 1384 μg g^{-1} (range 574 to 2612) for Cd, Cu, Pb and Zn, respectively. The enrichment ratios of Cd, Cu, Pb and Zn between dust

and soil are 3, 20, 10 and 10 respectively. No particular trend of seasonal variation is found. The higher metal contents tend to be associated with the finer particles.

Although there is no standard method of risk assessment for metal levels in urban dust, the average total Pb content of dust samples from London are up to two times higher than the GLC suggested guideline figure for soil (500 µg g^{-1}). It also falls into the DCI "clean-up investigation" category for soil (600 µg g^{-1}) while the average of Pb content of road dust samples from Hong Kong is slightly lower than the GLC suggested level.

The application of chemical speciation to dust has provided some consistent results with the literature. This is remarkable given that road dust is a complex mixture of different kind of particles and wide variation might be expected. In the present study, a considerable amount of Cd ($\approx$ 25%) is found in the exchangeable fraction. The carbonate fraction seems to have equal importance for four metals. Cu is the only element strongly associated with the organic fraction. The hydrous Fe-Mn oxides are shown to be an important fraction for Cd, Pb and Zn. Lead and Zn have similar patterns in all five fractions. About 10 % of Cd, Cu, Pb and Zn is in the residual fraction. According to the results the mobility of metal in dust can be summarised as:

Cd > Zn > Pb$\cong$Cu.

The sequential extraction method showed that heavy metals in dust were associated with different geochemical phases according to the operational definition of Tessier *et al.*, (1979) and that this approach may provide more realistic numerical values for assessing the environmental risk of exposure to metals through different pathways. Limitations to the Tessier's sequential extraction are recognised in this thesis and an operational interpretation of

the results is adopted. It is not assumed that each fraction represents the fraction of metal attached to a specific kind of particle. While using total metal concentration may not be a proper approach to assess the mobility and availability of metal in the environment, the sequential extraction approach still in practice suffers from its complexity and is difficult to perform on a routine monitoring basis.

Although chemical speciation has its limitations, it could be used to estimate the long-term effects of metal mobility and to give a general picture of the geochemical phases of metals. The implementation of the chemical speciation as criteria for risk assessment will be further investigated in the following chapters.

CHARACTERIZATION OF CADMIUM, COPPER, LEAD AND ZINC AND OTHER METALS IN URBAN DUST USING DIFFERENT CHEMICAL LEACHING METHODS AS CRITERIA FOR RISK ASSESSMENT

4.1 Introduction

The purpose of this chapter is to characterise urban dust using a variety of other chemical methods, namely leaching tests, acid titration and time dependent metal release kinetics, to evaluate the potential heavy metal release from urban street dust via different environmental pathways. The results obtained using the single leaching procedures will be related to those from the sequential extraction method, described in Chapter 3, to test the validity of the assumptions underlying the single extraction approach. The acid titration method will be used to assess the relationship between metal release and pH. A time dependent metal release mechanism was also studied to evaluate the metal release rate under highly acidic conditions (pH 1 to 4) which represents a worse case scenario. These chemical properties were also considered in relation to physical characteristics; the morphology and mineral structure of the dust samples were examined by X-ray diffraction and a scanning electron microscope used in conjunction with X-ray spectroscopy (SEM-EDS). The availability of Inductively Coupled Plasma Optical Emission Spectrometer (ICP-AES) instrumentation meant that a wider range of heavy metals could be studied in the various leaching test. Results of regarding the fraction extracted under various conditions are evaluated and for Cd, Cu, Pb and Zn are compared with the results reported in Chapter 3.

Besides sequential extraction, acid leaching is an alternative approach to total digestion for expressing the metal concentration of environmental particles (Reuther, 1996; Gupta *et al.*, 1996). This approach is widely used by industry, standardisation bodies, research institutes, commercial laboratories and government organisations to assess the hazard and bioavailability of heavy metals in soil, waste, sediment and compost materials since it is strongly linked to regulations (van der Sloot *et al.*, 1997). It has recently been proposed that a combination of single leaching procedures, such as the mobile, mobilisable and pseudo-total heavy metal fractions can be used to provide a more comprehensive evaluation of the environmental risk posed by heavy metal contamination (Gupta *et al.*, 1996; van der Sloot *et al.*, 1997).

It has become standard practice to assess the initial risk of metal leaching from hazardous waste materials using distilled water or weak acid (Reuther, 1996). Since the majority of environmental pollutants are not silicate-bound, the pseudo-total concentration using strong acid (HNO_3 / $HClO_4$) instead of hydrofluoric acid (HF) digestion is sufficient to assess the extent and risk posed by heavy metal pollution (Ure, 1996). The pseudo-total concentration measured using strong acid will give an indication of the total ion capacity in either dust or the soil. This can be used to assess the potential risk of metal release from the soil or of direct dust intake by small children or animals, because of the high acidity of stomach juice (Gupta, 1996).

Many factors affect the nature of metal leaching, such as the type of element complexes involved and extracting reagent used, but pH and contact time are the most common and simplest factors which govern the leaching behavior. Hence it is also important to study the metal release mechanism as a function of time and of pH as this information may provide further insight into the metal binding and release processes which can influence results from the chemical leaching method.

4.2 Materials and Methods

4.2.1 Sampling sites and sample preparation

The sampling sites and sampling strategies were described in Chapter 3. The dust samples chosen for more detailed analysis were from the batch taken in September 1995 at the London sites and in March 1996 at the Hong Kong sites. Two batches of dust samples with particle size <125, 125- 250 and 250- 500 μm were selected because they contained the highest quantities of dust collected which was the most important consideration during the sampling period to ensure that different risk assessment strategies could be satisfactorily performed. In addition, the concentrations of heavy metals in these two batches were within the 95% confidence limit of the average concentration in the dust during the sampling period. Therefore these two batches of dust samples can be regarded as representative of the dust samples collected during the whole of the sampling period. Soil samples taken in March 1995 in London and in July 1996 in Hong Kong were also studied.

4.2.2 Chemical analysis

Five chemical extraction approaches (the German standard method DIN 38414-S4), two USEPA methods SW-846 (Method 1310A) and SW-846 (Method 1311), a pseudo total digestion and Tessier's (1979) sequential extraction) were used to test the potential metal mobility from the dust under different simulated environmental conditions. These methods are first summarized in the following sections. In later sections results are presented and discussed.

4.2.2.1 DIN-S4 Method: Determination of leachability by water

The German standard method DIN 38414-S4 (Sludge and Sediments) for determination of the leachability by water were applied to dust samples.

This method is intended to determine the immediate effect of metal release from dust samples which are in contact with water.

10 g of dust were placed in 125 ml of acid washed polypropylene bottles, and 100 ml of deionised water (DIW) was added. The mixture was shaken at 100 rpm in an orbital shaker at a temperature of 25 ± 1 °C for 24 hours. Supernatants were separated by filtration (5C filter paper) and then the pH, conductivity and the concentration of metals were measured. A further 100 ml of DIW was added to the residue of the sample and the procedure described above repeated once more. Supernatants were acidified with nitric acid to pH < 2.0.

4.2.2.2 USEPA SW-846 Method 1310: A: Extraction Procedure (EP) Toxicity Test

The Extraction Procedure (EP) Toxicity Test method, Method 1310, is an attempt to model the leaching of pollutants from solid waste and is an interim method to determine whether a waste exhibits the characteristics of Extraction Procedure Toxicity (USEPA SW-846).

5 g of dust was placed in 125 ml acid washed polypropylene bottles, and 16 times the weight of the dust sample of DIW was added. The mixture was shaken for 24 hours at 100 rpm in an orbital shaker at a temperature of 25 ± 1 °C. The pH of the mixture was constantly measured during the extraction period. If the pH of mixture solution is greater than pH 5.0, the pH of the solution is adjusted to pH 5.0 ± 0.2 with 0.5 N acetic acid, while the total amount of acid added to the solution should not exceed 4 ml of acid per gram of solid. If the pH of mixture solution is less than pH 5.0, no acetic acid should be added. After the leaching period has elapsed, the supernatant

is separated by filtration through 5C filter paper and then adjusted to pH < 2.0 with concentrated nitric acid.

4.2.2.3 USEPA SW-846 Method 1311: Toxicity Characteristic Leaching

Procedure (TCLP)

The TCLP method is designed to determine the mobility of organic and inorganic pollutants in wastes and is part of the US Resource Conservation and Recovery Act (RCRA) regulation in USA. The method involves two stages; the preliminary evaluation and the actual leaching procedure. The initial procedure uses DIW as leaching solution to examine the acidity of the nature of the waste, in order to select which of two leaching fluids is to be used for the TCLP extraction of the waste. If a waste is more alkaline (pH > 5.0), the lower pH leaching fluid (pH 2.88 ± 0.05 acetic acid solution) is used to leach the waste, while if the pH of waste is less then 5.0, the higher pH leaching fluid (pH 4.93 ± 0.05 acetic acid and sodium hydroxide solution) is selected.

<u>Preliminary Evaluation:</u>

5 g of dust sample was placed in a 200 ml acid treated beaker, and 96.5 ml of DIW was added and vigorously stirred using a magnetic stirrer. The pH of the solution was measured after 5 minutes. If the pH was greater than 5.0, 3.5 ml 1M hydrochloric acid was added to the solution and the solution was heated to 50 °C for 10 minutes., The pH of the solution was measured after it had cooled. If the pH of the solution was still greater than pH 5.0, pH 2.88 ± 0.05 acetic solution was used as extraction fluid, whereas if the pH was less than 5.0, pH 4.93 ± 0.05 acetic acid and sodium hydroxide solution was used as extraction fluid.

<u>Actual leaching procedure:</u>

5 g of dust sample was placed in 125 ml acid washed polypropylene bottles and 20 times the weight of the sample of the selected extraction fluid was added. The mixed solution was shaken at 30 rpm in an orbital shaker at a temperature of 23 ± 2 °C for 18 ± 2 hours. Supernatants were then separated by filtration and adjusted to pH < 2.0 using concentrated nitric acid.

4.2.2.4 Pseudo total digestion of urban road dust and soil

Pseudo total digestion of dust sample was carried out by using nitric-perchloric acid. 0.5 g of dust sample was placed in a 50 ml acid washed polytetrafluoroethylene (PTFE) beaker and then was digested with 4:1 concentrated nitric-perchloric acid. The mixture solution was taken to near dryness for 24 hours, which included 3 hours at 50 °C, 3 hours at 150°C, 17.9 hours at 190 °C and 0.1 hour at 195 °C. The solution was then leached in 2 ml of nitric acid, made up to 100 ml with DIW.

4.2.2.5 Tessier's sequential extraction for ICP

The sequential extraction procedure followed Tessier's scheme (1979) which was summarized in Chapter 3, Flowchart 3.1. The residual fraction was modified by using the pseudo total digestion procedure described above. In order to standardize the solution to the uniform matrix for ICP-AES analysis, the supernatants from the exchangeable, carbonate, Fe-Mn oxide and organic fractions were digested with concentrated nitric acid (Li et al., 1995). 1 ml of concentrated nitric acid was added to the supernatant and left at 90 °C overnight and then slowly heated up to 140 °C and heated to near dryness. The residual was leached with 1 ml of concentrated nitric acid and made up to a volume of 50 ml with DIW.

4.2.2.6 Measurements

The concentrations of Al, Ca, Cd, Cr, Cu, Fe, K, Mn, Ni, Pb and Zn were measured using ARL 340 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES). The instrument was calibration by a multi-element synthetic standard solution in 2% nitric acid solution. The calibration standards for ICP-AES are shown in Table 4.1. The individual standard stock solutions of 1000 μg ml^{-1} of cadmium nitrate, copper (II) nitrate, chromic nitrate, nickel (II) nitrate, lead nitrate, aluminum nitrate, iron (III) nitrate, manganese nitrate, potassium nitrate and zinc nitrate were used to prepare the standard solutions of Cd, Cu, Cr, Ni, Pb, Al, Fe, Mn, K and Zn, while Ca standards were prepared from a 10,000 μg ml^{-1} standard stock solution of calcium nitrate.

4.2.2.7 ICP-AES

The technique of inductively coupled plasma-atomic emission spectrometry (ICP-AES) uses the emission source from a high temperature (6000-10000 K) plasma formed in the centre of quartz torch by coupling a radio-frequency electromagnetic field to ionized argon gas (Ure, 1990). The sample in nebulized and entrained in the flow of plasma through argon gas at high temperature and atomized for atomic emission spectroscopy using a high resolution optical instrument combined with a computer.

In contrast to the flame atomic absorption spectroscopy (AAS), ICP-AES has several advantages including lower detection limit, simultaneous multi-element analysis, wider linear calibration, less chemical and ionization interference effect (Potts, 1987).

Table 4.1 The calibration standards for ICP-AES

µg/ ml	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Ag, Cd	0.1	0.2	0.3	0.4	0.5
Cu, Cr, Ni, Pb	0.1	0.2	0.3	0.4	0.5
	*1	*2	*3	*4	*5
Al, Fe, Mn, Zn	1	2	3	5	10
K	1	5	10	15	20
Ca	5	10	25	50	75

*: These range of standards were used when measuring the pseudo total digestion of Cu, Cr, Ni and Pb in dust.

4.2.2.8 Quality control

All dust samples were analysed in triplicate and two blanks were used in each chemical extraction approach. Two certified reference materials (CRM), stream sediment GRM GBW07311 GSD-11 (China) and marine sediment PACS-1 (National Research Council, Canada) were used to monitor the metal recovery rates when the pseudo total digestion was performed using nitric-perchloric acid as the extractant. The use of matrix-matched CRM is an ideal way to assess whether a measurement system produces statistically valid results.

Each solution were measured twice and a drift correction inserted using the third standard solution every ten solutions to monitor performance of the ICP-AES. The Background Equivalent Concentration (BEC) and Detection Limit (DL) of the ICP-AES were calculated by testing ten double distilled water samples with two known standards.

4.2.3 Acid titration: metal release as function of pH

In order to study the importance of acidity to the metal release mechanism, a simple acid titration approach was applied to examine the metal release under different pH conditions.

The acid titration method was conducted by titrating each dust sample with different concentrations of nitric acid (HNO_3) solution. The concentration of 0, 0.0001, 0.0005, 0.001, 0.005, 0.008, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.06, 0.07, 0.08, 0.1 mole l^{-1} HNO_3 solutions were prepared and 20 ml of these solutions was then added to 1 g of dust in 30 ml centrifuge tubes at a ratio (w/v) of 1:20 for solid:acid solution.   Then the dust suspension was shaken in an orbital shaker at the temperature of 25 $\pm$ 1 °C for 7 days. Supernatant was separated and decanted by centrifuging dust suspension samples at 4000-4500 rpm for 30 minutes, filtered through 5C filter paper and then the pH and the concentrations of Cd, Cu, Pb and Zn of supernatant were measured. The residual dust on the filter paper and tubes were dried at 40°C in an oven for 7 days. The concentrations of Cd, Cu, Pb and Zn in the residual dust were measured after digesting with aqua regia.

4.2.4 Metal release as function of time

A time dependent kinetic experiment of Cd, Cu, Pb and Zn release for the dust samples of particle size < 125 μm in diameter was performed. At time zero, 40 g of dust was put into a 1000 ml of glass beaker, 800 ml of pH 1, 2, 3 and 4 HNO_3 solution was added and the suspension solution was mixed by a hydraulic stirrer at a temperature of 25 °C. The pH was controlled at set values of pH 1, 2, 3 and 4 by adding 1M HNO_3 and 1M NaOH solution from burettes. The ratio of dust:nitric acid solution was 1:20 at time zero, but the ratio altered slightly due to acid addition and dissolution of dust contents.

20 ml of suspension solution were withdrawn and filtered on 26 occasions over a 7 hour time interval (i.e. at time interval of 5, 10, 15, 20, 24, 29, 34, 39, 44, 49, 54, 62, 72, 82, 92, 102, 112, 142, 172, 202, 232, 262, 292, 322, 352 and 412 minutes). The 27th sample was taken at the end of 24 hours when it is assumed that equilibrium had been reached. For all samples taken it was assumed that the suspension solution was well mixed and had a nearly constant ratio of dust/acid solution. The constant ratio of dust/acid solution was calculated by measuring the amount of dust on the filter paper after oven drying at 40°C for 7 days. The concentrations of Cd, Cu, Pb and Zn in the solution of acid titration and the metal release as function of time were determined by using a flame atomic absorption spectrophotometer and anodic stripping voltameter (TraceLab^{TM} Radiometer, Copenhagen).

4.2.5 Physical analysis using SEM - EDS

The morphology and gross chemistry of the dust samples were analysed by a Scanning Electron Microscope (SEM) using a JEOL JSM-5310LV instrument and energy dispersive X-ray analysis (EDS). Dust samples were mounted on double sided adhesive carbon tabs and were coated with a thin layer of carbon using a high vacuum carbon evaporator. The dust particles were then analyzed on a SEM operated at an accelerating voltage of 15 kV. Imaging was performed in a backscattered electron mode, so that backscatter contrast thresholds could be set to isolate the elements with high atomic number in the dust particles in the specimen. The X-ray information was collected with a Si(Li) X-ray detector and a Oxford Instruments ISIS 300 microanalysis system.

4.2.6 X-ray powder diffraction of road dust samples

X-ray diffraction (XRD) provides a simple tool to characterize the mineralogy of the solid phase of fine-grained sediments (such as road dust

and river sediment). The dried sample was crushed to particles of less than 30 μm and back mounted into a Philips cavity powder mount. The back cover of the samples is removed and a glass plate is secured over the front of the cavity with Sellotape. The sample to be analyzed is loaded into the holder using a stainless steel spatula and the four corners are pressed down. A glass slide is then used to press the sample into the holder and to remove any surplus. The back cover is then replaced and the glass front cover is removed prior to loading into the machine for analysis. The sample was analyzed on a Philips p1830 diffractometer system using Cu Kα radiation, fitted with a PW1820 goniometer, an automatic divergence slit and a graphite monochromator. The generator setting was 40 kV and 50 mA. Philips PC-APD controlling, analysis and output software was used.

4.3 Results

4.3.1 Chemical analysis

The results of the German standard method DIN-S4, the two USEPA leaching methods (EPTox, TCLP), the pseudo total digestion method and the sequential extraction method are shown in Tables 4.2-4.6. A comparison of the levels of metal release using DIN-S4, EPTox, TCLP and pseudo total digestion are presented in Figure 4.1. The amounts of Cu, Pb, Zn, Al, Fe, Ca and Ni extracted from the dust did not show much difference between the USEPA TCLP and the EPTox extraction methods (Figures 4.1a and 4.1b). The result for Ca and Zn showed very close agreement using the EPTox, TCLP and pseudo total digesstion methods. The concentrations of metal release from the DIN-S4 method were lower than those for the other three single extraction methods.

Table 4.2 Metal release from the dust using the DIN-S4 method.

	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mn	Ni
						Concentrations ($\mu g\,g^{-1} \pm$ standard deviation)					
LDR1	0.00 ± 0.01	0.88 ± 0.05	1.37 ± 0.53	5.6 ± 0.8	7.1 ± 1.7	868 ± 11	0.02 ± 0.02	11.6 ± 2.8	76 ± 2	0.7 ± 0.0	0.00 ± 0.01
LDR2	0.02 ± 0.01	0.87 ± 0.13	1.82 ± 0.65	10.3 ± 2.5	12.2 ± 4.5	986 ± 64	0.07 ± 0.00	20.9 ± 7.8	75 ± 5	1.0 ± 0.3	0.03 ± 0.02
LDR3	0.03 ± 0.02	0.56 ± 0.03	2.34 ± 0.21	10.7 ± 1.6	15.4 ± 1.7	702 ± 15	0.05 ± 0.02	25.2 ± 3.8	45 ± 5	0.7 ± 0.1	0.01 ± 0.02
LDC1	0.02 ± 0.02	0.75 ± 0.20	0.84 ± 0.68	6.7 ± 0.2	6.8 ± 0.8	803 ± 269	0.01 ± 0.02	8.9 ± 3.4	80 ± 1	4.1 ± 3.0	0.08 ± 0.07
LDC2	0.02 ± 0.02	1.82 ± 0.18	2.80 ± 0.71	14.1 ± 1.5	10.3 ± 1.6	648 ± 19	0.03 ± 0.01	18.2 ± 2.9	111 ± 5	1.9 ± 0.4	0.06 ± 0.03
LDC3	0.03 ± 0.01	4.46 ± 0.75	2.85 ± 0.15	28.9 ± 4.5	9.8 ± 0.2	1168 ± 169	0.11 ± 0.04	18.3 ± 1.2	440 ± 82	6.8 ± 1.2	0.22 ± 0.08
HDR1	0.00 ± 0.01	3.27 ± 0.05	0.27 ± 0.04	2.8 ± 0.2	5.3 ± 1.9	1875 ± 55	0.12 ± 0.02	4.8 ± 0.4	410 ± 6	0.8 ± 0.1	0.01 ± 0.01
HDR2	0.01 ± 0.01	1.66 ± 0.03	0.36 ± 0.30	5.2 ± 0.1	2.1 ± 0.8	1576 ± 26	0.05 ± 0.02	2.7 ± 1.1	343 ± 10	1.2 ± 0.1	0.03 ± 0.01
HDR3	0.02 ± 0.02	1.42 ± 0.05	0.46 ± 0.06	7.0 ± 0.6	2.4 ± 0.5	1485 ± 30	0.05 ± 0.03	3.1 ± 0.6	263 ± 3	1.2 ± 0.1	0.03 ± 0.04
HDC1	0.02 ± 0.02	0.60 ± 0.04	0.35 ± 0.10	6.7 ± 0.3	3.7 ± 1.4	438 ± 8.4	0.03 ± 0.02	4.8 ± 0.9	85 ± 1	5.5 ± 0.3	0.09 ± 0.09
HDC2	0.01 ± 0.01	0.57 ± 0.05	0.13 ± 0.12	10.4 ± 0.5	2.5 ± 1.3	471 ± 5.6	0.06 ± 0.02	3.3 ± 0.6	81 ± 4	5.9 ± 0.1	0.10 ± 0.10
HDC3	0.02 ± 0.00	0.46 ± 0.04	0.33 ± 0.30	9.8 ± 0.4	3.8 ± 2.5	422 ± 21	0.04 ± 0.04	3.9 ± 0.8	65 ± 7	4.7 ± 0.2	0.11 ± 0.07
LBS	0.02 ± 0.01	0.62 ± 0.05	1.38 ± 0.20	1.3 ± 0.1	67.8 ± 10.8	205 ± 6.7	0.10 ± 0.05	88.0 ± 20.5	514 ± 6	5.6 ± 0.3	0.20 ± 0.10
HBS	0.01 ± 0.02	0.20 ± 0.06	0.49 ± 0.17	0.8 ± 0.1	155.1 ± 54.1	35 ± 3.5	0.07 ± 0.04	149.7 ± 58.3	39 ± 6	6.2 ± 1.2	0.07 ± 0.08

Table 4.3 Metal release from the dust using the EPTox method.

Concentations (μg g^{-1} ± standard deviation)

	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mn	Ni
LDR1	1.1 ± 0.1	14.8 ± 1.6	115.3 ± 13.2	2083 ± 249	37.3 ± 4.0	16363 ± 2389	0.1 ± 0.0	88.9 ± 5.6	138 ± 12	338 ± 4	1.8 ± 0.1
LDR2	0.6 ± 0.1	11.5 ± 0.6	68.5 ± 8.6	1717 ± 248	48.4 ± 1.6	16892 ± 1633	0.1 ± 0.1	207.5 ± 10.1	119 ± 6	298 ± 1	1.4 ± 0.2
LDR3	0.6 ± 0.4	9.1 ± 0.9	49.7 ± 7.1	1326 ± 100	55.1 ± 2.3	12545 ± 2606	0.2 ± 0.0	534.2 ± 47.2	85 ± 7	247 ± 7	0.9 ± 0.3
LDC1	0.3 ± 0.1	7.7 ± 1.3	31.1 ± 14.2	478 ± 69	62.2 ± 0.6	6243 ± 1549	0.1 ± 0.1	58.6 ± 11.0	128 ± 4	232 ± 3	3.7 ± 0.3
LDC2	1.0 ± 0.1	8.2 ± 0.1	29.7 ± 0.4	438 ± 17	11.6 ± 1.0	12330 ± 1203	0.0 ± 0.0	8.0 ± 0.9	147 ± 4	189 ± 1	1.7 ± 0.3
LDC3	1.3 ± 0.2	8.4 ± 0.2	22.1 ± 2.2	552 ± 44	11.4 ± 0.4	11886 ± 2256	0.1 ± 0.1	5.7 ± 0.5	517 ± 22	215 ± 2	2.0 ± 0.1
HDR1	0.3 ± 0.1	7.0 ± 0.8	1.8 ± 0.9	952 ± 150	5.5 ± 1.1	18640 ± 1992	0.4 ± 0.1	2.6 ± 0.2	611 ± 8	494 ± 3	1.6 ± 0.1
HDR2	0.6 ± 0.2	10.1 ± 0.6	15.9 ± 6.4	1702 ± 240	29.6 ± 1.3	16370 ± 1392	0.4 ± 0.0	19.9 ± 3.3	490 ± 9	447 ± 2	2.2 ± 0.3
HDR3	0.4 ± 0.1	8.5 ± 0.4	13.4 ± 6.3	1944 ± 270	38.2 ± 1.2	13308 ± 1257	0.4 ± 0.1	47.5 ± 9.0	409 ± 12	408 ± 4	2.1 ± 0.6
HDC1	0.2 ± 0.0	5.7 ± 0.4	7.3 ± 0.4	327 ± 32	87.5 ± 4.7	1901 ± 60	0.1 ± 0.0	46.2 ± 3.9	141 ± 5	119 ± 2	5.1 ± 0.3
HDC2	0.2 ± 0.0	4.4 ± 0.4	5.6 ± 0.5	532 ± 35	68.3 ± 2.7	2838 ± 183	0.2 ± 0.1	43.4 ± 2.7	146 ± 15	127 ± 2	4.1 ± 0.3
HDC3	0.1 ± 0.0	3.4 ± 0.3	5.6 ± 2.2	401 ± 30	55.7 ± 4.1	2358 ± 119	0.2 ± 0.0	47.1 ± 15.7	107 ± 3	94 ± 2	3.0 ± 0.5
LBS	0.0 ± 0.0	0.1 ± 0.0	0.2 ± 0.3	9 ± 0	168.5 ± 7.4	211 ± 16	0.1 ± 0.1	29.1 ± 0.8	72 ± 2	35 ± 0	0.1 ± 0.1
HBS	0.0 ± 0.0	0.4 ± 0.0	0.8 ± 0.1	8 ± 0	74.6 ± 1.9	1437 ± 77	0.1 ± 0.1	39.4 ± 0.6	717 ± 7	193 ± 3	0.3 ± 0.1

Table 4.4 Metal release from the dust using the TCLP method.

Concentrations ($\mu g\ g^{-1}$ ± standard deviation)

	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mn	Ni
LDR1	0.49 ± 0.09	9.9 ± 1.8	88.1 ± 11.6	1802 ± 164	57 ± 6	14183 ± 120	0.09 ± 0.02	94.1 ± 9.6	135 ± 5	61.2 ± 3.9	1.0 ± 0.2
LDR2	0.46 ± 0.06	8.8 ± 0.5	53.7 ± 6.6	1546 ± 151	63 ± 2	14466 ± 915	0.07 ± 0.06	162.9 ± 8.4	121 ± 4	56.0 ± 1.8	1.1 ± 0.1
LDR3	0.16 ± 0.09	7.3 ± 2.4	38.5 ± 11.7	568 ± 106	58 ± 2	11913 ± 1160	0.12 ± 0.02	393.2 ± 25.9	79 ± 9	44.3 ± 5.5	0.5 ± 0.2
LDC1	1.44 ± 0.19	12.1 ± 0.6	35.4 ± 1.9	1098 ± 10	36 ± 2	16459 ± 654	0.08 ± 0.08	24.6 ± 1.5	1005 ± 49	42.8 ± 1.2	3.0 ± 0.4
LDC2	0.80 ± 0.13	7.5 ± 0.4	27.0 ± 0.9	623 ± 83	19 ± 2	13611 ± 3099	0.00 ± 0.00	12.7 ± 0.8	149 ± 5	32.3 ± 1.8	1.0 ± 0.2
LDC3	1.06 ± 0.19	8.0 ± 0.9	26.4 ± 1.0	716 ± 115	19 ± 2	18642 ± 1359	0.01 ± 0.02	10.1 ± 0.2	446 ± 31	40.0 ± 1.0	1.6 ± 0.1
HDR1	0.24 ± 0.12	8.5 ± 0.4	14.5 ± 0.9	1010 ± 31	39 ± 2	14180 ± 200	0.26 ± 0.06	14.1 ± 0.1	545 ± 6	45.1 ± 0.1	1.5 ± 0.1
HDR2	0.56 ± 0.08	8.1 ± 0.9	18.1 ± 3.0	1317 ± 44	44 ± 1	12422 ± 513	0.27 ± 0.03	28.0 ± 0.7	435 ± 21	45.9 ± 3.1	1.5 ± 0.1
HDR3	0.18 ± 0.03	7.1 ± 1.0	10.9 ± 4.9	836 ± 43	43 ± 2	11989 ± 378	0.31 ± 0.07	48.9 ± 8.9	382 ± 5	43.6 ± 2.8	1.4 ± 0.1
HDC1	0.06 ± 0.03	5.4 ± 0.2	6.8 ± 0.4	327 ± 22	84 ± 3	1978 ± 92	0.10 ± 0.01	34.1 ± 1.8	141 ± 3	51.3 ± 2.6	4.7 ± 0.3
HDC2	0.06 ± 0.03	4.0 ± 0.6	6.0 ± 1.5	388 ± 37	66 ± 6	2284 ± 131	0.12 ± 0.08	31.2 ± 4.0	121 ± 3	39.7 ± 3.5	3.6 ± 0.8
HDC3	0.02 ± 0.01	4.7 ± 1.3	4.8 ± 0.5	366 ± 6	65 ± 2	2167 ± 15	0.09 ± 0.07	44.5 ± 6.3	103 ± 4	34.0 ± 1.1	3.1 ± 0.4
LBS	0.00 ± 0.00	0.0 ± 0.0	0.2 ± 0.1	8 ± 1	160 ± 6	236 ± 3	0.01 ± 0.02	15.8 ± 0.6	78 ± 4	39.4 ± 1.0	0.0 ± 0.0
HBS	0.00 ± 0.00	0.1 ± 0.1	0.5 ± 0.4	7 ± 3	68 ± 18	1173 ± 534	0.02 ± 0.03	30.0 ± 4.5	550 ± 311	33.4 ± 15.4	1.8 ± 2.8

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Table 4.5 Metal release from the dust using the pseudo-total digestion method.

	Concentrations (μg g^{-1} $\pm$ standard deviation)										
	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mn	Ni
LDR1	12 ± 1	376 ± 30	2918 ± 307	4843 ± 217	7930 ± 403	36632 ± 2750	93 ± 5	45082 ± 3996	1178 ± 92	902 ± 103	50 ± 8
LDR2	8 ± 2	174 ± 23	1592 ± 236	3225 ± 536	6181 ± 943	29350 ± 2903	61 ± 7	32127 ± 3911	993 ± 144	494 ± 56	31 ± 3
LDR3	7 ± 1	297 ± 74	878 ± 264	1639 ± 484	3273 ± 575	18216 ± 3918	43 ± 17	25826 ± 3948	522 ± 109	359 ± 64	20 ± 6
LDC1	8 ± 1	142 ± 22	849 ± 134	1890 ± 288	7772 ± 1563	14077 ± 2428	60 ± 9	32157 ± 4608	1035 ± 145	638 ± 85	81 ± 11
LDC2	8 ± 1	103 ± 16	1207 ± 148	2372 ± 295	4292 ± 139	31703 ± 934	31 ± 1	26114 ± 1473	858 ± 77	394 ± 19	32 ± 4
LDC3	10 ± 0	150 ± 53	1090 ± 278	2279 ± 161	5539 ± 327	56376 ± 5599	43 ± 5	31738 ± 2626	1210 ± 28	462 ± 45	35 ± 2
HDR1	10 ± 1	267 ± 47	1011 ± 191	3788 ± 639	10762 ± 755	35051 ± 2656	82 ± 6	38388 ± 2507	1526 ± 122	704 ± 64	39 ± 6
HDR2	9 ± 1	192 ± 31	737 ± 33	3259 ± 416	7767 ± 1427	25458 ± 4077	66 ± 7	39059 ± 7966	1183 ± 188	531 ± 116	27 ± 3
HDR3	8 ± 1	168 ± 77	549 ± 241	3102 ± 431	6119 ± 849	18470 ± 1483	53 ± 2	35589 ± 3925	1007 ± 71	487 ± 77	18 ± 2
HDC1	7 ± 0	69 ± 7	308 ± 29	965 ± 81	9027 ± 1292	4053 ± 290	48 ± 5	29431 ± 1654	993 ± 136	607 ± 41	99 ± 10
HDC2	6 ± 0	82 ± 20	347 ± 25	1618 ± 156	6893 ± 432	4537 ± 233	46 ± 4	25448 ± 692	956 ± 47	569 ± 37	94 ± 1
HDC3	6 ± 0	68 ± 27	269 ± 59	1154 ± 257	5081 ± 321	3785 ± 395	40 ± 6	25224 ± 1053	821 ± 87	526 ± 72	110 ± 27
LBS	4 ± 1	39 ± 24	125 ± 19	42 ± 44	11094 ± 1032	5779 ± 217	21 ± 2	15856 ± 752	2783 ± 90	246 ± 5	13 ± 1
HBS	4 ± 1	1 ± 1	6 ± 10	0 ± 0	21805 ± 3066	305 ± 35	11 ± 1	16230 ± 1666	2295 ± 527	123 ± 14	3 ± 1

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Table 4.6 Metal release from the dust using the sequential extraction method.

	Sequential extraction: Exchangeable fraction: concentrations (μg g^{-1} ± standard deviation)										
	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mg	Ni
LDR1	0.3 ± 0.2	5.3 ± 9.0	1.6 ± 1.3	24.6 ± 7.8	0.0 ± 0.0	1675.5 ± 40.6	0.4 ± 0.5	1.1 ± 0.7	115.2 ± 11.2	3.6 ± 0.1	0.4 ± 0.6
LDR2	0.2 ± 0.1	4.6 ± 8.0	0.0 ± 0.0	22.9 ± 9.8	0.0 ± 0.0	1380.2 ± 21.8	0.0 ± 0.1	1.3 ± 0.7	100.4 ± 11.6	2.6 ± 0.1	0.4 ± 0.3
LDR3	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	12.6 ± 3.5	0.0 ± 0.0	801.4 ± 18.6	0.1 ± 0.1	0.9 ± 0.6	86.7 ± 12.6	1.4 ± 0.1	0.8 ± 1.2
LDC1	1.0 ± 0.2	5.5 ± 9.5	2.1 ± 1.5	92.8 ± 6.1	0.0 ± 0.0	1942.2 ± 175.2	0.1 ± 0.2	4.6 ± 0.2	617.5 ± 39.7	8.0 ± 0.7	3.1 ± 1.9
LDC2	0.3 ± 0.1	2.1 ± 3.6	0.3 ± 0.4	46.3 ± 13.3	0.0 ± 0.0	776.1 ± 36.4	0.1 ± 0.1	6.2 ± 7.7	96.7 ± 18.8	3.2 ± 0.0	0.2 ± 0.3
LDC3	0.8 ± 0.2	0.0 ± 0.0	0.3 ± 0.5	66.4 ± 9.2	0.0 ± 0.0	1233.4 ± 189.4	0.0 ± 0.0	2.2 ± 1.5	287.1 ± 21.3	5.8 ± 0.8	7.0 ± 10.6
HDR1	0.3 ± 0.1	12.9 ± 4.4	4.7 ± 2.4	66.1 ± 25.3	0.0 ± 0.0	2295.0 ± 196.9	3.2 ± 1.5	3.3 ± 2.3	296.7 ± 26.1	4.7 ± 0.1	5.8 ± 3.8
HDR2	0.2 ± 0.2	12.2 ± 3.9	1.5 ± 2.7	33.3 ± 9.3	0.0 ± 0.0	1526.8 ± 36.2	0.2 ± 0.4	3.0 ± 0.5	229.6 ± 9.7	3.2 ± 0.1	0.0 ± 0.1
HDR3	0.1 ± 0.1	4.4 ± 3.4	1.2 ± 1.0	26.1 ± 1.1	0.0 ± 0.0	1192.2 ± 42.2	0.3 ± 0.3	1.7 ± 0.4	189.4 ± 26.4	2.7 ± 0.1	0.3 ± 0.5
HDC1	0.2 ± 0.2	0.4 ± 0.8	0.0 ± 0.0	50.5 ± 3.5	0.0 ± 0.0	666.7 ± 54.5	0.0 ± 0.1	1.7 ± 0.6	90.3 ± 25.1	5.0 ± 0.4	4.6 ± 4.9
HDC2	0.2 ± 0.1	1.8 ± 3.2	0.0 ± 0.0	52.0 ± 3.7	0.0 ± 0.0	613.0 ± 27.6	0.2 ± 0.3	1.3 ± 0.1	89.6 ± 19.6	4.5 ± 0.2	12.1 ± 15.6
HDC3	0.1 ± 0.1	0.0 ± 0.0	1.9 ± 1.7	35.7 ± 1.5	0.0 ± 0.0	452.6 ± 29.0	0.2 ± 0.3	1.2 ± 1.0	69.2 ± 9.7	3.4 ± 0.4	3.6 ± 5.1
LBS	0.0 ± 0.1	0.0 ± 0.0	0.6 ± 0.9	0.0 ± 0.1	0.0 ± 0.0	1449.1 ± 69.7	0.0 ± 0.0	16.5 ± 1.2	725.3 ± 18.7	25.0 ± 1.1	3.2 ± 3.9
HBS	0.1 ± 0.1	0.0 ± 0.0	0.8 ± 1.3	0.0 ± 0.0	58.8 ± 27.8	134.3 ± 20.9	0.0 ± 0.0	8.5 ± 3.6	72.7 ± 21.5	17.8 ± 2.2	0.4 ± 0.4

Table 4.6 (cont.) Metal release from the dust using the sequential extraction method.

	Sequential extraction: Carbonate fraction: concentrations ($\mu g\,g^{-1}$ ± standard deviation)										
	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mg	Ni
HDR1	0.7 ± 0.1	24.1 ± 4.2	113 ± 3	1209 ± 40	70.6 ± 3.5	21784 ± 760	2.6 ± 0.4	87 ± 3	432 ± 15	66 ± 1.9	3.4 ± 5.8
HDR2	0.3 ± 0.0	10.6 ± 1.2	116 ± 2	1135 ± 40	71.4 ± 3.0	14882 ± 272	1.5 ± 0.3	141 ± 11	344 ± 27	50 ± 1.3	0.2 ± 0.3
HDR3	0.3 ± 0.3	3.2 ± 1.1	73 ± 7	968 ± 113	64.0 ± 13.3	11420 ± 993	1.5 ± 0.1	153 ± 36	257 ± 54	39 ± 5.1	0.0 ± 0.0
HDC1	0.7 ± 0.9	12.3 ± 5.6	170 ± 249	686 ± 837	66.6 ± 38.5	7709 ± 1687	0.5 ± 0.4	141 ± 205	161 ± 15	43 ± 28.6	0.0 ± 0.0
HDC2	0.2 ± 0.3	1.9 ± 1.1	22 ± 2	322 ± 23	44.7 ± 3.4	1557 ± 92	0.5 ± 0.4	31 ± 10	139 ± 7	24 ± 1.7	0.0 ± 0.0
HDC3	0.0 ± 0.0	0.4 ± 0.2	17 ± 4	224 ± 7	36.5 ± 1.8	1291 ± 22	0.7 ± 0.6	25 ± 7	85 ± 16	18 ± 1.2	0.0 ± 0.0
LDR1	0.7 ± 0.5	12.2 ± 2.1	376 ± 299	1039 ± 729	80.3 ± 33.0	12619 ± 1072	0.6 ± 0.5	222 ± 173	101 ± 11	56 ± 26.1	1.9 ± 3.3
LDR2	0.5 ± 0.1	8.6 ± 4.9	323 ± 23	1120 ± 125	115.5 ± 10.1	14851 ± 1552	1.0 ± 0.6	359 ± 19	81 ± 13	55 ± 5.9	0.4 ± 0.6
LDR3	0.4 ± 0.1	6.4 ± 2.2	249 ± 42	513 ± 53	69.3 ± 7.4	10421 ± 1155	0.8 ± 0.4	373 ± 90	48 ± 28	50 ± 5.6	0.0 ± 0.0
LDC1	1.5 ± 0.4	10.9 ± 7.5	338 ± 87	806 ± 122	30.3 ± 5.7	19912 ± 4906	0.8 ± 0.1	35 ± 8	272 ± 31	37 ± 6.9	2.2 ± 3.5
LDC2	0.9 ± 0.5	8.2 ± 0.7	173 ± 22	317 ± 49	25.8 ± 3.7	14147 ± 2091	0.2 ± 0.2	56 ± 17	71 ± 12	28 ± 4.5	0.0 ± 0.0
LDC3	0.8 ± 0.1	6.4 ± 1.1	239 ± 38	496 ± 65	19.7 ± 0.6	25180 ± 1565	0.1 ± 0.1	51 ± 17	117 ± 13	38 ± 0.9	0.0 ± 0.0
HBS	0.0 ± 0.1	0.4 ± 0.8	2 ± 2	0 ± 0	97.8 ± 21.3	81 ± 14	0.2 ± 0.2	29 ± 8	20 ± 5	10 ± 1.4	0.0 ± 0.0
LBS	0.0 ± 0.1	0.0 ± 0.0	22 ± 5	0 ± 0	56.2 ± 7.4	435 ± 84	0.0 ± 0.0	39 ± 6	290 ± 38	15 ± 1.1	11.0 ± 19.1

Table 4.6 (cont.) Metal release from the dust using the sequential extraction method.

Sequential extraction: Fe-Mn oxides fraction: concentrations ($\mu g\,g^{-1}$ ± standard deviation)

	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mg	Ni
LDR1	3.3 ± 1.1	50.8 ± 6.9	1206 ± 80	871 ± 34	2099 ± 96	14915 ± 271	33.4 ± 2.2	6938 ± 131	177 ± 11	334 ± 5	15.8 ± 1.5
LDR2	3.1 ± 1.8	44.5 ± 7.4	610 ± 79	512 ± 29	1526 ± 74	9075 ± 362	19.3 ± 1.0	4662 ± 117	128 ± 18	171 ± 12	6.4 ± 0.3
LDR3	0.9 ± 0.2	31.1 ± 8.4	449 ± 104	387 ± 81	1129 ± 29	6657 ± 1572	15.6 ± 2.6	3846 ± 135	89 ± 16	160 ± 38	4.9 ± 0.4
LDC1	4.1 ± 0.6	44.7 ± 25.0	916 ± 152	973 ± 138	1666 ± 32	22428 ± 5993	17.9 ± 2.0	4878 ± 366	202 ± 18	231 ± 23	22.5 ± 4.2
LDC2	1.8 ± 0.6	18.6 ± 7.0	344 ± 24	547 ± 232	916 ± 157	10280 ± 2769	9.6 ± 1.4	2337 ± 361	95 ± 32	95 ± 11	10.6 ± 5.9
LDC3	1.9 ± 0.4	31.3 ± 9.5	446 ± 33	658 ± 151	1141 ± 11	25030 ± 2378	13.4 ± 4.1	2937 ± 52	164 ± 16	145 ± 8	8.8 ± 2.0
HDR1	2.1 ± 0.5	82.3 ± 13.3	377 ± 12	880 ± 55	2649 ± 140	10559 ± 616	20.3 ± 1.2	5148 ± 320	247 ± 58	257 ± 8	15.1 ± 1.1
HDR2	1.2 ± 0.1	56.6 ± 13.7	250 ± 18	703 ± 94	1598 ± 104	5503 ± 148	17.1 ± 2.5	3865 ± 210	168 ± 35	150 ± 6	9.0 ± 0.3
HDR3	1.1 ± 0.4	48.3 ± 13.8	250 ± 75	633 ± 92	1298 ± 35	4401 ± 169	15.1 ± 1.6	3277 ± 159	133 ± 16	154 ± 30	6.1 ± 1.5
HDC1	0.8 ± 0.2	76.4 ± 18.2	256 ± 17	404 ± 53	1044 ± 19	1135 ± 68	17.3 ± 2.1	2645 ± 50	123 ± 6	162 ± 3	44.6 ± 1.2
HDC2	1.0 ± 0.2	71.3 ± 17.3	251 ± 53	594 ± 330	842 ± 58	1134 ± 122	20.9 ± 5.0	2269 ± 186	104 ± 24	127 ± 4	47.5 ± 4.3
HDC3	0.6 ± 0.1	56.2 ± 31.3	219 ± 98	463 ± 309	616 ± 46	979 ± 42	20.8 ± 6.9	2082 ± 68	81 ± 17	117 ± 28	45.8 ± 12.5
LBS	0.3 ± 0.1	28.2 ± 12.7	45 ± 11	127 ± 160	700 ± 55	2389 ± 38	1.6 ± 1.5	1655 ± 62	186 ± 6	80 ± 2	3.1 ± 2.6
HBS	0.6 ± 0.1	23.4 ± 14.4	19 ± 19	113 ± 157	1057 ± 31	74 ± 11	2.6 ± 2.1	2739 ± 142	38 ± 5	46 ± 1	2.2 ± 3.6

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Table 4.6 (cont.) Metal release from the dust using the sequential extraction method.

Sequential extraction: Organic fraction: concentrations ($\mu g\,g^{-1} \pm$ standard deviation)

	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mg	Ni
LDR1	0.6 ± 0.1	224.3 ± 33.2	228 ± 12	151 ± 33	1569 ± 101	1701 ± 46	3.9 ± 0.3	1592 ± 92	102 ± 12	37 ± 1.3	10.9 ± 4.6
LDR2	0.5 ± 0.1	125.5 ± 11.3	135 ± 41	97 ± 14	1222 ± 60	1054 ± 65	2.2 ± 1.0	1186 ± 91	133 ± 4	26 ± 2.4	0.6 ± 0.7
LDR3	0.4 ± 0.3	88.5 ± 3.2	192 ± 125	108 ± 20	644 ± 37	762 ± 154	1.4 ± 1.3	1490 ± 72	87 ± 14	29 ± 7.0	0.8 ± 0.5
LDC1	0.7 ± 0.3	95.2 ± 6.1	150 ± 3	183 ± 3	1695 ± 57	1990 ± 119	3.6 ± 0.4	1812 ± 40	142 ± 7	34 ± 1.8	8.8 ± 2.8
LDC2	0.8 ± 0.2	123.2 ± 7.0	46 ± 9	131 ± 7	968 ± 32	1052 ± 74	0.6 ± 0.5	1146 ± 33	112 ± 18	21 ± 4.1	3.1 ± 1.3
LDC3	0.8 ± 0.3	144.6 ± 25.0	106 ± 47	260 ± 123	1088 ± 24	1803 ± 154	2.2 ± 1.8	1350 ± 87	111 ± 11	28 ± 6.5	4.0 ± 0.9
HDR1	0.8 ± 0.2	198.3 ± 11.6	123 ± 10	161 ± 6	1698 ± 43	1010 ± 30	4.1 ± 0.8	1453 ± 44	124 ± 19	51 ± 1.0	5.6 ± 2.9
HDR2	0.6 ± 0.3	126.3 ± 35.7	87 ± 11	137 ± 15	1213 ± 98	630 ± 80	3.7 ± 0.3	1525 ± 47	137 ± 15	46 ± 1.5	2.5 ± 2.5
HDR3	0.4 ± 0.0	68.7 ± 50.2	76 ± 26	166 ± 16	1175 ± 68	590 ± 68	3.4 ± 0.1	1612 ± 237	161 ± 22	45 ± 1.3	0.0 ± 0.0
HDC1	0.6 ± 0.1	98.8 ± 2.6	20 ± 4	122 ± 6	1189 ± 64	705 ± 8	6.2 ± 1.6	1952 ± 140	150 ± 19	89 ± 5.3	13.7 ± 1.7
HDC2	0.6 ± 0.2	96.8 ± 5.8	16 ± 5	144 ± 37	927 ± 40	543 ± 72	6.3 ± 1.2	1730 ± 94	131 ± 25	67 ± 5.0	19.3 ± 9.7
HDC3	0.4 ± 0.3	124.6 ± 32.7	43 ± 61	140 ± 53	651 ± 32	491 ± 57	4.9 ± 0.9	1306 ± 65	113 ± 12	57 ± 5.6	10.0 ± 4.8
LBS	0.5 ± 0.2	104.6 ± 91.0	36 ± 15	317 ± 192	1876 ± 115	555 ± 49	2.6 ± 2.0	1670 ± 55	141 ± 21.2	28 ± 1.2	5.2 ± 2.3
HBS	0.5 ± 0.2	59.7 ± 39.7	0 ± 0	107 ± 13	2631 ± 32	26 ± 9	0.0 ± 0.0	919 ± 11	43 ± 13	10 ± 0.4	0.0 ± 0.0

Table 4.6 (cont.) The metal release from the dust using sequential extraction method.

Sequential extraction: Residual fraction: concentrations ($\mu g\,g^{-1} \pm$ stnadard deviation)

	Cd	Cu	Pb	Zn	Al	Ca	Cr	Fe	K	Mg	Ni
LDR1	4.8 ± 2.1	7.9 ± 0.7	81 ± 4	56 ± 1	4047 ± 279	1237 ± 19	45.8 ± 3.8	0.0 ± 0.0	751 ± 130	207 ± 9	20.8 ± 2.7
LDR2	3.6 ± 1.2	16.4 ± 20.8	47 ± 9	68 ± 62	2829 ± 277	670 ± 70	31.4 ± 5.2	0.0 ± 0.0	628 ± 92	109 ± 5	11.1 ± 1.0
LDR3	2.3 ± 0.2	7.9 ± 7.0	47 ± 23	37 ± 25	1604 ± 169	478 ± 57	21.0 ± 3.7	0.0 ± 0.0	307 ± 49	97 ± 19	6.2 ± 1.9
LDC1	3.7 ± 0.1	10.8 ± 5.6	76 ± 5	124 ± 17	3100 ± 281	980 ± 42	30.1 ± 4.3	0.0 ± 0.0	620 ± 28	136 ± 5	21.8 ± 0.6
LDC2	1.3 ± 0.1	33.3 ± 51.4	31 ± 17	140 ± 146	1944 ± 182	383 ± 3	13.5 ± 1.0	0.0 ± 0.0	536 ± 84	51 ± 1	9.6 ± 1.8
LDC3	3.3 ± 1.4	55.5 ± 87.2	47 ± 18	292 ± 275	1918 ± 87	551 ± 50	15.8 ± 4.0	0.0 ± 0.0	372 ± 42	74 ± 6	14.2 ± 4.8
HDR1	3.0 ± 0.4	7.3 ± 1.5	44 ± 3	90 ± 6	5045 ± 390	165 ± 6	50.1 ± 0.5	0.0 ± 0.0	527 ± 10	167 ± 8	16.0 ± 1.7
HDR2	2.3 ± 0.3	9.9 ± 5.5	30 ± 3	89 ± 20	3394 ± 253	140 ± 1	32.6 ± 5.5	0.0 ± 0.0	408 ± 55	133 ± 9	10.4 ± 3.5
HDR3	2.1 ± 0.2	2.9 ± 0.4	32 ± 9	58 ± 9	3543 ± 291	166 ± 10	33.7 ± 7.3	0.0 ± 0.0	418 ± 10	119 ± 4	6.5 ± 1.2
HDC1	1.5 ± 0.3	3.4 ± 4.4	13 ± 2	59 ± 19	3199 ± 500	172 ± 40	10.2 ± 1.6	0.0 ± 0.0	358 ± 67	137 ± 20	32.5 ± 16.6
HDC2	1.4 ± 0.2	2.2 ± 1.6	10 ± 1	69 ± 6	2821 ± 249	242 ± 19	8.7 ± 0.1	0.0 ± 0.0	417 ± 52	140 ± 4	28.7 ± 0.9
HDC3	1.5 ± 1.0	10.9 ± 9.1	14 ± 5	92 ± 30	2240 ± 148	317 ± 9	8.6 ± 1.2	0.0 ± 0.0	408 ± 4	141 ± 15	25.1 ± 5.2
LBS	0.5 ± 0.2	14.3 ± 9.6	14 ± 3	51 ± 27	6679 ± 102	157 ± 14	14.0 ± 0.3	0.0 ± 0.0	1354 ± 9	36 ± 2	8.7 ± 0.7
HBS	1.2 ± 0.2	17.3 ± 30.0	10 ± 8	60 ± 86	13683 ± 137	24 ± 6	6.6 ± 1.3	0.0 ± 0.0	1417 ± 282	14 ± 1	2.0 ± 1.8
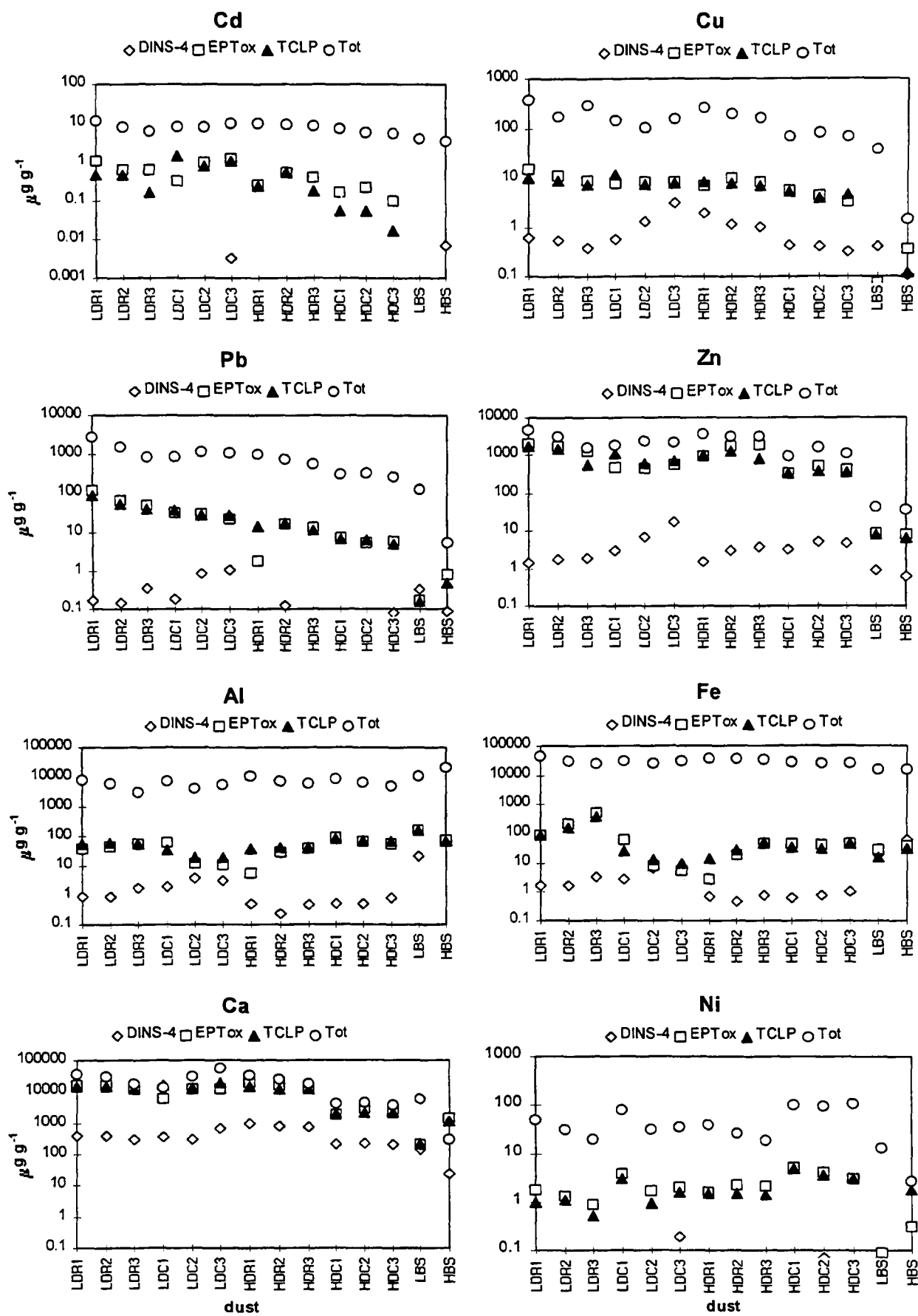
Figure 4.1 Al, Ca, Cd, Cu, Fe,Ni, Pb and Zn released from the dust samples using the different extraction Methods, DIN-S4, TCLP, EPTox and the pesudo-total digestion.

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The average percentages derived from Tables 4.2 to 4.6 of metal extracted using the DIN-S4, EPTox and TCLP methods and the pseudo total metal content, together with the average percentages of the metal in different fractions of the sequential extraction are shown in Table 4.7.

The amounts of Cd, Pb, Al, Cr, Ni and Fe extracted using the DIN-S4 method are less than 0.5 % (see Table 4.7) of the amounts extracted using the pseudo total digestion. The percentages of Cd, Cu, Pb, Zn, Al, Ca, Cr, Fe, K and Ni extracted from the dust showed no significant differences ($p < 0.05$) between the EPTox and TCLP leaching methods. More than 50 % of Fe and Pb were bound to the Fe-Mn oxides fraction (III) and for Ca was bound to the carbonate fraction (II). More than 60% of Cu was bound to the organic fraction (Table 4.7). In general the average percentage of metal extracted by the DIN-S4 method to the pseudo total metal concentrations showed much lower percentages than in the exchangeable fraction of the sequential extraction. The average percentages of Cd, Cu, Zn, Ca, Al and K extracted from the EPTox and TCLP methods to the pseudo total metal concentrations were very close to the sum of percentages of the exchangeable and the carbonate fractions of sequential extraction. The percentages of Pb and Fe extracted in the EPTox and TCLP methods to the pseudo total metal concentrations were just slightly above the exchangeable fraction in the sequential extraction and Cr and Ni were lower than the exchangeable fraction in the sequential extraction.

Figure 4.2 compares the effect of particle size on the concentrations of Cd, Cu, Pb and Zn extracted using different leaching methods. The Cd, Cu, Pb and Zn released using the DIN-S4, EPTox, TCLP and pseudo total digestion approaches showed no significant differences ($p < 0.05$) according to particle

size, using size ranges of less than 125 μm, between 125 and 250μm and between 250 and 500 μm in diameter.

Table 4.7 Average percentages of metal content extracted by the DIN-S4, EPTox, TCLP procedures compared to the pseudo total metal content in all dust samples, and the average percentages of metal content in each fraction in the sequential extraction procedure.

Metal	Leaching methods(%)			Sequential Extraction Method (%)				
	DIN-S4 /total	TCLP /total	EPTox /total	f(I)	f(II)	f(III)	f(IV)	f(V)
Cd	0.2	5.3	6.5	4.9	9.5	29.3	11.6	44.8
Cu	0.9	5.2	5.3	1.9	4.1	26.0	61.1	6.9
Pb	0.1	2.6	2.7	0.2	22.0	60.0	12.8	5.0
Zn	0.5	34.9	40.6	2.8	42.5	38.9	9.6	6.2
Al	0.1	0.8	0.7	0.0	1.1	24.4	21.2	53.4
Ca	5.9	54.7	53.1	6.5	52.5	32.7	5.6	2.7
Cr	0.1	0.2	0.4	0.6	1.7	40.3	8.0	49.4
Fe	0.0	0.3	0.3	0.1	2.5	67.7	29.8	0.0
K	15.5	28.3	23.1	15.5	14.8	12.8	12.0	44.9
Mn	0.5	8.3	49.6	1.1	11.0	44.4	11.6	32.0
Ni	0.1	4.0	5.3	5.9	1.5	40.0	11.6	41.0

f(I): exchangeable fraction, f(II): carbonate fraction, f(III): Fe-Mn fraction, f(IV): organic fraction, f(V): residual fraction.
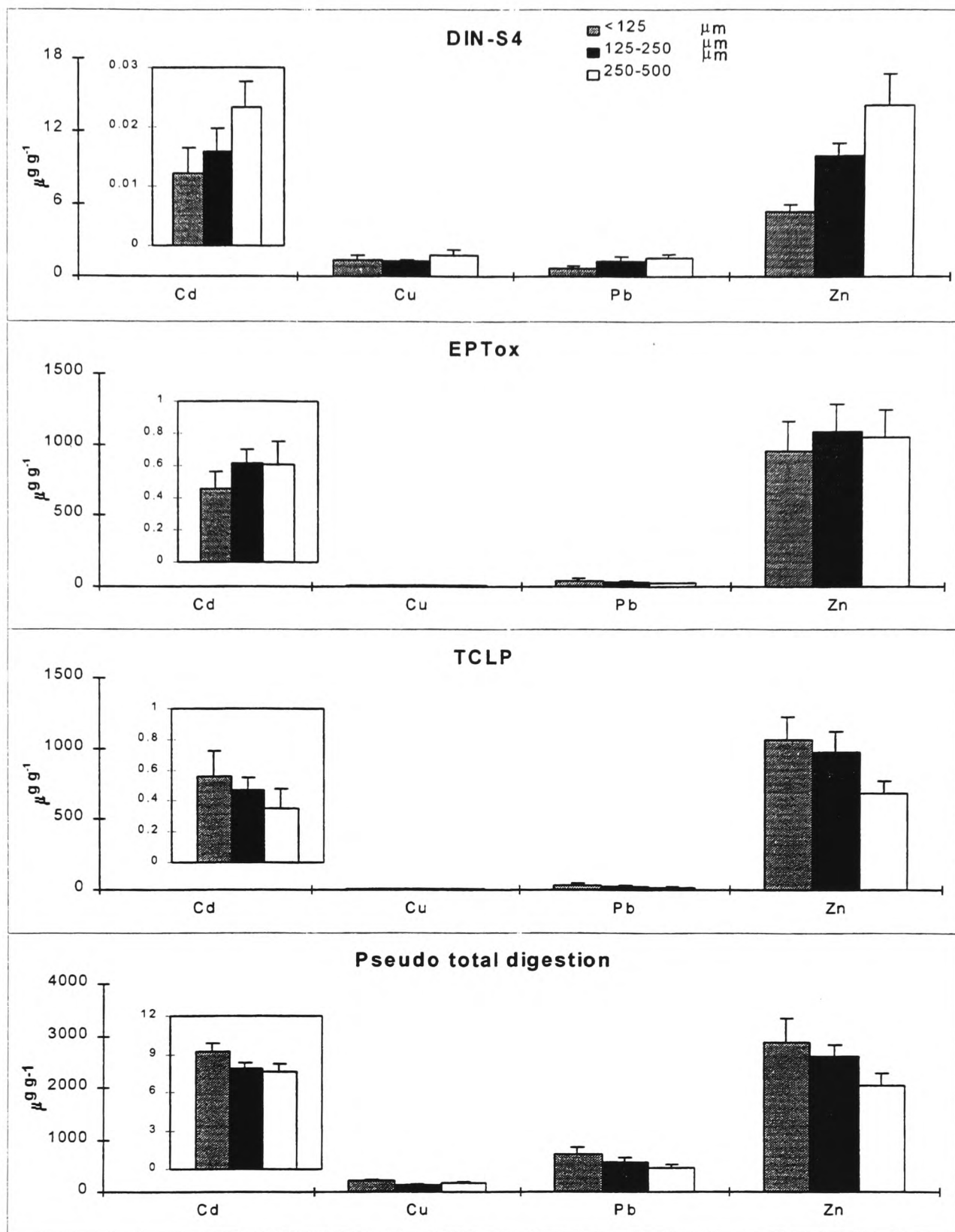
Figure 4.2 Comparison the concentration ($\mu g\ g^{-1}$, mean $\pm$ standard error, $n = 12$) of Cd, Cu, Pb and Zn in different size ranges of dust particles using different extraction methods. Note: data were analysed using one-way ANOVA.

Figure 4.3 shows the concentration of Cd, Cu, Pb and Zn extracted by the DIN-S4, EPTox, TCLP and pseudo total digestion approaches from each sampling site. Zinc, Pb and Cu show similar release pattern using the pseudo total digestion, EPTox, and TCLP approaches. In general, significantly higher amounts of Cd, Cu, Pb and Zn were released from road dust than from car park dust both from the London and Hong Kong sites. Similar amounts of Cd, Cu and Zn were released from the road dusts both from the London and Hong Kong sites except for Cd using EPtox approach, while the amount of Pb released from London road dust was significantly higher than that from Hong Kong road dust. The Cd, Cu, Pb and Zn release patterns showed very different behavior using the DIN-S4 approach; Cd showed no significant difference among the dust samples from the four sampling sites but the amount of Cu release showed a significant difference between the road and car park dust both from the London and Hong Kong sites.

Figure 4.4 shows the difference in the average concentrations of Cd, Cu, Pb and Zn measured using the ICP-AES (this chapter) and the AAS (Chapter 3). For some metals and some fractions significant differences are seen. The concentrations of Cu in the different fractions of sequential extraction showed no significant differences using these two techniques.

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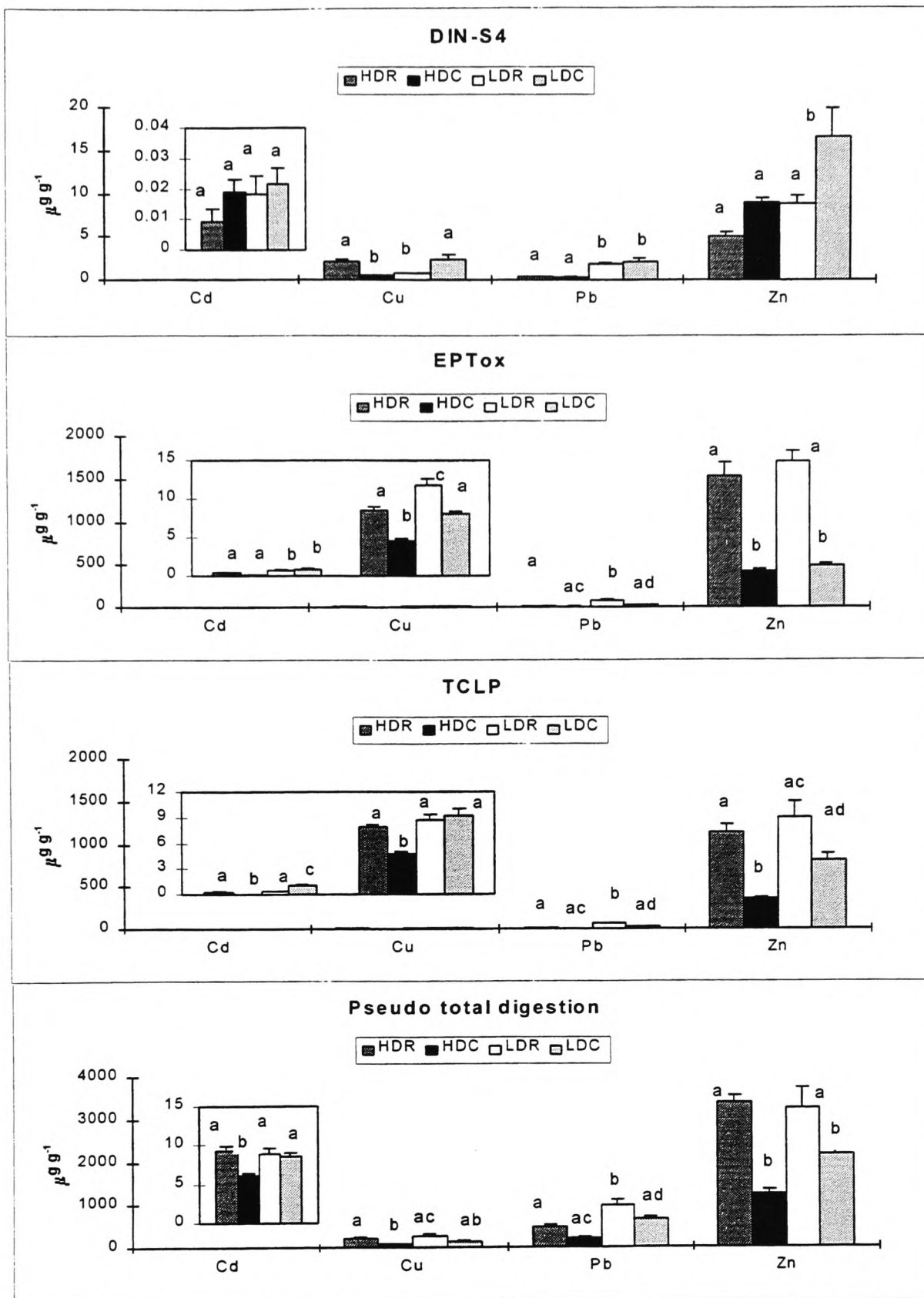
Figure 4.3 Comparison of the concentration (μg g⁻¹, mean ± standard error, n=9) of Cd, Cu, Pb and Zn at different sites using different extraction methods. Note: (1) data were analyed using one-way ANOVA, different letter in different sites indicate significant difference at the $p < 0.05$ probability level (2) difference scales used on y-axis.

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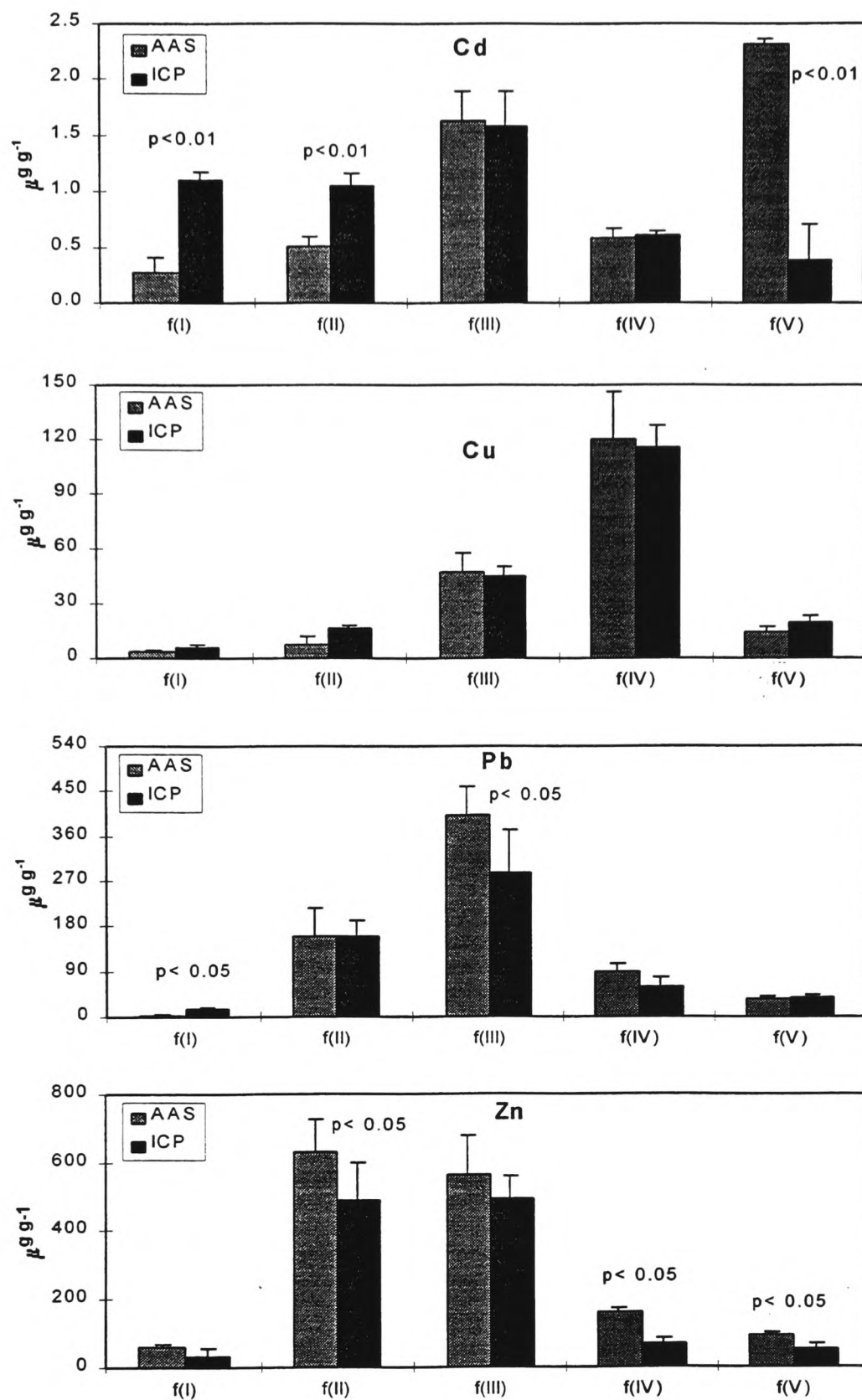
f(I): exchangeable fraction; f(II): carbonate fraction; f(III): Fe-Mn oxides fraction; f(IV): organic fraction; f(V): residual fraction.

Figure 4.4 Comparison of the average concentrations (μg g^{-1}, mean $\pm$ standard error) of Cd, Cu, Pb and Zn measured using ICP-AES and AAS techniques.

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The differences are not readily explained and may arise from measurement error. The following section considers quality control for chemical analysis using the ICP-AES.

4.3.2 Quality control

The results of total digestion and the certified values of Cd, Cu, Pb, Zn, Al, Ca, Cr, Fe, K, Mn and Ni in CRM PACS-1 (marine sediment) and GSC-11 (stream sediment) using the ICP-AES are compared in Table 4.8. The concentration of Cd, Cu, Pb, Zn and Ni found for the total digestion agree well with the certified values (PACS-1 and GSC-11) with recovery rates greater than 80%. Fe and Mn have a fair recovery rate around 60% while Al and K showed very poor recovery rates around 20% with the CRM PACS-1 and GSC-11. Cadmium, Ca and Cr in the CRM PACS-1 sample and Cd and Pb in the CRM GSC-11 sample have recovery rate of greater than 100%, which may represent errors in the instrument calibration.

The instrument detection limit has been related to different confidence levels such as the lower limit of detection, the limit of determination and the limit of quantitation in analytical techniques (Potts, 1987), Table 4.9 shows some of these values calculated from the instrument noise of ICP-AES by testing with double distilled water. In this study six times the standard deviation (6σ) was chosen as the detection limit where the standard deviation were calculated by testing ten DIW samples.

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Table 4.8 Total concentration data for certified reference materials (PACS-1 marine sediment and GSD-11 stream sediment).

	PACS-1			GSD-11		
	Certified value	Total digestion value (n=3)	Recovery %	Certified value	Total digestion value (n=3)	Recovery %
Cd	2.38	4 ± 1.0	158	2.3	3.9 ± 0.5	167
Cu	452	363 ± 25.6	80	78.6	64.4 ± 11.4	82
Pb	404	377 ± 42.6	93	636	668.0 ± 78.3	105
Zn	824	724 ± 65.5	88	373	352.0 ± 31.6	94
Al	64747	17584 ± 1707	27	54900	23585 ± 1502	43
Ca	20857	7957 ± 892.1	38	3357	2487 ± 130.0	74
Cr	113	53 ± 4.6	47	40	10.5 ± 1.7	26
Fe	48720	40360 ± 2011	83	30730	28306 ± 2355	92
K	12447	2845 ± 348	23	27217	6331 ± 376	23
Mn	470	269 ± 48.6	57	2490	1679 ± 573	67
Ni	44.1	42 ± 14.1	96	14.3	13.2 ± 5.2	92

Table 4.9 Different level of detection limit ($\mu g\ ml^{-1}$)

Element	the lower limit of detection (3σ)	the limit of determination (6σ)	the limit of quantitation (10σ)
Al	0.04	0.07	0.12
Ca	0.02	0.04	0.06
Cd	0.01	0.01	0.02
Cr	0.01	0.01	0.02
Cu	0.01	0.01	0.02
Fe	0.25	0.51	0.84
K	0.48	0.96	1.59
Mn	0.00	0.00	0.00
Ni	0.02	0.03	0.06
Pb	0.03	0.06	0.10
Zn	0.00	0.00	0.00

4.3.3 Acid titration: metal release as a function of pH

Results from the leaching test described in earlier sections show a complex pattern which is not easy to interpret. The single most important factor which brings an ordering to the fraction of an element released is the pH with higher fraction removed at lower pH. Given that metals are sometimes present at very low (trace) concentrations considerable scatter in the results is to be expected. The following sections consider release purely as a function of the acidity of the solution with which the dust is in contact.

4.3.3.1 The relationship of acid input and pH change in dust solution

Figure 4.5 shows the titration curves (acid input *vs* pH) for dust samples collected from the London and Hong Kong sites. The suspension of London road dust (LDR) has a higher initial pH (≈ 8.2) than that of London car park dust (LDC) (pH ≈ 7.0). However, the Hong Kong car park dust samples(HDC) have a higher initial pH (≈ 8.0) than the road dust samples (HDR) (pH ≈ 7.3) except for HDR1 (pH ≈ 9.0). Most of interest is directed toward the metal release within the range of pH values between 2 to 6.
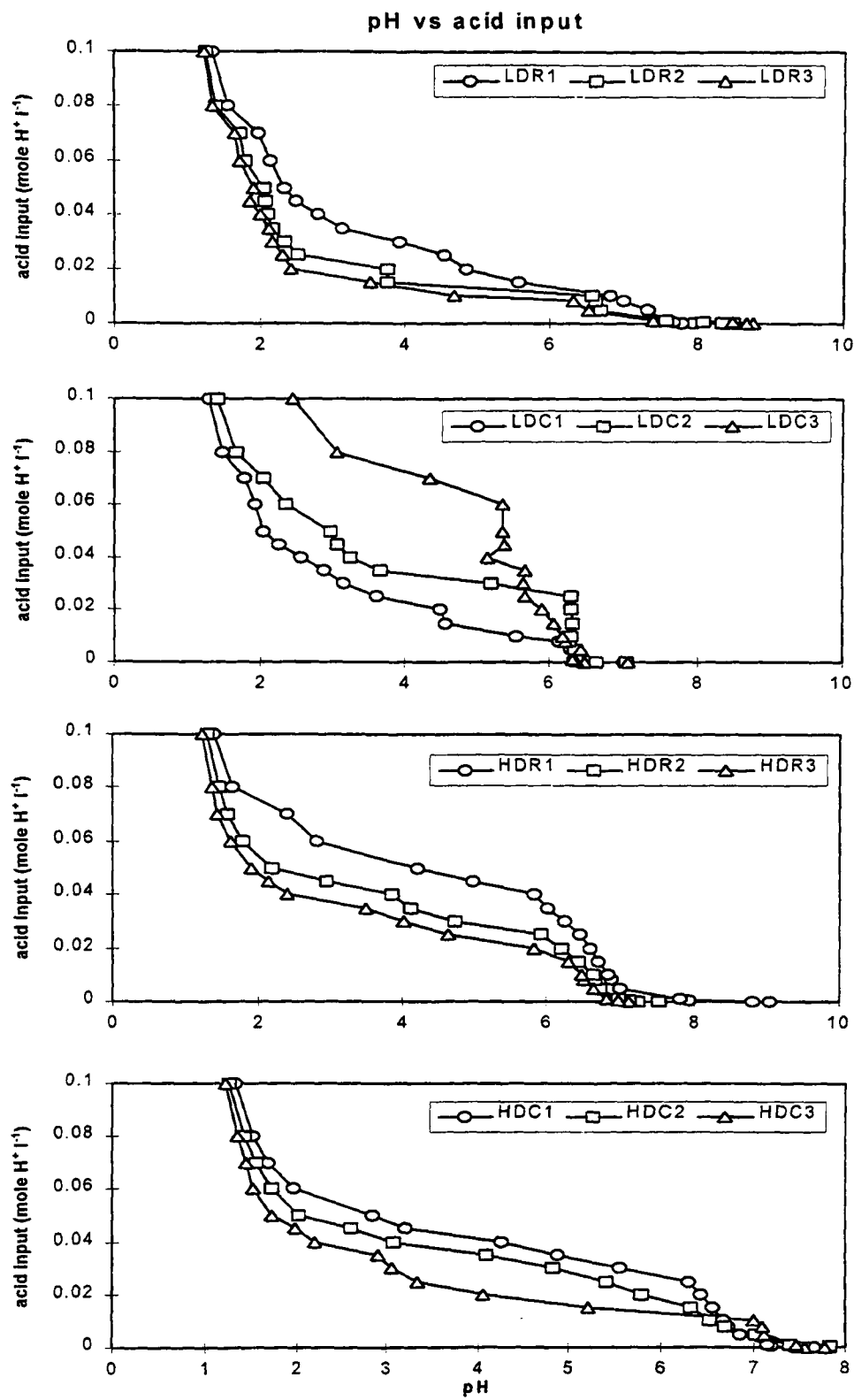
pH vs acid input

LDR1, LDR2, LDR3/ LDC1, LDC2, LDC3 : London road dust/ London car park dust 0-125 μm, 125-250μm, 250-500 μm, respectively.

HDR1, HDR2, HDR3/HDC1, HDC2, HDC3: Hong Kong road dust/Hong Kong car park dust 0-125 μm, 125-250μm, 250-500 μm, respectively.

Figure 4.5 pH-titration curves of pH *vs* acid input for the dust samples.

4.3.3.2 Metal released from dust as a function of pH

The dissolution of Cd, Cu, Pb and Zn from dust samples was investigated by using various concentrations of dilute nitric acid solution. Figure 4.6a and Figure 4.6b show the percentages of Cd, Cu, Pb and Zn released from the dust samples as a function of pH. In general, the dust samples exhibit the capability of retaining Cu and Pb at pH values greater than 6, while Cd and Zn show certain levels of release when the pH is less than 7. As the amount of acid input increases, the amount of Cd, Cu, Pb and Zn released from dust tends to increase. For London dust (Figure 4.6a and 4.6b), when the pH value has dropped from 6 to 4, the dissolution of Cd, Zn, Cu and Pb in dust increases by 20-30%, 10-30%, 0-3%, 0-20%, respectively. Similar trends can be found in Hong Kong dust (Figure 4.6a and 4.6b). At pH 6 the percentages of metal released (Cd: 5- 40%; Cu: 1-2%; Pb: 1-2% and Zn: 15-30%) are less than those of pH 4 (Cd:15- 50%; Cu: 10- 20%; Pb: 5-18% and Zn: 20- 70%). In general, dust with particle sizes less than 125 μm (LDR1, LDC1, HDR1 and HDC1) had higher percentages of metal release at lower pH than for coarser dust particles except for Cd from LDC1 sample and Zn from HDR1. Higher percentages of Cd, Cu, Pb and Zn were released from the London dust samples than from the Hong Kong dust samples.

The fractions of the metals released depend strongly on the pH of the contact solution. However, as presented in Figures 4.6a and 4.6b the results would be hard to apply to a risk assessment. In the next section results are presented using the concept of a partition coefficient.
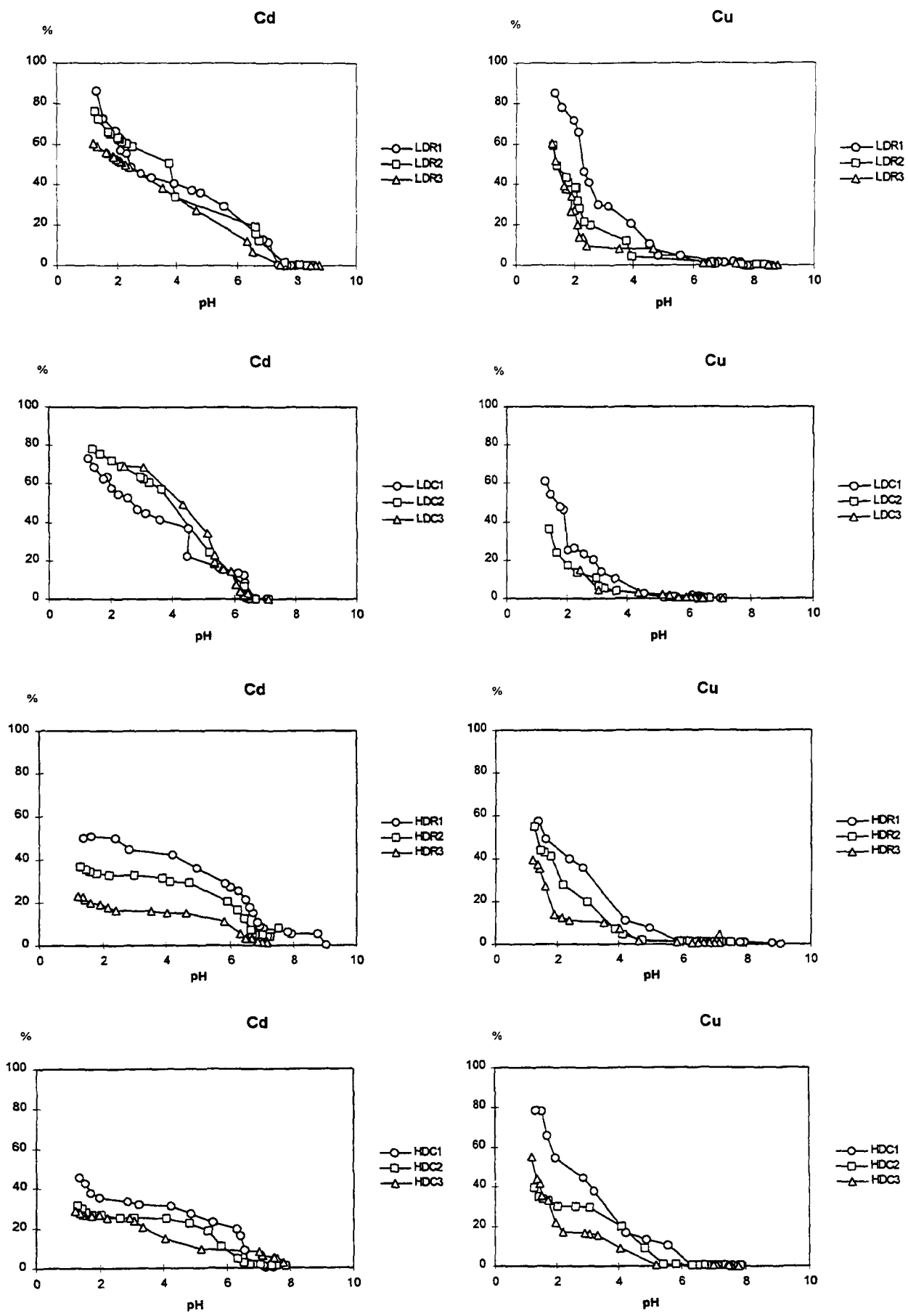
Figure 4.6a The Cd and Cu release (μg g^{-1}) as function of pH.

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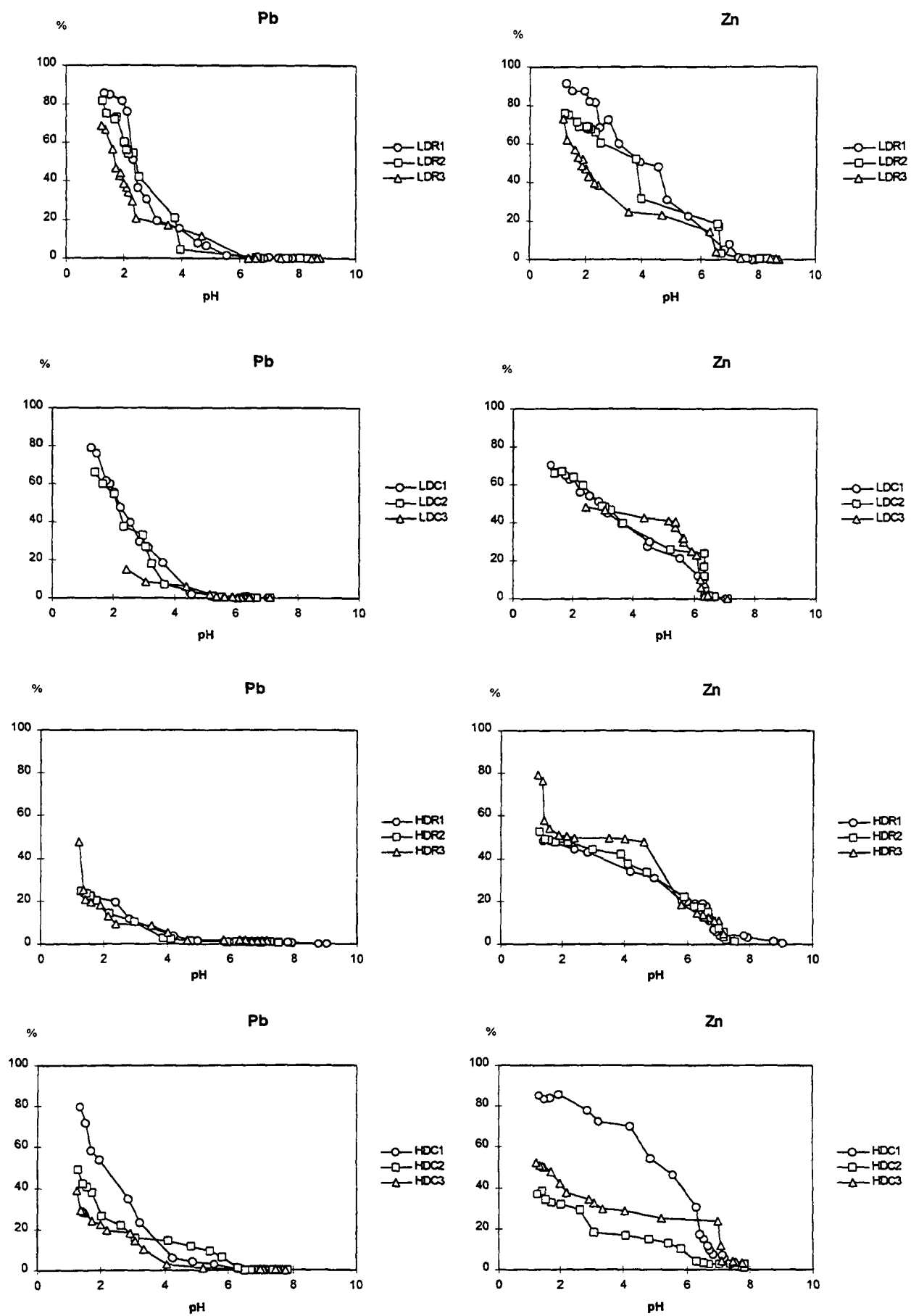
Figure 4.6b The Pb and Zn release (μg g^{-1}) as function of pH.

4.3.3.3 Partition coefficients for Cd, Cu, Pb and Zn by acid titration

The total metal content in dust samples is assumed to be equal to the amount of metal retained in the dust sample plus the amount of metal released to the contact solution during a seven day period in which each dust sample was left to equilibrate. Under this operationally defined equilibrium concept, a relatively simple approach for calculating the distribution of heavy metal between the solid phase and water in contact with the dust can be used, based on partition coefficient. Partition coefficients have been widely used for assessing the fate of heavy metal in runoff such as USEPA Water Quality Model WASP4 (Ambrose *et al.*, 1988). More commonly, partition coefficients under a simple linear isotherm assumption were applied for assessing the mobility of heavy metal in urban roadway storm water and field soil (Sansalone and Buchberger, 1997; Janssen *et al.*, 1997, Benoit and Rozan, 1999).

Assuming a linear isotherm to describe the relationship between adsorbed and dissolved metal molecules, a partition coefficient (k_{sw}) can be defined as the ratio between the metal concentration in dust and that in solution as follows:

$$k_{sw} = \frac{C_d}{C_w} \qquad (4.1)$$

where C_d (μg g^{-1}) is the metal concentration retained in the dust and C_w (μg ml^{-1}) is the concentration of metal in the solution at the ratio (w:v) of 1:20 for dust:water at 25 °C. The k_{sw} (ml g^{-1}) values of dust in different acidic solutions are plotted on a logarithmic scale against pH (Figure 4.7a and 4.7b). The values of k_{sw} of each metal in dust are strongly pH dependent; the lower

the pH, the lower the k_{sw}. In general, Cd and Zn have lower k_{sw} values than Cu and Pb for pH values between 4 and 6.

Variations in the pH dependence of k_{sw} for different size ranges of dust particles collected at the same sites are not seen to be large (see Figures 4.7a and 4.7b). There appears to be some variation between the partition coefficient for samples collected at different sites, but if attention is confined to pH in the range 2 to 6 the pattern for dust samples at different sites looks consistent and a linear relation between the $\log(k_{sw})$ and the pH of the solutions is observed. Linear regression equations between the $\log(k_{sw})$ and the pH of the solutions for each metal were determined at pH range between 2 and 6 (Table 4.10). The regression analysis was performed by means of the Microsoft Office Excel program and the adjusted r^2 value, where r is the correlation coefficient. r^2 is the fraction of the variation explained by the linear regression equation, was used as a measure of the goodness-of-fit.

The regression equations are reasonably fitted to the observed data of four metals with high r^2 values (between 0.66 to 0.94) except for Zn at the HDC site ($r^2 = 0.26$) and Cd at the HDR ($r^2 = 0.38$) and at the HDC sites($r^2 = 0.45$).
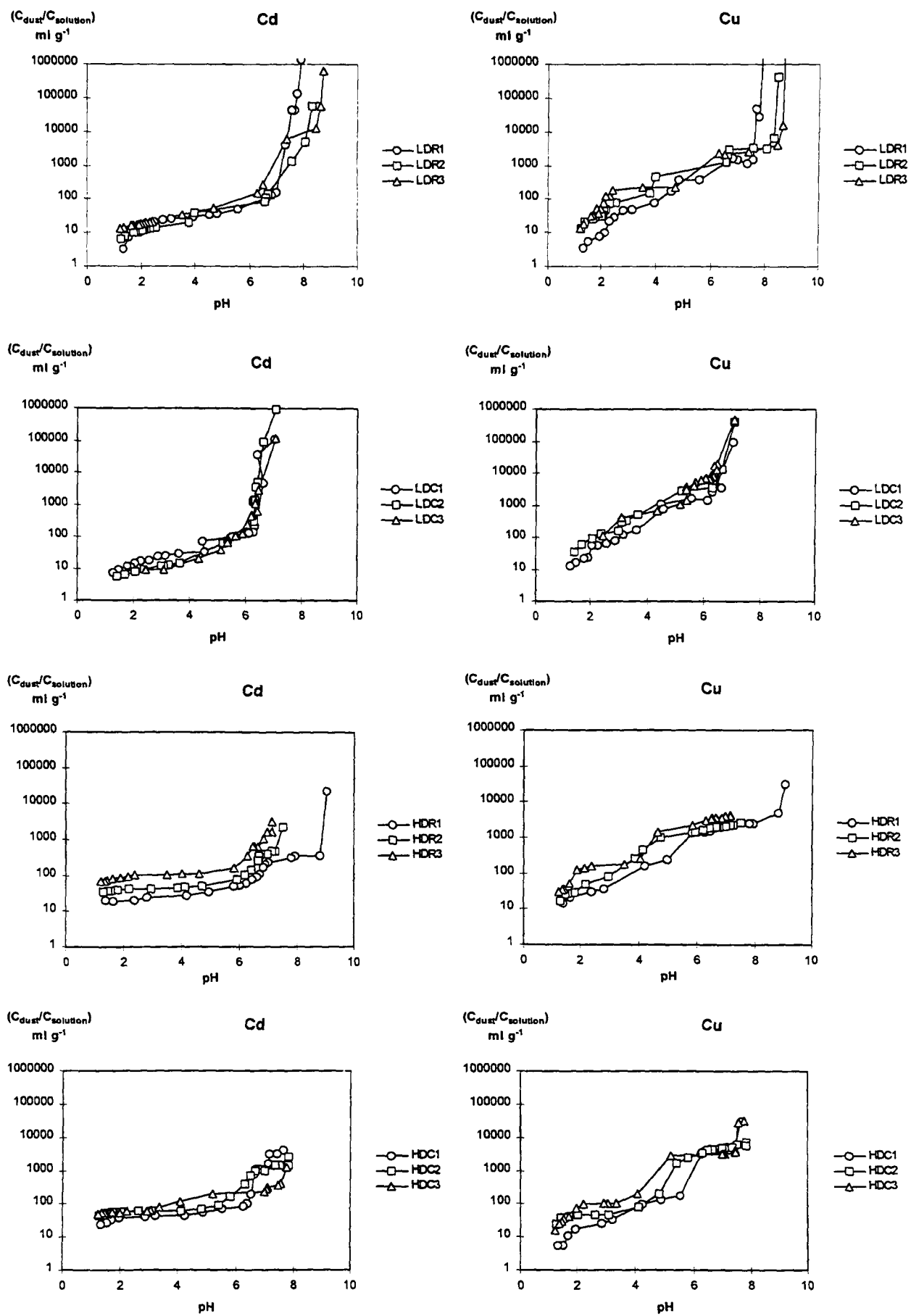
Figure 4.7a The partition coefficients of Cd and Cu of dust at different pH in acidic conditions.
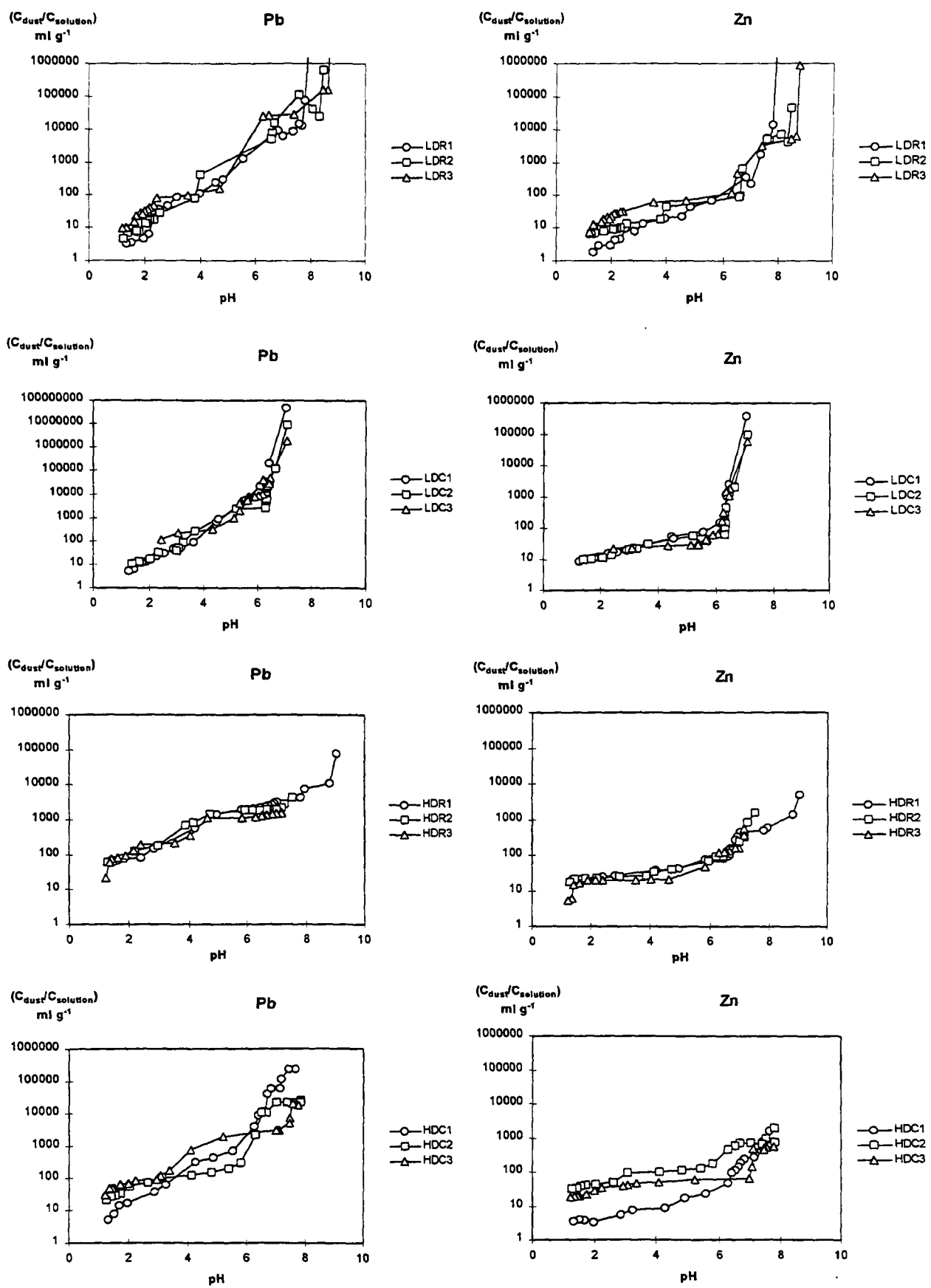
Figure 4.7b The partition coefficients of Pb and Zn of dust at different pH in acidic conditions.

Table 4.10 The linear regression equations of the relations between log (k_{sw}) and pH of solution.

	Regression equations	
dust	Cd	
LDR	log (k_{sw}) = 0.2079 pH + 0.7148	r^2 = 0.90
LDC	log (k_{sw}) = 0.3129 pH + 0.2703	r^2 = 0.86
HDR	log (k_{sw}) = 0.1599 pH + 1.2185	r^2 = 0.38
HDC	log (k_{sw}) = 0.1184 pH + 1.3882	r^2 = 0.45
	Cu	
LDR	log (k_{sw}) = 0.3431 pH + 0.8821	r^2 = 0.74
LDC	log (k_{sw}) = 0.4751 pH + 0.8031	r^2 = 0.91
HDR	log (k_{sw}) = 0.3664 pH + 1.0105	r^2 = 0.80
HDC	log (k_{sw}) = 0.4476 pH + 0.4524	r^2 = 0.74
	Pb	
LDR	log (k_{sw}) = 0.568 pH + 0.0335	r^2 = 0.89
LDC	log (k_{sw}) = 0.674 pH - 0.1568	r^2 = 0.94
HDR	log (k_{sw}) = 0.3096 pH + 1.4231	r^2 = 0.89
HDC	log (k_{sw}) = 0.3353 pH + 0.9979	r^2 = 0.70
	Zn	
LDR	log (k_{sw}) = 0.2543 pH + 0.4761	r^2 = 0.66
LDC	log (k_{sw}) = 0.1608 pH + 0.8186	r^2 = 0.78
HDR	log (k_{sw}) = 0.1516 pH + 0.9264	r^2 = 0.81
HDC	log (k_{sw}) = 0.1895 pH + 0.8406	r^2 = 0.26

4.3.4 Time dependency of Cd, Cu, Pb and Zn release kinetics

The concept of a partition coefficient assumes that heavy metal concentrations in solid and dissolved form have reached an equilibrium. The question raised as to how quickly this equilibrium is established.

Figures 4.8a and 4.8b show the time-dependency of the concentrations ($\mu g \ g^{-1}$) of Cd, Cu, Pb and Zn released from dust at London and Hong Kong sites during extraction in constant pH 1, 2, 3 and 4 nitric acid solutions. Cadmium, Cu, Pb and Zn release was dependent on pH: the lower the pH, the higher the amount of metal released from the dust samples. Two different patterns of Cd, Cu, Pb and Zn release were found. In one pattern, the metal release was very sharp and fast within the first 30 minutes followed by much slower release until 24 hours later (e.g. Figure 4.8a LDR1: Cd and Zn at pH 1 and 2); the other pattern involved a much slower release mechanism throughout the whole extraction period (e.g. Figure 4.8a LDR1: Cu and Pb at pH 3 and 4). Figure 4.9a and 4.9b show the percentages of Cd, Cu, Pb and Zn released as a function of time. The dissolution of Cd, Cu, Pb and Zn for the HDR1 sample showed a smaller percentage of metal released ($\leq 50\%$) in the kinetic experiment than HDC1, LDR1 and LDC1. At pH 3 and 4, Cu and Pb had the smallest release ($\leq 20\%$) among all the dust samples.
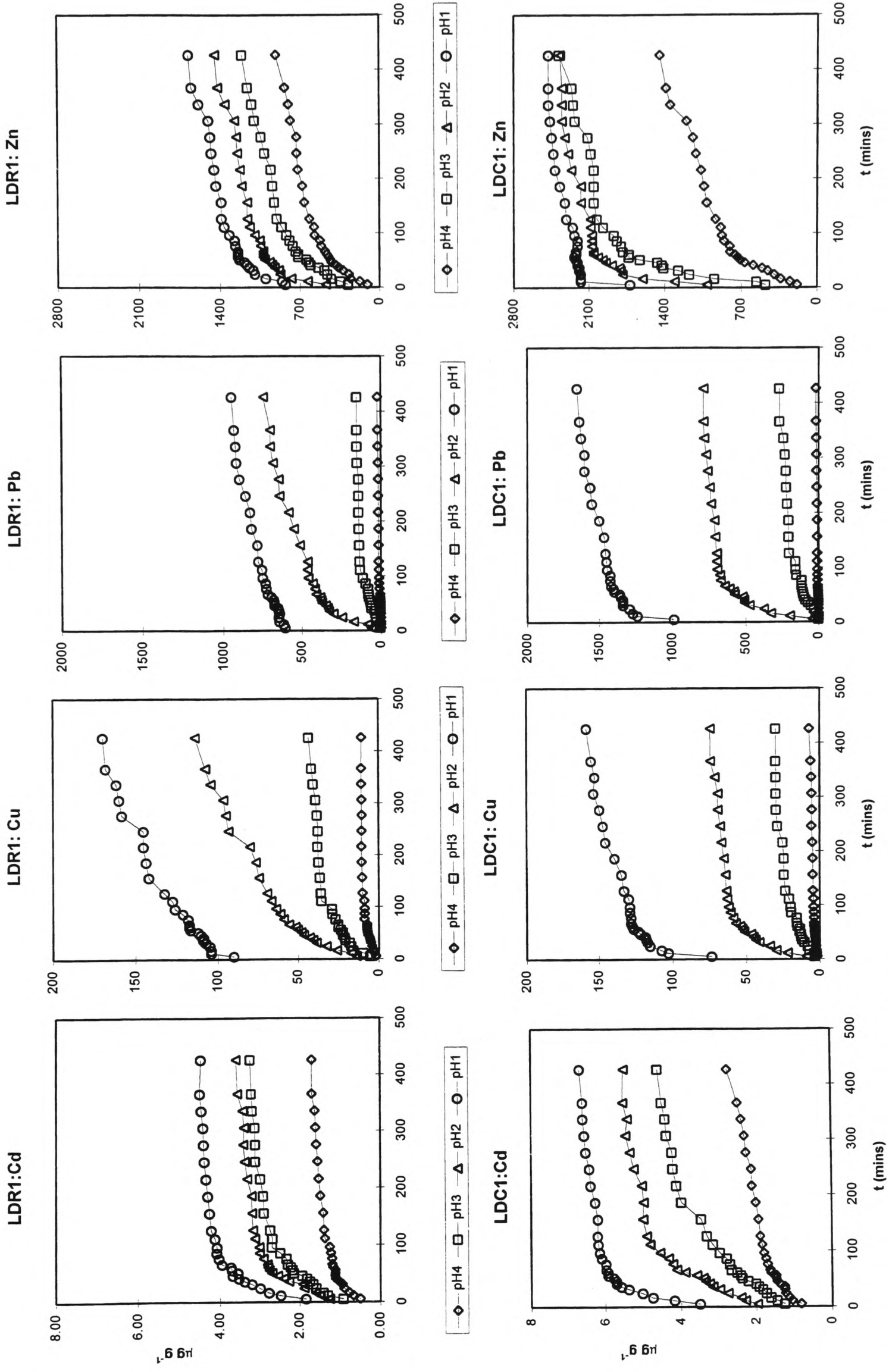
LDR1, LDC1: London road dust and Lodon car park dust particle size < 125 µm respectively.

Figure 4.8a Concentration (µg g^{-1}) of Cd, Cu, Pb and Zn release from London site dust in pH = 1, 2, 3 and 4 nitric acid solution versus extraction time.

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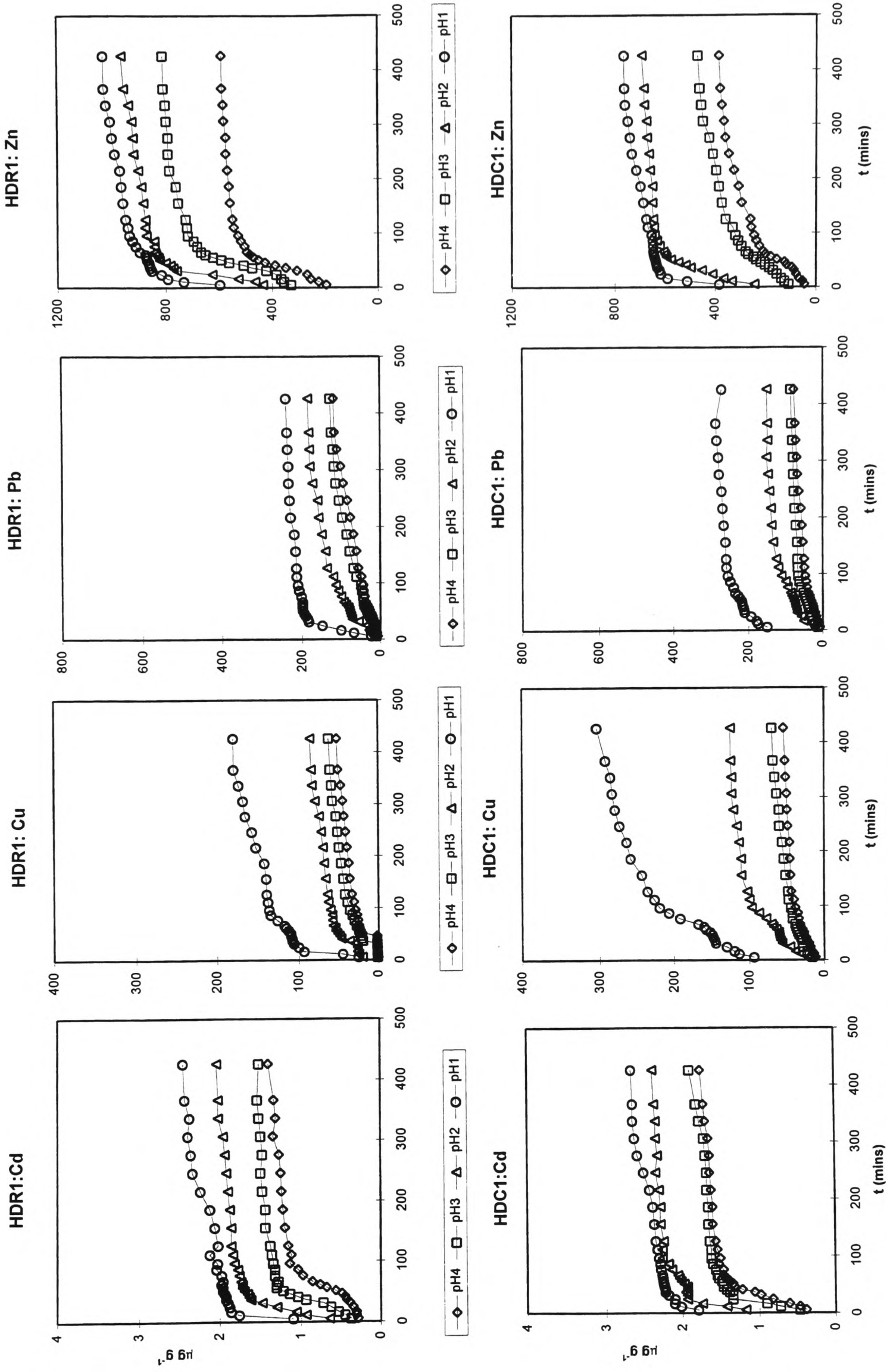
HDR1, HDC1:Hong Kong road dust and Hong Kong car park dust particle size < 125 μm respectively.

Figure 4.8b Concentrations (μg g^{-1}) of Cd, Cu, Pb and Zn release from Hong Kong site dust in pH= 1, 2, 3 and 4 nitric acid solution versus extraction time.

130
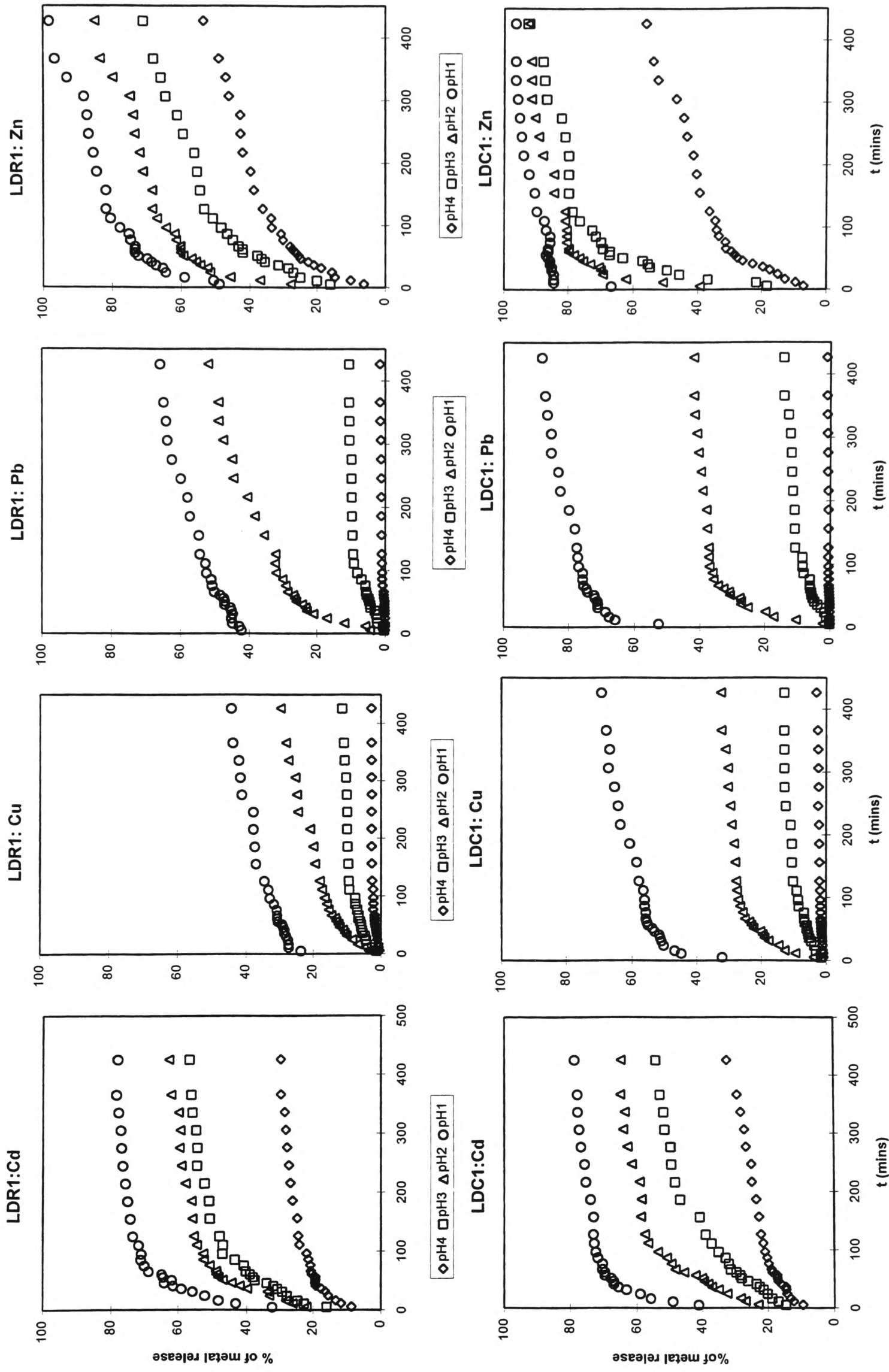
LDR1, LDC1: London road dust and Lodon car park dust particle size < 125 mm respectively.

Figure 4.9a Percentages of Cd, Cu, Pb and Zn release from London site dust in pH = 1, 2, 3 and 4 nitric acid solution versus extraction time.
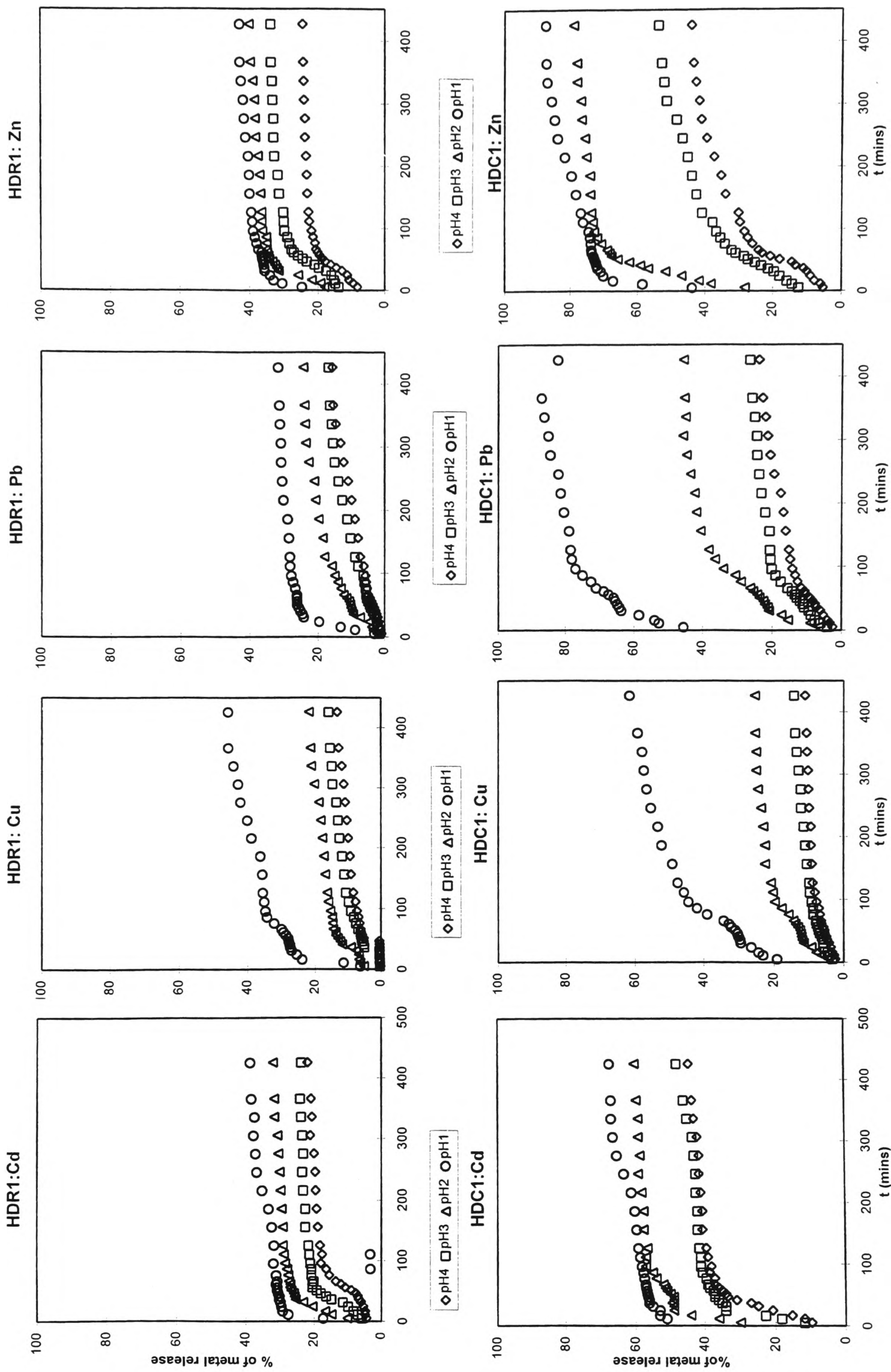
Figure 4.9b Percentages of Cd, Cu, Pb and Zn release from Hong Kong sites dust in pH = 1, 2, 3 and 4 nitric acid solution versus extraction time.

HDR1, HDC1: Hong Kong road dust and Lodon car park dust particle size < 125 mm respectively.

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4.3.4.1 Kinetic analysis

Many researcher have proposed that the ionic adsorption and desorption processes in clay and soil can be described by first order reactions, which include a single first order reaction (e.g. Sivasubramaniam and Talibudeen, 1972; Spark et al., 1980; Spark and Jardine, 1984; Jardine and Spark, 1984) and multiple first order reactions (e.g. Griffin and Burau, 1974; Griffin and Jurinak, 1974; Tuin and Tels, 1990). In this study, a model of two first order reactions was used to describe the metal release kinetics (Figures 4.8a and 4.8b) from the dust. This model was first constructed by Tuin and Tels (1990) to study metal clean up kinetics by acid solution of metal contaminated soil. The approach can be equally well be applied to the leaching of dust particles in acid solution. The model assumes that metal release follows two different first order reactions, one fast and irreversible reaction and the other a slow and reversible reaction. These reactions are assumed to behave as follows:

$$\text{reaction A: } Surf_1 - O^- Me^{2+} + H^+ \xrightarrow{k_1} Surf - O - H + Me^{2+} \qquad (4.2a)$$

$$\text{reaction B: } Surf_2 - O^- Me^{2+} + H^+ \underset{k_3}{\overset{k_2}{\longleftrightarrow}} Surf - O - H + Me^{2+} \qquad (4.2b)$$
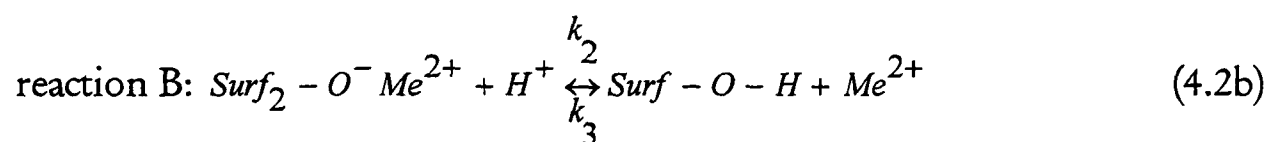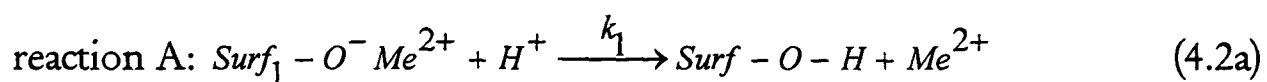
where $Surf_1$ and $Surf_2$ are the active surface binding sites on the soil particle, Me represents a metal ion, and k_1, k_2 and k_3 are reaction rate constants. The equations are only illustrative and are not meant to represent balanced chemical reactions.

The model assumes that metal release in an acid solution first follows a fast forward reaction (reaction A) during the first few minutes, and then follows a much slower reversible reaction (reaction B). In reaction A, it is assumed

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that the metal binding sites are destroyed by the strong acid intrusion. The metal binding in reaction B is assumed to be stronger than in reaction A and it cannot be dissolved easily in the acidic solution. It is assumed that the metal release kinetics are coupled by these two reactions. For simplicity, it is further assumed that all the reactions (two forward and one backward) are pseudo first order reactions. Although reactions A and B are both simple, the system is quite involved and the two equations are strongly coupled. Metal released in reaction A, for example, may be re-absorbed by reaction B.

The mathematical expressions for the two reactions rates are as follows:

$$R_a = \frac{dA}{dt} = -k_1 A \tag{4.3}$$

$$R_b = \frac{dB}{dt} = -k_2 B + k_3 C \tag{4.4}$$

where,

R_a = rate of metal release according to reaction A,

R_b = rate of metal release according to reaction B,

k_1, k_2 = reaction rate constants (min^{-1})

k_3 = reaction rate constant $(min^{-1}$ volume liquid/ mass dust),

A = heavy metal concentration in the dust that reacts according to reaction A,

B = heavy metal concentration in the dust that reacts according to reaction B,

C = heavy metal concentration in the extraction liquid.

At time $t=0$, the initial total heavy metal concentration in the dust is taken to be A_0+B_0 and it is assumed that A_0 is the part subject to reaction A and that B_0 is the part subject to reaction B. The heavy metal concentration in the extraction liquid is equal to C_0 at time $t=0$ and is subject to the reaction

$$\frac{L}{M}\frac{dC}{dt} = k_3 C - k_2 B - k_1 A \tag{4.5}$$

where L is the volume of extraction liquid and M is the mass of dust. It is assumed that the volume of liquid of liquid and the mass of dust remains unchanged, so

$$L=L_0 \text{ and } M=M_0 \tag{4.6}$$

where L_0 and M_0 are the volume of liquid and mass of dust at time $t=0$.

The mass balance of heavy metal in the system is as follows,

$$M(A+B) + LC = M_0\left(A_0 + B_0\right) + L_0 C_0 \tag{4.7}$$

Thus $C = \dfrac{M}{L}\left(A_0 + B_0 - A - B\right) + C_0$

and equations (4.3) and (4.4) can be written as

$$A = A_0 \exp\left(-k_1 t\right) \tag{4.8}$$

$$\frac{dB}{dt} + \left(k_2 + \frac{k_3 M}{L}\right)B = k_3 C_0 + \frac{k_3 M}{L}\left(A_0 + B_0 - A\right) \tag{4.9}$$

Writing $k'_3 = k_3(M/L)$ and $k'_2 = k_2 + k'_3$, where k'_3 and k'_2 are reaction rates per minute, then the equation (4.9) can be solved.

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$$B = \frac{k_3}{k_2'} C_0 \left\{ (1 - \exp(-k_2' t)) \right\} + \frac{k_3'}{k_2'} (A_0 + B_0)(1 - \exp(-k_2' t))$$

$$- \frac{k_3'}{k_2' - k_1} \left(\exp(-k_1 t) - \exp(-k_2' t) \right) + B_0 \exp(-k_2' t) \tag{4.10}$$

The expression for total metal concentration in the dust (A+B) as a function of time t can be obtained

$$A + B = \frac{k_3}{k_2'} C_0 \left\{ (1 - \exp(-k_2' t)) \right\} + \frac{k_3'}{k_2'} (A_0 + B_0) + \frac{k_2 - k_1}{k_2' - k_1} A_0 \exp(-k_1 t)$$

$$+ \left((k_2 - k_1) B_0 + \frac{k_1 k_3'}{k_2'} (A_0 + B_0) \right) \frac{\exp(-k_2' t)}{k_2' - k_1} \tag{4.11}$$

One may note that at $t = 0$

$$A + B = A_0 + B_0 \tag{4.12}$$

and when $t \to \infty$ the equation (4.11) is given by

$$A + B = \frac{k_3}{k_2'} \left(C_0 + \frac{M}{L}(A_0 + B_0) \right) \tag{4.13}$$

The concentration of metal in solution when $t \to \infty$ is as follows:

$$C = \frac{k_2}{k_2'} \left(C_0 + \frac{M}{L}(A_0 + B_0) \right) \tag{4.14}$$

This corresponds to equilibrium conditions expected to apply after 24 hours of extraction under which

$$\frac{A + B}{C} = \frac{k_3}{k_2} = \frac{k_3'}{k_2} \frac{L}{M} \tag{4.15}$$

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where $(A+B)/C$ at $t \to \infty$ represents an equilibrium between metal in solid and liquid and is equivalent to the partition coefficient k_{sw}. Thus in this model, k_{sw} can be given by equation (4.16).

$$k_{sw} = \frac{k_3}{k_2} \qquad (4.16)$$

The ratio k_3/k_2 in equation (4.16) is determined from experiments at a fixed pH which assumes that the dust and extracting agent reached chemical equilibrium after 24 hours of extraction by the HNO_3 solution

At time $t=0$, the initial metal concentration in the dust is taken to be (A_0+B_0) and the initially metal concentration in the extraction liquid is equal to 0 $(C_0=0)$. It assumed that β is the fraction of metal in dust subject to the slow reversible reaction B and $(1-\beta)$ is the fraction of dust subject to the fast irreversible reaction A. Hence equation (4.11) can be written as follows:

$$A+B = \frac{k_3}{k_2'} C_0 \left\{ (1-\exp(-k_2't)) \right\} + \frac{k_3'}{k_2'}(A_0+B_0) + \frac{k_2-k_1}{k_2'-k_1}(1-\beta)(A_0+B_0)\exp(-k_1t)$$
$$+ \left((k2-k1)\beta(A_0+B_0) + \frac{k_1k_3'}{k_2'}(A_0+B_0) \right) \frac{\exp(-k_2't)}{k_2'-k_1} \qquad (4.17)$$

Hence the time dependence of metal release given by the model in equation (4.17) is a function of k_1, k_2 k_{sw} (through k_3 and k_3') and β.

The parameters k_1, k_2 and β can be determined by fitting the measurement data points $(A(t)+B(t), t)$ shown in Figure 4.8a and 4.8b to equation (4.17). The data from the kinetic experiments were fitted to this solution of the two reaction model using the Solver function in Microsoft Excel, which

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minimises the sum of squares of the differences between measurement data and the model described by equation (4.17).

The two reaction model provided a good fit to the data of experimental measurement in all cases (see examples in Appendices Figure 3). The model contains enough parameters to provide a good description of the experimental data without containing too many parameters whose values could not be uniquely determined by the curve fitting technique. The calculated parameters of k_1, k_2, k_{sw} (given by equation (4.16)) and β together with the corresponding half life of the reaction ($t_{1/2}$) and correlation coefficient (r) of this kinetic model are given in Table 4.11, 4.12, 4.13 and 4.14 The reaction rate constants k_1 and k_2 correspond to the fast irreversible and slow reversible forward reactions, respectively. The half life of a reaction is defined as the time required to consume half of the original amount of metal in dust. In general, the k_1 value increases as pH decreases while β and k_{sw} decrease. This shows a shorter half life for the fast reaction at pH 1 than at other pH values. Table 4.15 presents the results in another way and shows the percentages of Cd, Cu, Pb and Zn released after 10, 30 and 120 minutes according to the two reaction model.

Table 4.11 Selected parameters for the two reaction model of Cd dissolution from dust from all samples at different pH values and half lives ($t_{1/2}$:min). β refers to the percentage of metal that followed the slow reaction; k_{sw} is the ratio of metal in the dust to metal in the solution, which is similar to the partition coefficient, and r^2 is the correlation coefficient between the data of the kinetic model and the experimental data. LDR1, LDC1, HDR1 and HDC1 refer to particle < 125 μm in diameter from London road dust, London car park dust, Hong Kong road dust and Hong Kong car park dust respectively.

	Cd	k_1 (min^{-1})	k_2 (min^{-1})	β (ratio)	k_{sw}(ml g^{-1})	r^2
LDR1	pH =1	0.0949	0.0019	0.38	5.00	0.90
	$t_{1/2}$	7.3	370.4			
	pH =2	0.0510	0.0009	0.49	10.77	0.91
	$t_{1/2}$	13.6	774.7			
	pH = 3	0.0476	0.0011	0.58	14.48	0.88
	$t_{1/2}$	14.6	658.7			
	pH =4	0.0266	1.0E-16	0.72	40.61	0.90
	$t_{1/2}$	26.1	6.9E+15			
LDC1	pH =1	0.1410	0.0015	0.32	5.00	0.86
	$t_{1/2}$	4.9	477.6			
	pH =2	0.0568	0.0017	0.54	10.30	0.86
	$t_{1/2}$	12.2	418.8			
	pH = 3	0.0743	0.0015	0.74	11.25	0.93
	$t_{1/2}$	9.3	449.6			
	pH =4	0.0227	0.0004	0.77	37.14	0.9
	$t_{1/2}$	30.6	1949.5			
HDR1	pH =1	0.0674	0.0008	0.68	28.78	0.8
	$t_{1/2}$	10.3	914.2			
	pH =2	0.0652	0.0002	0.72	37.14	0.95
	$t_{1/2}$	10.6	3636.3			
	pH = 3	0.0286	0.0000007	0.77	56.92	0.97
	$t_{1/2}$	24.3	9.9E+05			
	pH =4	0.0081	1E-10	0.74	63.33	0.93
	$t_{1/2}$	85.9	6.9E+09			
HDC1	pH =1	0.3493	0.0010	0.46	8.99	0.92
	$t_{1/2}$	2.0	729.3			
	pH =2	0.1204	0.0012	0.56	10.77	0.83
	$t_{1/2}$	5.8	577.6			
	pH = 3	0.0637	0.0004	0.62	16.36	0.97
	$t_{1/2}$	10.9	1903.4			
	pH =4	0.0348	0.0002	0.61	17.74	0.98
	$t_{1/2}$	19.9	3478.5			

Table 4.11 Selected parameters for the two reaction model of Cd dissolution from dust from all samples at different pH values and half lives ($t_{1/2}$:min). β refers to the percentage of metal that followed the slow reaction; k_{sw} is the ratio of metal in the dust to metal in the solution, which is similar to the partition coefficient, and r^2 is the correlation coefficient between the data of the kinetic model and the experimental data. LDR1, LDC1, HDR1 and HDC1 refer to particle $<$ 125 μm in diameter from London road dust, London car park dust, Hong Kong road dust and Hong Kong car park dust respectively.

	Cu	k_1 (min^{-1})	k_2 (min^{-1})	β (ratio)	k_{sw}(ml g^{-1})	r^2
LDR1	pH =1	0.4928	0.0019	0.75	24.44	0.99
	$t_{1/2}$	1.4	356.3			
	pH =2	0.0521	0.0011	0.91	40.61	0.99
	$t_{1/2}$	13.3	602.8			
	pH = 3	0.0275	0.0002	0.93	113.33	0.97
	$t_{1/2}$	25.2	3132.7			
	pH =4	0.0208	1.8E-06	0.97	380.00	0.97
	$t_{1/2}$	33.3	3.9E+05			
LDC1	pH =1	0.2050	0.0029	0.52	8.17	0.99
	$t_{1/2}$	3.4	240.8			
	pH =2	0.0360	0.0006	0.75	34.05	0.99
	$t_{1/2}$	19.2	1095.3			
	pH = 3	0.0169	0.0003	0.91	89.24	0.99
	$t_{1/2}$	41.0	2685.4			
	pH =4	0.0221	1E-10	0.98	343.64	0.80
	$t_{1/2}$	31.4	6.9E+09			
HDR1	pH =1	0.0749	0.0018	0.75	20.82	0.97
	$t_{1/2}$	9.3	395.1			
	pH =2	0.0362	0.0005	0.87	54.07	0.96
	$t_{1/2}$	19.1	1280.3			
	pH = 3	0.0078	1.2E-06	0.84	60.00	0.97
	$t_{1/2}$	88.4	5.9E+05			
	pH =4	0.0065	1E-10	0.86	85.26	0.91
	$t_{1/2}$	106.9	6.9E+09			
HDC1	pH =1	0.3633	0.0038	0.79	10.77	0.98
	$t_{1/2}$	1.9	183.5			
	pH =2	0.0243	0.0008	0.84	51.43	0.98
	$t_{1/2}$	28.5	836.4			
	pH = 3	0.0885	0.0005	0.95	91.11	0.98
	$t_{1/2}$	7.8	1410.2			
	pH =4	0.0275	0.0003	0.94	133.85	0.98
	$t_{1/2}$	25.2	2297.2			

Table 4.13 Selected parameters for the two reaction model of Pb dissolution from dust from all samples at different pH values and half lives ($t_{1/2}$:min). β refers to the percentage of metal that followed the slow reaction; k_{sw} is the ration of metal in the dust to metal in the solution, which is similar to the partition coefficient, and r^2 is the correlation coefficient between the data of the kinetic model and the experimental data. LDR1, LDC1, HDR1 and HDC1 refer to particle < 125 μm in diameter from London road dust, London car park dust, Hong Kong road dust and Hong Kong car park dust respectively.

	Pb	k_1 (min⁻¹)	k_2 (min⁻¹)	β (ratio)	k_{sw}(ml g⁻¹)	r^2
LDR1	pH = 1	0.0980	0.0032	0.55	1.83	0.99
	$t_{1/2}$	7.1	218.9			
	pH = 2	0.0995	0.0018	0.89	13.33	0.98
	$t_{1/2}$	7.0	375.4			
	pH = 3	0.0045	1.0E-07	0.81	80.00	0.89
	$t_{1/2}$	154.0	6.9E+06			
	pH = 4	0.0048	1.2E-12	0.98	113.33	0.98
	$t_{1/2}$	145.3	6.0E+11			
LDC1	pH = 1	0.2784	0.0033	0.24	2.13	0.94
	$t_{1/2}$	2.5	209.0			
	pH = 2	0.0341	0.0008	0.65	24.44	0.99
	$t_{1/2}$	20.3	891.7			
	pH = 3	0.0109	0.0002	0.90	104.64	0.98
	$t_{1/2}$	63.3	3145.3			
	pH = 4	0.0045	1.0E-10	0.99	698.01	0.96
	$t_{1/2}$	152.7	6.9E+09			
HDR1	pH = 1	0.0483	0.0005	0.73	37.09	0.98
	$t_{1/2}$	14.3	1467.0			
	pH = 2	0.0170	0.0007	0.86	48.97	0.99
	$t_{1/2}$	40.8	992.4			
	pH = 3	0.0045	1.0E-7	0.80	70.91	0.99
	$t_{1/2}$	154.2	6.9E+06			
	pH = 4	0.0031	0.0003	0.86	90.17	0.99
	$t_{1/2}$	224.2	2411.3			
HDC1	pH = 1	0.3924	0.0102	0.50	3.53	0.98
	$t_{1/2}$	1.8	67.8			
	pH = 2	0.0231	0.0013	0.69	16.36	0.98
	$t_{1/2}$	30.0	547.4			
	pH = 3	0.0216	0.0005	0.82	42.29	0.98
	$t_{1/2}$	32.1	1370.8			
	pH = 4	0.0221	0.0006	0.90	43.25	0.99
	$t_{1/2}$	31.4	1083.9			

Table 4.14 Selected parameters for the two reaction model of Zn dissolution from dust from all samples at different pH values and half lives ($t_{1/2}$:min). β refers to the percentage of metal that followed the slow reaction; k_{sw} is the ratio of metal in the dust to metal in the solution, which is similar to the partition coefficient, and r^2 is the correlation coefficient between the data of the kinetic model and the experimental data. LDR1, LDC1, HDR1 and HDC1 refer to particle < 125 μm in diameter from London road dust, London car park dust, Hong Kong road dust and Hong Kong car park dust respectively.

	Zn	k_1 (min^{-1})	k_2 (min^{-1})	β (ratio)	k_{sw}(ml g^{-1})	r^2
LDR1	pH =1	0.2463	0.0055	0.40	0.12	0.95
	$t_{1/2}$	2.8	127.1			
	pH =2	0.1251	0.0040	0.50	3.29	0.98
	$t_{1/2}$	5.5	174.5			
	pH = 3	0.0193	1.0E-13	0.38	6.67	0.93
	$t_{1/2}$	35.9	6.9E+12			
	pH =4	0.0415	0.0021	0.79	16.36	0.99
	$t_{1/2}$	16.7	328.3			
LDC1	pH =1	0.3362	0.0048	0.17	0.41	0.97
	$t_{1/2}$	2.1	145.5			
	pH =2	0.1323	0.0055	0.31	1.05	0.98
	$t_{1/2}$	5.2	126.9			
	pH = 3	0.0418	0.0032	0.34	0.62	0.99
	$t_{1/2}$	16.6	218.4			
	pH =4	0.0364	0.0020	0.77	12.79	0.98
	$t_{1/2}$	19.1	349.3			
HDR1	pH =1	0.2256	0.0013	0.66	24.44	0.97
	$t_{1/2}$	3.1	530.5			
	pH =2	0.0807	0.0009	0.67	27.61	0.94
	$t_{1/2}$	8.6	732.7			
	pH = 3	0.0301	1.0E-7	0.68	35.55	0.92
	$t_{1/2}$	23.0	6.9E+06			
	pH =4	0.0047	0.0047	0.61	51.42	0.95
	$t_{1/2}$	147.6	147.6			
HDC1	pH =1	0.1957	0.0042	0.32	2.47	0.99
	$t_{1/2}$	3.5	166.2			
	pH =2	0.0604	0.0028	0.35	4.10	0.96
	$t_{1/2}$	11.5	250.9			
	pH = 3	0.0497	0.0027	0.79	14.48	0.98
	$t_{1/2}$	14.0	257.1			
	pH =4	0.0146	0.0018	0.76	24.44	0.99
	$t_{1/2}$	47.5	379.5			

Table 4.15 Percentages of Cd, Cu, Pb and Zn release after 10, 30 and 120 min according to the kinetic model.

	Metal release after											
	pH 1			pH =2			pH = 3			pH =4		
	10 min	30 min	2 hr	10 min	30 min	2 hr	10 min	30 min	2 hr	10 min	30 min	2 hr
Cd release (%)												
LDR1	39	60	67	21	41	54	17	33	46	6	15	26
LDC1	52	68	71	21	40	52	15	26	36	5	12	24
HDR1	16	28	34	14	24	29	6	14	23	2	6	16
HDC1	53	55	57	53	54	57	18	33	40	12	26	39
Cu release (%)												
LDR1	26	28	34	5	10	18	2	5	9	1	1	2
LDC1	43	51	58	8	17	27	2	4	9	<1	1	2
HDR1	15	26	35	4	10	16	1	3	10	1	2	7
HDC1	23	28	44	4	10	20	4	6	9	2	4	8
Pb release (%)												
LDR1	30	47	61	8	14	26	1	2	8	<1	<1	1
LDC1	72	77	81	11	24	38	1	3	9	<1	<1	<1
HDR1	11	21	29	3	7	17	1	3	9	1	2	7
HDC1	53	61	78	7	18	36	4	10	20	3	7	15
Zn release (%)												
LDR1	57	66	79	38	54	66	11	27	56	9	19	35
LDC1	80	85	90	52	72	82	24	50	76	9	19	36
HDR1	31	36	38	19	31	36	8	19	31	4	11	26
HDC1	59	70	77	30	57	72	10	22	38	5	12	31

LDR1, LDC1: London road dust and Lodon car park dust particle size < 125 µm respectively.

HDR1, HDC1: Hong Kong road dust and Lodon car park dust particle size < 125 µm respectively.

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At pH 4 the results (Tables 4.11-4.14) of two reaction model show that $\beta \geq$ 0.9 and $\geq$ 0.7 for Cu/Pb and Cd/Zn release respectively from the dust sample so that the fraction dissolved by the fast reaction is generally small. These results are consistent with the results of the sequential extraction described in Chapter 3.

If one assumed $k_3 = 0$ so that reaction B was irreversible, then equation (4.11) reduces to

$$A + B = A_0 \exp\left(-k_1 t\right) + B_0 \exp\left(-k_2 t\right) \tag{4.18}$$

In this study if f is the fraction of metal released during the time dependent extraction process, then f is given by

$$f = 1 - \frac{B(t)}{A_0 + B_0} \tag{4.19}$$

and when $t \rightarrow \infty$

$$f \rightarrow \frac{1}{1 + \dfrac{k_3}{k_2}\dfrac{M}{L}} = \frac{1}{1 + k_{sw}\dfrac{M}{L}} \tag{4.20}$$

Equation (4.20) illustrates the difference between a sequential extraction and a time dependent extraction. If a sequential extraction was performed and all the metal subject to the fast irreversible reaction was removed during the first extraction, the fraction removed would be $A_0/(A_0 + B_0) = 1 - \beta$ which is not equal to the fraction given by equation (4.20). However it may be seen that the model is an approximate way of representing each stage of sequential extraction in which a reagent has been chosen to dissolve particles associated with certain geochemical forms.

4.3.5 Scanning Electron Microscopy (SEM)

The techniques of SEM can be used to characterize the dust in individual particles. The morphology of dust varies according to their size and shape (see Figure 4.10). In general, the assemblage of dust from the London site includes fragments of mineral, elongated objects and aggregate particles. Occasionally fly ash, small bright smooth sphere particles (the bright particle shows higher atomic number) were identified among the samples. Normally the small pieces of dust were attached to or adhered to the surface of bigger dust particles. The mineral phases were analyzed by an X-ray detector. The majority of the particles were dominated by Si, Ca and Fe phases. Zn, Zr, S and Ba was occasionally found in the car park dust from the London sites. Dust particles from the Hong Kong sites do not show much difference to the dust from the London sites in terms of the morphology of the dust. Fragments of mineral, elongated objects and aggregate particles were the main constituents of dust, while less bright round sphere particles were found among the dust from the Hong Kong sites. Dust particles from the Hong Kong sites were found have sharper edges than the dust from London and this suggests that more immature weathering products were in the dust from the Hong Kong sites. There is less Fe phase in the dust from Hong Kong sites than the dust from London sites.
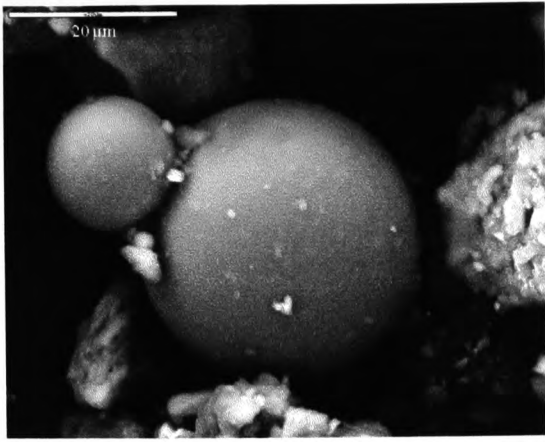
LDR1 (Fe phase)
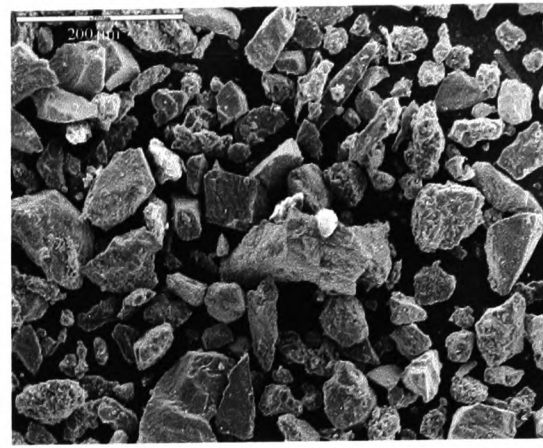
HDR1
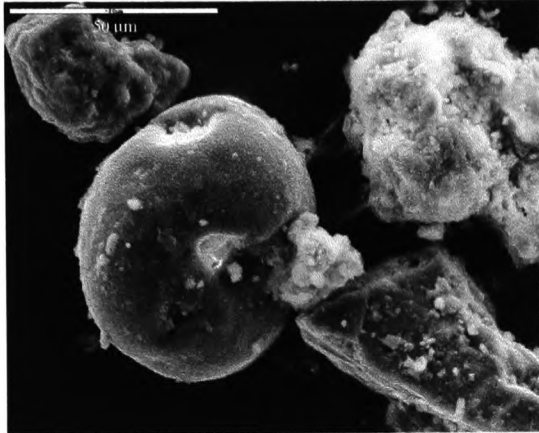
HDR1 (Fe phase)
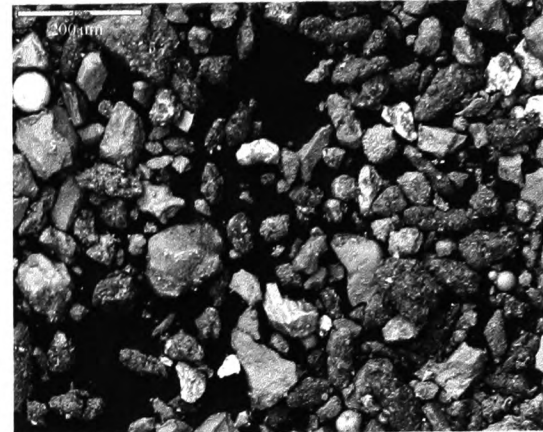
LDR1
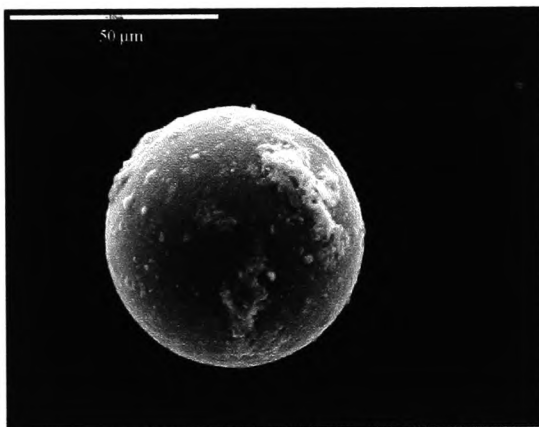
LDC1(Fe phase)
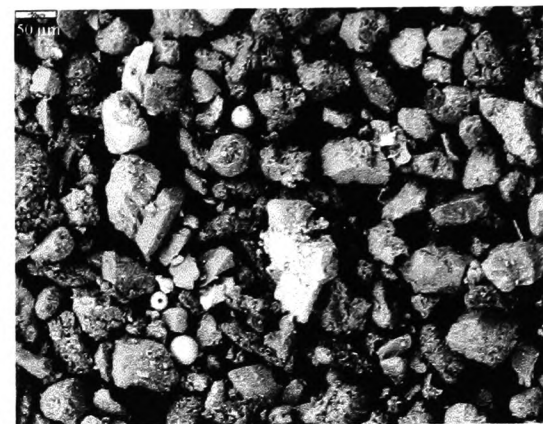
LDC1

LDR1(fly ash)

LDC1(Zr phase)
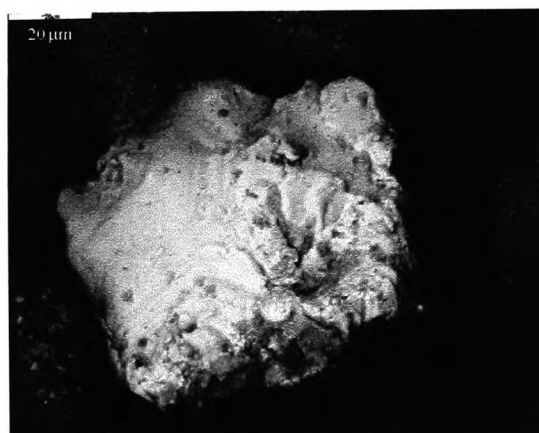
LDC1(Zn phase)
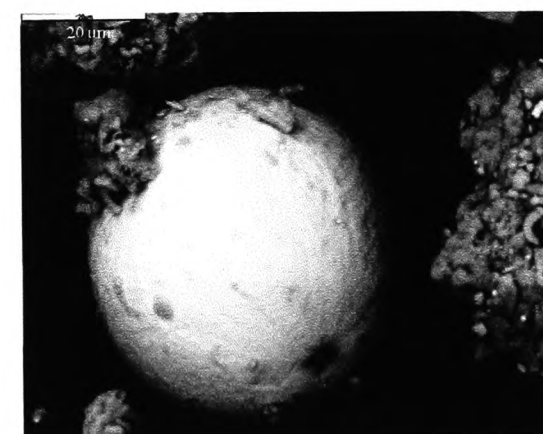
LDR1 (Fe phase)

Figure 4.10 SEM images.

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4.3.6 X-ray diffraction

The technique of X-ray diffraction was used to provide additional information on some of the mineral forms seen in a small selection of the dust samples. The results of X-ray diffraction analysis (see an examples in Appendices Figure 4) showed that the dust samples were dominated by the highly crystallized forms of mineral because the X-ray lines have very narrow and sharp peaks, in contrast to the poorly crystallized forms of mineral for which the X-ray lines have wider smaller peaks of low intensity. The major mineral was identified using computer programs Philips PC-APS 1700 and Philips PC-IDENTIFY, to match the fingerprint of the mineral structure of rock. Quartz (SiO_2) and Calcite($CaCO_3$) were two minerals which could be clearly identified by the computer program with good matches of peaks in the X-ray line. Although Microcline ($KAlSi_3O_8$), Albite ($NaAlSi_3O_8$), Lanrkite (PB_2OSO_4), Ankerite ($Ca(Fe, Mg)(CO_3)_2$) were identified by the computer program as the most possible minor mineral appearing in the dust samples, the overlap among the peaks and the similarity of the different matches caused confusing results. The identification of the mineral structure of the dust turns out to be very difficult when there are many small peaks appearing in the samples and this further demonstrated the complex composition of the urban dust.

4.4 Discussion

4.4.1 Chemical analysis

The different leaching methods together with the sequential extraction are discussed in this section. Although the results of these methods are available for eleven elements, the discussion will be mainly focused on the four elements Cd, Cu, Pb and Zn which are of most concern in urban dust and in urban runoff.

4.4.1.1 DIN-S4 Leaching Test

The purpose of the German standard method DIN-S4 (DIN 38414 S4, 1984) is to determine the likelihood of heavy metals being leached from the solid waste material into rivers and lakes when it comes into contact with water. The test identifies the dust particles that are immediately available to the natural environment and can give a reliable estimate of the bioavailability of different minerals (Sterckeman *et al.*, 1996). Less than 1% of Cd, Cu, Pb, Zn, Al, Cr, Fe, Mn and Ni were released using water extraction compared to the pseudo total digestion method while showed relatively high percentages of K and Ca (10 and 2.9 % respectively) were released. The absence of electrolyte may cause the dispersion of the dust or soil colloids, which is unable to separate the phases and this may be the reason why the concentration of extracted metals are very low (Sterckeman *et al.*, 1996). The other limitation of using DIW as an extractant is the different solubility of univalent and divalent ions. The relative and total dissolved constituents will change when increasing the water content and the processes involve exchange reactions in which dissolved divalent cations replace adsorbed univalent cations (Black et al, 1965).

4.4.1.2 TCLP Leaching Method

The USEPA Toxicity Characteristic Leaching Procedure (TCLP) is designed to determine the mobility of both organic and inorganic compounds present in liquid, solid and multi-phase waste (USEPA SW 846 method 1311, 1998). The USEPA examined a variety of methods to test the potential to leach toxic constituents from waste. The rationale of using acetic acid as a leaching fluid in the TCLP test is that acetic acid is found in the liquids from municipal landfills as a result of the normal degradation of organic materials, and the value of pH 5 adopted was the observed acidity of fluids found in actual landfill leachates (Mice Service, personal communication, 1998). One

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of two leaching fluids with different pH values was used depending upon the nature of the waste to be leached. If a waste is more alkaline or has a large inherent buffer capacity, the lower pH leaching fluid was used to leach the waste. The rationale is that a short term leaching test must use strong acid to overcome the buffer capacity of the waste itself when the pH of the waste is higher, such as in the case of dust. This change will help to simulate what would happen over the long term if a waste were placed in an uncontrolled landfill and leached over a longer period.

4.4.1.3 EPTox Leaching Test

The leaching test SW486 Method 1310 Extraction Procedure Toxicity Test Method (EPTox) attempts to model the leaching of pollutants from a solid waste. It was developed after early experiments with reagent water (water in which an interference is not observed at or above the method's detection limit of the compound of interest. De-ionized water was used in this study). Acetic acid was used to adjust the pH to 5 ± 0.2.

The EPTox and TCLP methods were designed similarly to expose waste to a final solution with a pH around 5, but the TCLP method has the options to choose different extraction solutions in relation to the alkalinity of the material. Very similar amounts of metal are released using the TCLP and EPTox methods except for Mn (Table 4.7). This suggests that the pH value of the solution may be the governing parameter in these two leaching methods.

When compared with the sequential extraction method, the average percentage of metal released using the TCLP and EPTox methods, showed values generally located between the exchangeable fraction and the carbonate fraction (see Table 4.7). The exchangeable and carbonate fraction of Tessier's sequential extraction reflects the fraction which is most mobile and becomes

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mobile when the pH is about 5 in the natural environment, such as when exposed to acid rain. Hence the EPTox and TCLP tests can also used to simulate exposure to acid rain conditions when rainfall percolates through a landfill site during the rain event.

4.4.1.4 Comparison of pseudo total digestion and total sequential extraction

In general, Cd, Pb, Zn, Al, Cr, Fe, Mn and Ni showed (see Table 4.16) higher amounts of metal released when the total digestion approach was applied, while Cu, Ca and K showed higher amount of metal release in all fractions of the sequential extraction. Very little of iron was released using sequential extraction. Higher amounts of Cd, Pb, Zn, Al, Cr, Fe, Mn and Ni might have been found using total digestion because of losses during the different stages of sequential extraction. On the other hand, the higher amounts of Cu, Ca and K may be due to the highly acidic leaching fluid (HNO_3 and $HClO_4$) and these metals may not be efficiently digested using the pseudo total digestion approach.

Recalling that Cd, Cu, Pb and Zn are the elements analysed in detail in Chapter 3 for dust under a wide range of conditions, the differences of ± 17-34% (see Table 4.16) between the techniques suggest that no great significance should be placed on some of the differences between techniques. For most elements the spread in results between samples described by the standard deviation is larger than the percentage difference between techniques. This suggests that the techniques are sufficiently reliable to detect major sample differences.

Table 4.16 The average percentages differences of pseudo total metal concentration (μg g^{-1} $\pm$ standard deviation) to the sum of five fractions of sequential extraction.

	Total of sequential extraction	Total digestion	Mean difference (%)
Cd	6 ± 3	8 ± 2	29
Cu	204 ± 59	174 ± 96	-17
Pb	791 ± 495	979 ± 728	19
Zn	1664 ± 501	2511 ± 1158	34
Al	5578 ± 1813	6720 ± 2086	17
Ca	25021 ± 15676	23142 ± 15837	-8
Cr	49 ± 20	55 ± 18	12
Fe	5397 ± 1551	32182 ± 6343	83
K	1112 ± 356	1024 ± 246	-9
Mn	391 ± 115	556 ± 146	30
Ni	47 ± 33	53 ± 33	11

4.4.1.5 Size and site effects

Size effects (Figure 4.2) are seen to make no significant difference on Cd, Cu, Pb and Zn release in the four leaching/digestion approaches (DIN-S4, EPTox, TCLP and pseudo total digestion). This suggests that the size ranges (less than 125 μm, between 125-250 μm and between 250-500 μm) in this study are not important parameters in these leaching methods. In general, the road site dust shows higher amounts of Cd, Cu, Pb and Zn release than the car park dust both at the London and Hong Kong sites when using the pseudo total digestion, TCLP and EPtox methods (Figure 4.3).

4.4.1.6 Correlation between different leaching methods

Given the expected difference inherent in the results of the different leaching methods, it was decided to compare the order with which metal was released from the various samples. The Spearman rank correlation of Cd, Cu, Pb

and Zn release between different leaching methods is shown in Table 4.17. The Cd, Cu, Pb and Zn concentrations using EPTox, TCLP extraction methods and the pseudo total digestion method were significantly positively correlated.

Table 4.17 Spearman rank correlation of metal release between different methods.

	Cd			
	DIN-S4	EPTox	TCLP	Tot
EPTox	0.1			
TCLP	-0.1	0.7 *		
Tot	-0.5	0.6 *	0.6 *	
F(I)	-0.1	0.3	0.7 **	0.4
	Cu			
	DIN-S4	EPTox	TCLP	Tot
EPTox	0.3			
TCLP	0.4	0.6 *		
Tot	0.3	0.8 **	0.6 *	
F(I)	0.6 *	0.0	0.6 **	-0.1
	Pb			
	DIN-S4	EPTox	TCLP	Tot
EPTox	0.8 **			
TCLP	0.7 **	0.9 **		
Tot	0.7 *	0.7 *	0.9 **	
F(I)	-0.3	-0.2	0.0	0.0
	Zn			
	DIN-S4	EPTox	TCLP	Tot
EPTox	-0.2			
TCLP	-0.4	0.8 **		
Tot	-0.5	0.8 **	0.9 **	
F(I)	-0.1	-0.6 *	-0.2	-0.2

F(I): the exchangeable fraction of sequential extraction.
*: $p < 0.05$; **: $p < 0.01$

The DIN-S4 approach involves the leachability of metal by de-ionized water which suggest that only the most available metal cations can be released to the natural environment, regardless of the amount of other forms of metal held in the dust. One therefore does not expect any correlation with the other methods. However in the case of Pb a good correlation is found between the DIN-S4 approach and the results from other tests. The good correlation may due to the very small amount of Pb released when using any (DIN-S4, TCLP and EPTox) of the leaching tests. The general poor correlation between results from the leaching tests and the pseudo total metal concentration suggests that using the pseudo total metal concentration may not be a proper way to evaluate the bioavailability and mobility of metal in typical environmental conditions.

4.4.1.7 Comparison of measurements by using AAS and ICP

Figure 4.4 compares the measurements obtained using atomic absorption spectrometry (AAS) and ICP-AES in the measurement of Cd, Cu, Pb and Zn in the different fractions of sequential extraction. AAS is a technique used to measure the metal ions in solution of concentration normally greater than 1 ppm in a limited number of samples while ICP-AES is normally used to measure the metal cations at concentrations greater than 100 ppb and can applied to multi-element analysis with a large amount of samples. Copper does not show any significant differences between the two techniques. Significantly higher concentrations of Cd and Pb appeared in the exchangeable fraction using ICP, while higher concentration appeared in the Fe-Mn oxide fraction with AAS. Significant higher levels of Zn were found in the carbonate, organic and residual fraction when the measurements were performed using AAS. The differences between these two techniques may

be caused by the techniques themselves because of the different detection limits. Furthermore sequential extraction is unable to clearly separate different fractions and this may alter the distribution of the metals in the fractions. This result suggests that no significance should be attached to some of the sample differences obtained using the AAS described in Chapter 3.

4.4.1.8 Partition coefficient

In the present study, the term of partition coefficient was used as a simplified parameter to describe the ratio of metal retained in dust and metal dissolved in the solution under assumed equilibrium condition without considering the complicated thermodynamic processes involved in adsorption. Although the partition coefficient can be used to quantify the solid solution partitioning of a constituent in an adsorption experiment and is a useful parameter for comparing the sorptive capacities of different soil or solid materials for any particular ion at equilibrium (Alloway, 1992, Millward and Turner, 1994), the definition may not apply strictly in this study.

In this research, it is assumed that after the extraction time elapsed in each of the leaching methods, the solid-liquid solution reaches an equilibrium condition. In practice this may not be true in all cases, though it can be used to provide a simplified, operational description of the complicated conditions found in natural environment. Assuming that in the DIN-S4, TCLP, EPTox and Tessier's sequential extraction methods at the end of the leaching or partial leaching procedures the solid and liquid are under equilibrium or quasi-equilibrium conditions, a partition coefficient [k_{sw} equal to the metal in the solid (C_d) divided by the concentration of metal in the liquid (C_w)] can be calculated using the measured fraction of the metal released in the liquid, where C_d, C_w, k_{sw} have units of $\mu g\ g^{-1}$, $\mu g\ ml^{-1}$, $ml\ g^{-1}$,

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respectively. In this study, it is assumed the ratio of metal released from the different leaching methods to the concentration of metal released from the pseudo total digestion is approximately equal to the ratio of metal released from the solid to liquid form. This can be described by a simple mathematical equation as follows:

$$f = \frac{C_w}{C_w y + C_d y} = \frac{1}{1 + \dfrac{C_d}{C_w} y} = \frac{1}{1 + k_{sw} y}$$ (4.21)

where f is the fraction of metal released from the solid form to liquid form; C_w and C_d are the metal concentration in liquid ($\mu g\ ml^{-1}$) and in solid ($\mu g\ g^{-1}$) and y is the ratio of solid to liquid (g ml $^{-1}$) in each leaching method. The sum of ($C_w + C_d y$) is assumed to be the metal released by the pseudo total digestion. The partition coefficient can then be calculated as follows:

$$k_{sw} = \left(\frac{1}{f} - 1\right)\frac{1}{y}$$ (4.22)

The calculated partition coefficients for Cd, Cu, Pb and Zn are shown in Figure 4.11. If the value of k_{sw} is low, it shows a high potential for release of metal present to the liquid and depending on conditions it may show a high risk to the environment. In Figure 4.11, the k_{sw} values of Cd, Cu and Zn in EPTox and TCLP methods were similar to the k_{sw} values of first three fractions (exchangeable, carbonate and Mn-Fe oxides fractions) of the sequential extraction method, while the k_{sw} value of Pb in the EPTox and TCLP method was similar to the first two fractions of the sequential extraction.

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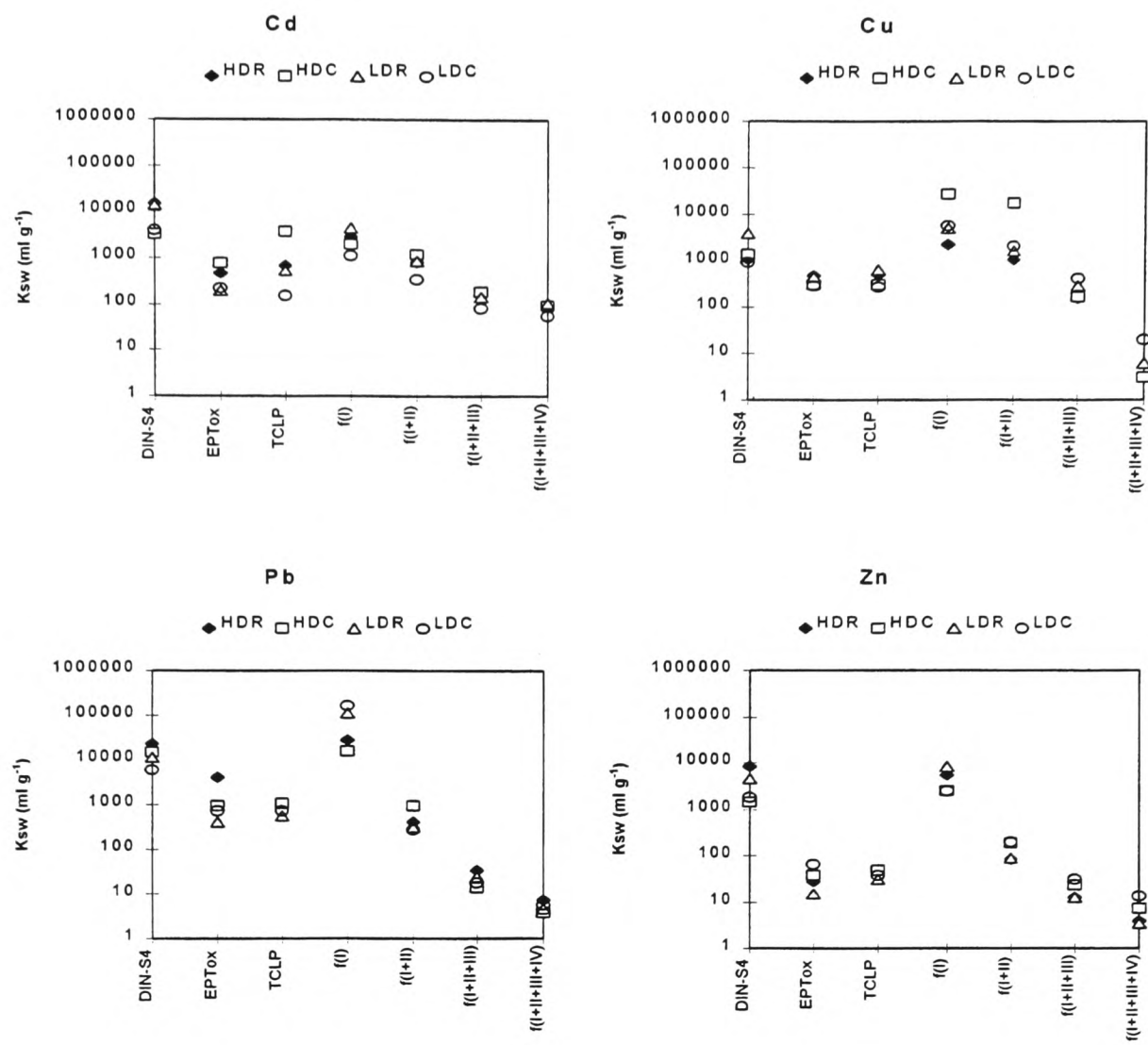
Figure 4.11 Partition coefficients of Cd, Cu, Pb and Zn according to different extraction methods and at different sites

Although the partition coefficient may not describe fully the release of a metal into solution it is a simple way of comparing the potential for leaching under different conditions. Although Figure 4.11 uses a logarithmic scale the partition coefficient appears to be an effective way of summarising data from a large number of experiments performed under different conditions.

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4.4.2 Acid titration: metal release as function of pH

4.4.2.1 Buffer capacity of dust samples

Soil and dust have the ability to withstand or buffer acid precipitation according to the type of bedrock, the kind of soil and its composition (Environmental Resource Limited, 1983). This is the buffer capacity, a mechanism for soil to resist changes in pH (Brady and Weil, 1996). The more easily weathered a bedrock, the faster the release of its buffering metallic cations, and the stronger its resistance to acidification. Most soils and dusts in rural areas have sufficient concentrations of weathered base cations as well as inorganic/organic phosphates, insoluble carbonates, bicarbonates, hydroxides and silicates to provide buffering capacity to negate the acidification effect of acid rain (Kennedy, 1992). However, in areas where the natural buffer effect is lacking, acid rain can more easily induce an increase in the acidity of the soil and dust solution and hence enhance the release of heavy metals.

Buffer capacity is an index used to indicate the degree of buffering. It can be determined by plotting a titration curve (pH versus acid/base input) which captures the tendency of the solution at any point in the titration curve to change pH upon the addition of acid/base (Stumm and Morgan, 1970). The buffer capacity at any point of the titration is the slope of the titration curve at that point when a strong base is added, or the negative slope of the tangential line when a strong acid is added. Mathematically, that may be defined as follows (Pankow, 1991):

$$\eta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \qquad (4.23)$$

where dC_B and dC_A are the increment of mole l^{-1} of η strong base and strong acid required to produce a change in dpH. η is called the buffer capacity or the buffer index, which is a measure of how well a solution is able to resist pH change when either strong acid or strong base is added.

In Figure 4.5 the highest buffer capacities can be found in the regions of pH between 6 to 7. Similar trends were found in the graph of dust titration curves presented by Serrano-Belles et al., (1997) and on the smectite titration curve by Yong et al., (1990). At the pH range between 6 and 7, the high buffer capacity can be explained by the slightly alkaline nature of the dust samples, which creates the buffering effect that prevent pH from dropping immediately and quickly as the concentration of acid input increases. There are several different buffer systems in natural soil system such as calcium carbonate-bicarbonate at pH buffer range between 8 to 6.2 and silicate-bicarbonate exchange at pH buffer range between 6.5 to 5 (Wellburn, 1988).

Figures 4.6a and 4.6b show that at pH > 6 the percentages of metal release from the dust samples are generally low (under 20%). This could be due to the buffering effect of dust samples which prevent pH from dropping below 6. If the amount of acid input is insufficient to overcome the buffering effect, the metals in dust remain bound to particles, especially Cu and Pb. Once the buffering effect reduces, pH will drop sharply and high amounts of metal are released from the dust. Hence, when the pH of solution is lower than 6 buffering may not be an important mechanism affecting metal release from dust.

4.4.2.2 Metal release from dust as function of pH

In urban runoff, the contamination is predominately associated with particles but the proportions of dissolved trace metals may increase when the

pH is lowered by, for instance, acid precipitation (Dempsey *et al.*, 1993). The pH value is likely to dominate the adsorption processes of heavy metal onto clay minerals. Heavy metals might therefore be released because the H^+ ions compete with heavy metal ions for the exchange sites in the system. In the case of the reaction B equation (4.2b) in Section 4.3.4.1 which is assumed to be in pseudo-equilibrium conditions, an equilibrium constant k can be expressed as:

$$k = \frac{[surf - O - H][Me^{2+}]}{[surf_2 - O - Me^+][H^+]}$$

or

$$k_{sw} = \frac{[surf_2 - O - Me^+]}{[Me^{2+}]} = \frac{1}{k}\frac{[surf - O - H]}{[H^+]} \tag{4.24}$$

where bracket denote concentration, surf denotes a surface site and Me^{2+} is a metal ion and k_{sw} is the partition coefficient using the definition in equation (4.1). Hence k_{sw} is proportional to $1/[H^+]$. Figures 4.7a and 4.7b show the partition coefficients k_{sw} are dependent on pH which is equal to log $(1/[H^+])$. More generally the form of the partition coefficient is more complex than the simple inverse dependence suggested by equation (4.24). For instance, a set of lumped equations for the adsorption of metal on solid and the formation of metal complexes in water may be considered as follows:

$$S - Me + H^+ \leftrightarrow S - H + Me^+ \qquad k_1 \tag{4.25a}$$

$$Me^+ + L^- \leftrightarrow MeL \qquad k_2 \tag{4.25b}$$

$$H^+ + L^- \leftrightarrow HL \qquad k_3 \tag{4.25c}$$

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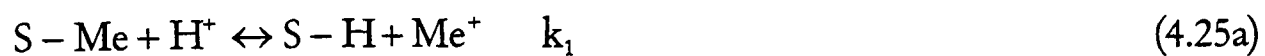
where k_1, k_2 and k_3 are equilibrium constants, S denotes a surface site, Me^+ is a metal ion and L is a ligand. The partition coefficient k_{sw} is then given by

$$k_{sw} = \frac{[S-Me]}{[Me]+[MeL]} = \frac{\frac{1}{k_1}[S-H]}{[H^+][1+k_2[L^-]]} = \frac{\frac{1}{k_1}[S-H]}{[H^+]\left\{1+k_2\frac{[HL]}{k_3[H^+]}\right\}}$$

$$= \frac{a}{[H^+]+b}$$

(4.26)

where a and b are functions of equilibrium constants for surface site and solution reaction. In general much more complex relationships are expected, but equation (4.26) still illustrates an inverse dependence on an increasing function of $[H^+]$. The empirically derived relationships represented graphically by Figures 4.7a and 4.7b are an approximate form of the $[H^+]$ dependence when the values of equilibrium constants and ligand concentrations are not known, as would be the case in most environmental assessments.

Cadmium Cd, Cu, Pb and Zn released from dust in the acidic solution are clearly dependent on pH; the extent of the metals released decreases by more than one half when the pH is increased from 4 to 6 (Figure 4.6a and 4.6b). In nearly neutral conditions (pH 6 to 7), Cd, Cu Pb and Zn are predominately retained in the dust by precipitation and adsorption reactions. Higher percentages of Cd and Zn are released than those of Pb and Cu at pH values between 4 to 6 (see Figure 4.6a and 4.6b). Similar Pb release patterns from urban dust were shown by Serrano-Belles, *et al.*, (1997).

For the roadside dust studied in this thesis the natural exposure to leaching conditions is likely to be associated with runoff and will therefore depend on the pH of precipitation. Strong acid cations (SO_4^{2-} and NO_3^-) along with H^+

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in acid rain will enhance the base-forming cations and mobilisation of metals in road dust (Brady and Weil, 1996). Metal desorption using diluted nitric acid could be used to simulate the metal release from urban dust during periods when rain is highly acidic such as pH 4. The buffering effects of dust only prevent the pH change at pH around 6 in the present study. According to the data of UK Acid Deposition Networks, the typical pH of rainfall in Britain in normally between 4 to 7. For instance in Compton, near the upper Thames, the pH of rainfall was measured as being between 3.7 to 7.0 in 1995 (Clark, 1996). In the present study (see Figures 4.6a and 4.6b) when the pH lay in the range between 4 to 7, Cu and Pb were mainly retained in dust particles, while Cd and Zn showed less affinity to the dust particles. Therefore, Cd and Zn in urban dust is expected to be more mobile than Cu and Pb. The results indicate that estimates of metal release from dust should take into account the pH of the water with which the dust comes into contact.

4.4.2.3 *Dust partition coefficients for Cd, Cu, Pb and Zn by acid titration*

Samples were assumed to have reached equilibrium after 7 days, since the American Society for Testing and Materials (ASTM, 1991) method 4319 specifies a minimum contact time of 3 days and a maximum of at least 14 days and therefore a partition coefficient k_{sw} may be used operationally to estimate mobility and/or bioavailability of metals for environmental risk assessments.

In general, Cd, Cu, Pb and Zn have higher k_{sw} value at pH value greater than 6 (see Figures 4.7a and 4.7b). Hence less Cd, Cu, Pb and Zn are desorbed from dust in the lower acidic solution (e.g. pH >6) than from the higher acidic solution (pH <6). Under the same pH condition at pH 4 to 6, Cd and Zn had a lower k_{sw} than Cu and Pb in the dust samples. A practical

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solution to assessing the availability of metal ions from an unknown constituent of particles, such as dust, would be to define a partition coefficient as function of pH or concentration of H^+, which can provide information on metal release in different acidic environmental conditions.

4.4.2.4 *The relationship between the acid titration and leaching methods*

The relationships of Cd, Cu, Pb and Zn released under acid titration and single leaching methods are presented in Figure 4.12a and 4.12b. The results from different single leaching methods are marked on each of the figures according to the pH of the solution under which the leaching test was conducted. Broadly the pH conditions of each leaching test is consistent with the acid titration data for Cd, Cu, Pb and Zn, although the different metals have different release patterns as a function of pH. Van der Slooter *et al.* (1996) found that the leachability of Cd from a wide range of coal ashes as function of pH showed a very systematic relationship between leaching and pH. This supports the use of pH as the key parameter to describe the amount of metal released to solution. The metal release as function of pH appears to explain wide range of release patterns.

4.4.3 *Time dependent metal release kinetics*

4.4.3.1 *Heavy Metal (Cd, Cu, Pb and Zn) release kinetics*

In general, the results of the kinetic experiments show reasonable support for two different types of reactions, one fast and irreversible and one slow and reversible first order reaction. Although Cd, Cu, Pb and Zn release kinetics generally followed the two reaction model, the model shows that the individual metals were released in different ways for the different dust samples.
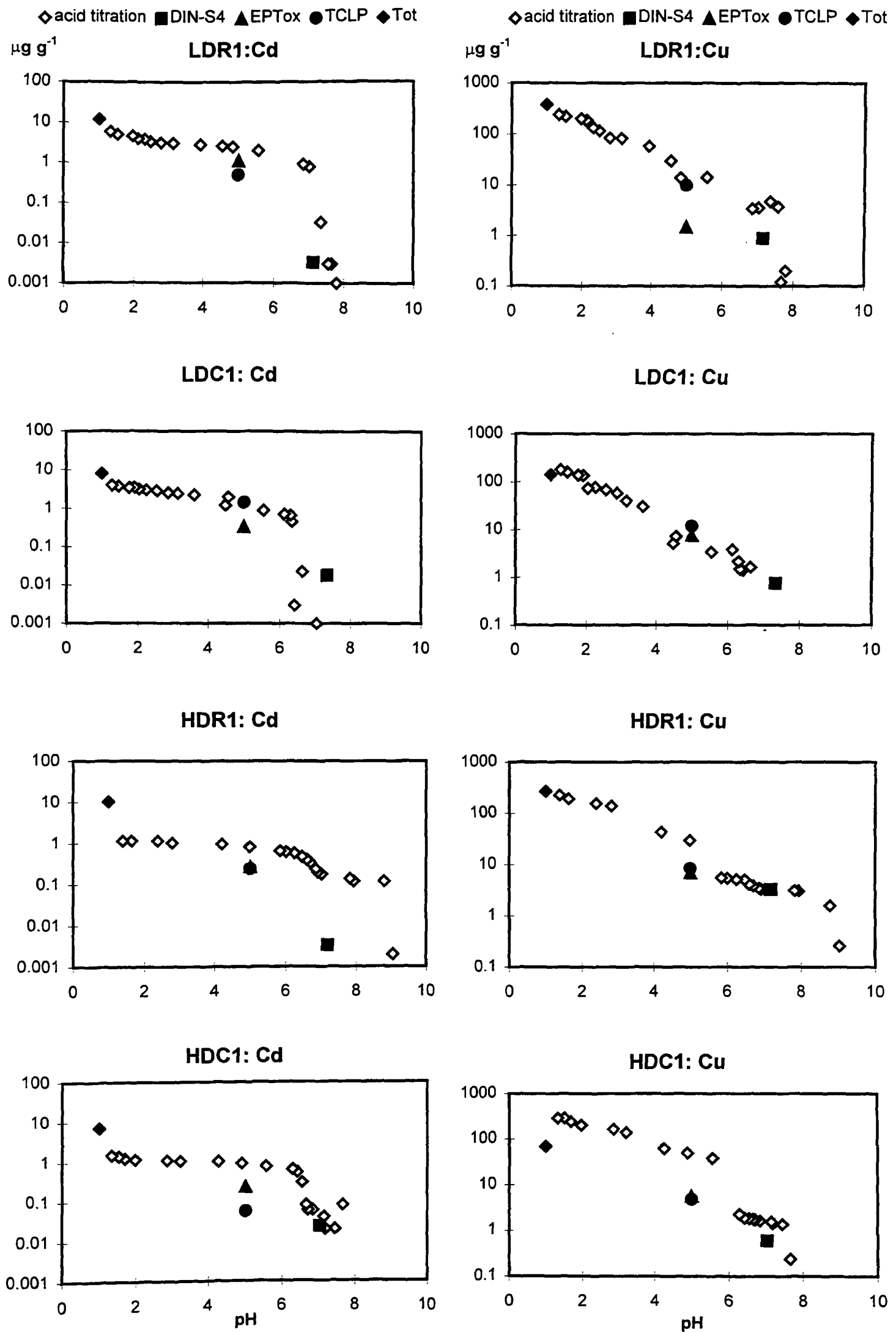
Figure 4.12a Cd and Cu release ($\mu g\ g^{-1}$) under different leaching methods.
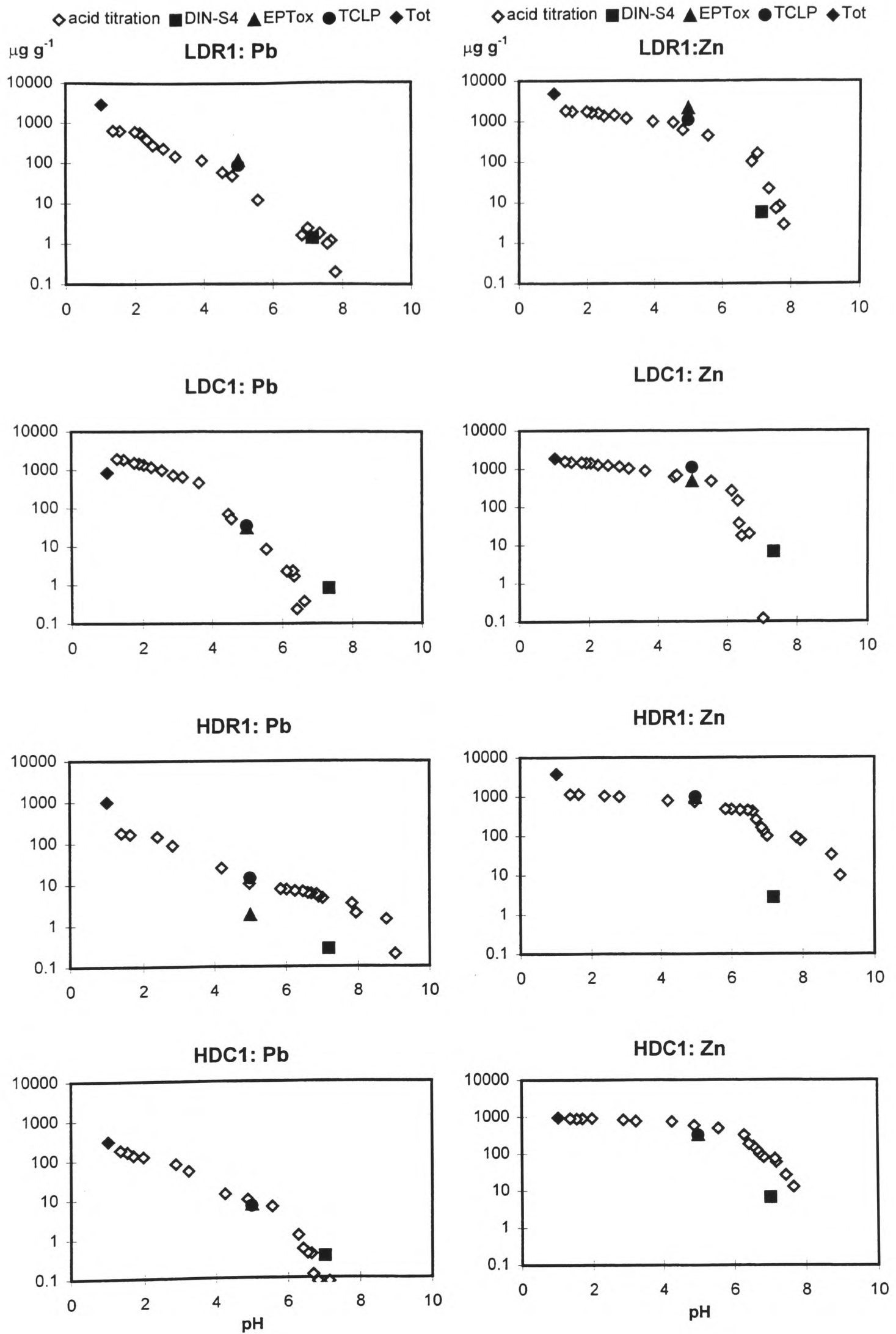
Figure 4.12b Pb and Zn release (μg g^{-1}) under different leaching methods.

The different metals have different metal binding patterns as shown by the sequential extraction (see Chapter 3), and these different binding characteristics may dominate the metal release mechanism of dust in the aquatic environment. The main factors governing the amount of Cd, Cu, Pb and Zn released in the present study are the time of extraction, the pH of the extraction solution and the composition of the dust itself.

All of the k_1 values are somewhat greater than the reaction rate of the forward reversible reaction, k_2 (Table 4.11, 4.12, 4.13 and 4.14). In general, the rates k_1 and k_2 decrease relative to a decrease of pH. This indicates a shorter half life of reaction at low pH which means that the reaction takes less time to reach completion. The values of k_2 are relatively small at pH 3 and 4 (see Table 4.11- 4.14) when compared with the value at pH 1 and 2. These represent a very slow reversible reaction B (see equation (4.2b)). This is probably an artificial feature of the curve fitting, but it could also be that the metal does not react at these pH values.

The trend in metal release rate at pH 1 is $Zn > Cu > Cd > Pb$; at pH 2 is $Zn > Cd > Pb \geq Cu$; at pH 3 is $Cd > Cu \geq Zn > Pb$ and at pH 4 is $Cd \geq Zn \geq Cu > Pb$.

The values of the reaction constant k_2 and k_3 of the slow forward and backward reactions are limited by the value of equilibrium constant of k_{sw}. The quasi-equilibrium constant k_{sw} (see equation (4.16)) can be treated as partition coefficient k_{sw} with pH dependence. A high value of k_{sw} indicates that metals prefer to bound to dust particles and relatively little metal dissolves in the contact solution.

A general relationship cannot be found between β, the fraction of metal subject to slow reversible reaction, and the experimentally determined metal

fraction of the dust, because of the complicated composition of the dust. If the fraction β is greater than 0.5 then the metal release mechanism is dominated by the slow reversible reaction. Hence, if a high k_{sw} and a large fraction of β appear in the reaction, the metal release will be dominated by the slow reaction. In the present study, the values of β are much greater than 0.5 for Cd, Cu, Pb and Zn release kinetics at pH 4, which shows that at pH 4 the Cd, Cu, Pb and Zn dissolution kinetics are dominated by the slow reaction. In particular at pH 4, the range of β is between 0.86 to 0.99 for Cu and Pb. When this fraction is related to sequential extraction, it is seen to lie in the exchangeable and part of the carbonate fraction (see Table 4.7). Thus for these metals the kinetic model may be a good presentation of the first and second stage of sequential extraction.

It may seen that the k_{sw} derived from the metal release kinetics experiments reported in Table 4.11 to Table 4.14 are in qualitative agreement with the partition coefficients obtained in the acid titration experiments reported in section 4.3.3.2. Both show the release fraction as a function of pH over the range 2 to 4. Although the correspondence is not exact both sets of data show that systematic differences arise according to the metal release considered.

4.4.4 Scanning Electron Microscopy

SEM-EDS is unable to detect the metal present at concentrations less than 1%, although it provides a very good tool to look at the morphology of single particle. Moreover, the complexity of mixtures and the heterogeneity of urban dust presents technical difficulties in the detection of particles which are too close to each other, or big aggregated particles, because these interfere with the detection of X-rays.

4.4.5 X-ray diffraction

X-ray diffraction has provided good results on the major mineral structure of the major element. However as in the case of the SEM, the technique of X-ray diffraction is used to examine mineral structure when the mineral present have concentrations greater than 2%. Hence for the analysis of trace metals such as Cd, Cu, Pb and Zn, it may not an appropriate technique to identify the possible mineral structure associated with these metals.

4.5 Summary

Cadmium, Cu, Pb and Zn showed consistent leaching patterns using the pseudo total digestion, EPTox and TCLP methods. The Cd, Cu, Pb and Zn release patterns were very similar when these metals extracted using the pseudo total digestion, the EPTox and TCLP methods, though the amount of metal released are very different between the pseudo total digestion and EPA leaching methods (EPTox and TCLP). In contrast, these heavy metals showed very different release patterns using the DIN-S4 approach which involves de-ionized water.

The results from the single leaching methods (DIN-S4, EPTox, TCLP and pseudo total digestion) are consistent with the acid titration data for Cd, Cu, Pb and Zn although the different metals have different release patterns as a function of pH. This further emphasized the importance of the pH in the metal leaching methods.

The average fractions of metal released from the DIN-S4, EPTox and TCLP approaches compared to the pseudo total digestion method may be related to the fraction released during the Tessier's sequential extraction approach. The fractions of metals released using the EPTox and TCLP methods are located between the exchangeable and carbonate fractions of the results of Tessier's

method while the fraction released in the DIN-S4 method correlated with a much lower fraction than the exchangeable fraction of Tessier's method.

Under laboratory conditions, the simple approaches based on a single constant partition coefficient describing the equilibrium between metal dissolved in different acidic solution and metal held on particles is a gross simplification in an assessment of the mobility of metals in the different solid-liquid conditions. The partition coefficients of Cd, Cu, Pb and Zn are seen to be affected by the pH of the contact solution. The results indicate that in a weak acidic solution at pH in the range of between 4 to 6, Cd and Zn were more mobile than Cu and Pb, and therefore are less likely to remain within dust particles. Defining the partition coefficients of metals as a function of $[H^+]$ or pH, the acidity of the contact solution, is seen to be a possible practical way of using partition coefficients in risk assessments.

The main factors which control Cd, Cu, Pb and Zn release from urban dust are the pH of the solution and the time of dust contact with the solution. Release kinetics are well described by a two reaction (fast irreversible and slow reversible reactions) model. The fractions of metal released correspond approximately to the exchange and carbonate fractions in the sequential extraction. The two reaction model provides useful information on predicting metal release rate at different pH as a function of time.

The results of the SEM and X-ray diffraction experiments confirm as expected that the dust samples contained particles of many different forms and composition.

In recent years, there have been a growing effort to harmonize leaching methods in order to establish standard methods yielding comparable results (e.g. Van der Sloot, 1997, Ure, 1996). It is also very useful to select or to

generalize the important parameters in leaching which can be used in the risk assessments for both analytical as well as in modelling.

Owing to the complicated chemical reaction of solid-liquid solution such as adsorption and desorption, dissolution and precipitation and complexation and decomplexation processes, neither total metal concentration nor any single extraction procedure can provide very detailed information to predict the mobility and bio-availability of metal in dust and soil profile. However some assumption regarding the metal distribution in solid and solution phases is necessary to assess the risk of heavy metals in dust and to provide reliable predictions for risk management. The following chapter makes use of the partition coefficient as an operational parameter dependent on pH to do a risk assessment based on a theoretical model.

Chapter Five

RISK ASSESSMENT OF CADMIUM, COPPER, LEAD AND ZINC
IN URBAN DUST USING A THEORETICAL MODEL

5.1 Introduction

The applications of mathematical modelling to environmental pollution have been used to gain a better understanding of the fate and transport of chemical pollutants, to determine chemical exposure concentration to the biota and to predict future conditions under various loading scenarios or better management options (Schnoor, 1996). Modelling a complex environmental problem is also an important decision making tool even when there is lack of good scientific data and the model can simply give an qualitatively overall picture of the causes, transmission routes and the possible effects (Whyte and Burton, 1980). Since international guidelines do not exist for the heavy metal content of street dust, a theoretical model was developed to assess whether Cd, Cu, Pb and Zn in road dust pose a risk during road surface storm runoff to the soil adjacent to a road. Elevated levels of Cd, Cu, Pb and Zn have been found in urban runoff (Ellis *et al.* 1987), but the transfer pathway is not straight forward as heavy metals (e.g. Cd, Cu, Pb and Zn) within urban street dust may become mobile when they come to contact with acidic water in runoff from streets. The natural soil layer and the runoff sludge has a potential for retaining pollution and becoming contaminated from the infiltration of road runoff (Mikkelsen *et al.*, 1995).

The aim of this chapter is to construct a theoretical model to calculate the dust accumulation under dry and wet weather conditions and to assess the parameters which influence metal release from dust during rain runoff to the

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soil adjacent to a road. From this, an assessment of the risk of the heavy metal release from urban street dust to the environment can be made. The starting point to the assessment is the acidity of the water with which the dust comes to contact. The acidity of precipitation is first reviewed, since earlier chapters have shown that the release of metal from dust is dependent on the pH of the water with which it comes to contact.

5.1.1 Acid rain

Rain with a pH of less than 5.6 has been considered acidic while a number of studies show evidence of unpolluted rainfall having a pH in the range of 4.5 to 7.4. Acid rain or precipitation is defined as the wet precipitation of airborne pollutants, largely oxides of sulphur and nitrogen (SO_2/SO_4 and NO_2/HNO_3) which have dissolved in cloud and rain droplets to form sulphuric and nitric acids (Environmental Resource Limited, 1983). Acid rain is naturally associated with the volcanic and thunderstorm activity (Kennedy, 1992) but the impact of acid in rain on the environment is almost entirely associated with modern industrialisation. Nitrogen oxides and sulphur-containing gases enter the atmosphere as a result of the combustion of petrol (e.g. motor vehicles), coal (e.g. power plants), and other fossil fuels (e.g. incinerators) as well as from the burning of forests and agriculture residues (Brady and Weil, 1996). The problem has been found in many regions of the world, for instance in Northern Europe, America and Asia.

Acid precipitation has long been reported to have potentially damaging effects on the terrestrial and aquatic environment (EUR 8684m, 1983), for instance:

- in forests (e.g., acute damage to pine and spruce in USA, Canada, Czech and Slovak Republics),

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- in crops and vegetables (e.g., acute damage to tobacco in southern USA and growth impairments on wheat, soya, peanuts, radishes and grapes in USA),

- in terrestrial flora and fauna (e.g., damage to and disappearance of lichen, cantharella, certain fungi and reduced diversity of flora close to urban community).

- in aquatic flora and fauna (e.g., change and/or loss in phyto- and zoo-plankton, benthic communities, cycling of nutrients, decomposition of organic matter and diversity of flora for example in Canada, parts of the USA, Scandinavia, Scotland and Eastern Europe).

- in fish populations (e.g., acid precipitation is a possible cause of the fish loss in lakes and rivers in southern Norway, south and central Sweden, Canada and USA).

Moreover, acid precipitation is thought to disrupt the normal pedological cycle of minerals in forest soils such as aluminium (Cronan and Schofield, 1979). Forster (1990) showed that urban metal roofs and gutter materials such as Zn, are good buffers for acid rain but elevated concentrations of metals and other pollutants are found in the runoff from these surfaces. Hence high acidity (low pH) of rain may accelerate the solubility of metals on the urban surface.

There are two processes which involve the mobilisation of metal from the urban street dust by rain. Firstly, rainfall provides the removal mechanism that washes off the dust from the street surface to the drainage system or to the environment adjacent to the road. Secondly, the acidity in the rain could be a crucial factor dominating the transport of Cd, Cu, Pb and Zn in urban dust to the dissolved phase during rain events.

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As shown in Chapters 3 and 4, the mobilisation of metals in dust can be dependent on its properties. Hence it is appropriate to consider which are the most important parameters in the release of Cd, Cu, Pb and Zn from the dust during rain runoff as this may directly affect the neighbourhood environment such as soil next to the road.

5.1.2 Rain composition in Compton, (UK Acid Deposition Network site nearest to London) in 1995 and Hong Kong in 1996

The acidity of the extractant solution with which dust could come into contact has been found to an important factor governing the release of Cd, Cu, Pb and Zn from street dust according to the chemical leaching methods and kinetic studies (see Chapter 4). It is therefore important to review the typical acidity and composition of rain in Hong Kong and in London.

Hong Kong and London are both densely populated urban cities. They are located in subtropical and temperate zones, respectively. The two cities are subject to very different rainfall patterns. London has a high frequency of rainfall which is generally of low intensity; Hong Kong, on the other hand, in the rainy season has very high frequency and intensity of rainfall.

In 1995, there were 27 sites across the UK that gathered rainfall composition data under the UK Acid Deposition Network (National Air Quality Information Archive, the Department of the Environment, Clark, 1996). Compton was the only site located in the Thames region (grid reference 4512, 1804) and the closest one to the dust sampling sites in London. The Compton site was operated and monitored by AEA Technology plc and the data was collected on a weekly basis. The measurements of rainfall composition included rainfall pH, SO_4^{2-} (sulphate), NO_3^- (nitrate), NH_4^+ (ammonium), Na^+ (sodium), Mg^{2+} (magnesium), Ca^{2+} (calcium), Cl^- (chloride), K^+ (potassium), $nssSO_4^{2-}$ (non sea salt sulphate), conductivity, H^+

and the amount of the rain. According to rainfall composition data from the UK Acid Deposition Network, the pH and the amount of rainfall for any sampling site reveal large weekly variations (see Figure 5.1(a)) but less variation in annual averages (see Figure 5.1(b)). At Compton, according to weekly data for 1995, the lowest rainfall pH was found in May (pH$\approx$ 3.7) and the highest rainfall pH (pH$\approx$ 7.0) was found between the middle of March and the middle of April. In addition, the amount of rainfall did not specifically influence the rainfall pH (Figure 5.1(a)). The total of annual rainfall at Compton in 1995 was 579mm and the monthly rainfall distribution is shown in Figure 5.1(c) (Clark, 1996).

The monthly rainfall distribution in Hong Kong during 1996 is presented in Figure 5.1(d) with the total annual rainfall being 2249 mm (Hong Kong Observatory, 1997). Approximately four times as much rain fell in Hong Kong, 1996 than in Compton, 1995. None of the officially published data of routinely monitored rainfall pH is available during the sampling period in Hong Kong. In Hong Kong the rainfall is concentrated between March to September; on the other hand, at Compton the highest intensity of rain occurs in winter (January, February, November and in September. Correlation between rainfall constituents at Compton are shown in Table 5.1. The amount of rainfall has a significant negative correlation with the other rain components (SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, K^+, $nssSO_4^{2-}$, conductivity and H^+). A significant correlation was found between SO_4^{2-} and NO_3^- ($r = 0.7$ $p < 0.05$).

(a) Compton: weekly rainfall and rainfall pH data

(b) Compton: yearly rainfall and rainfall data

(C) Compton: monthly rainfall data

(d) Hong Kong: monthly rainfall data
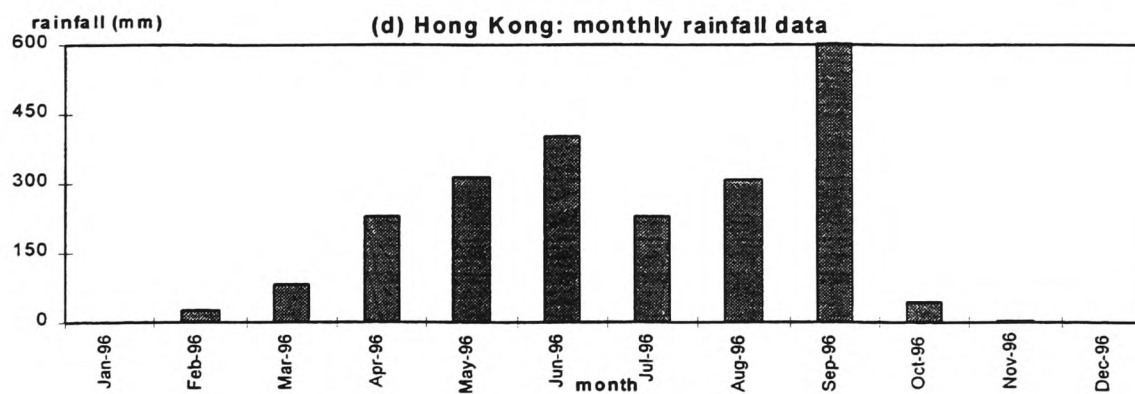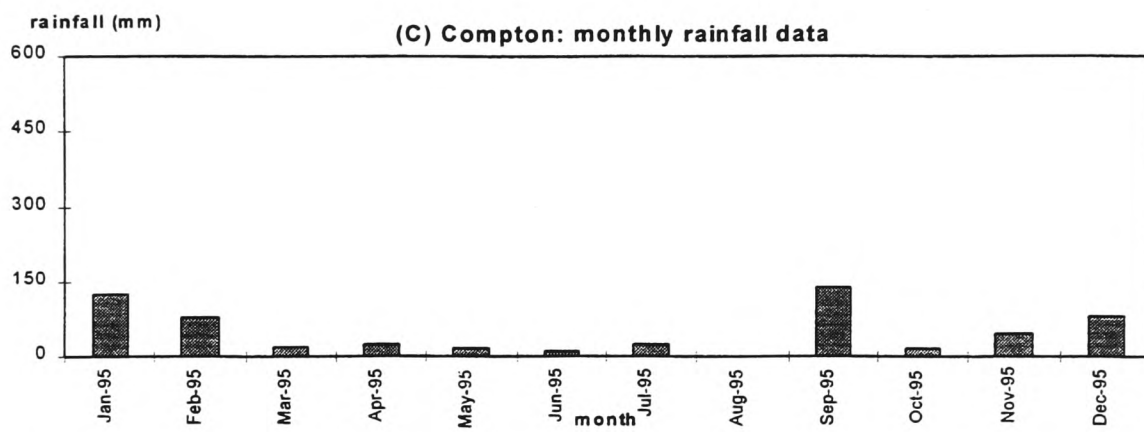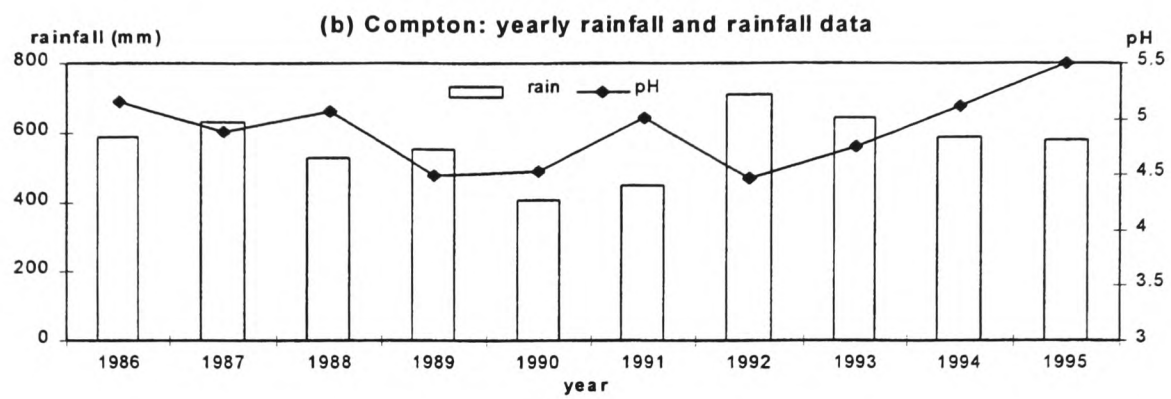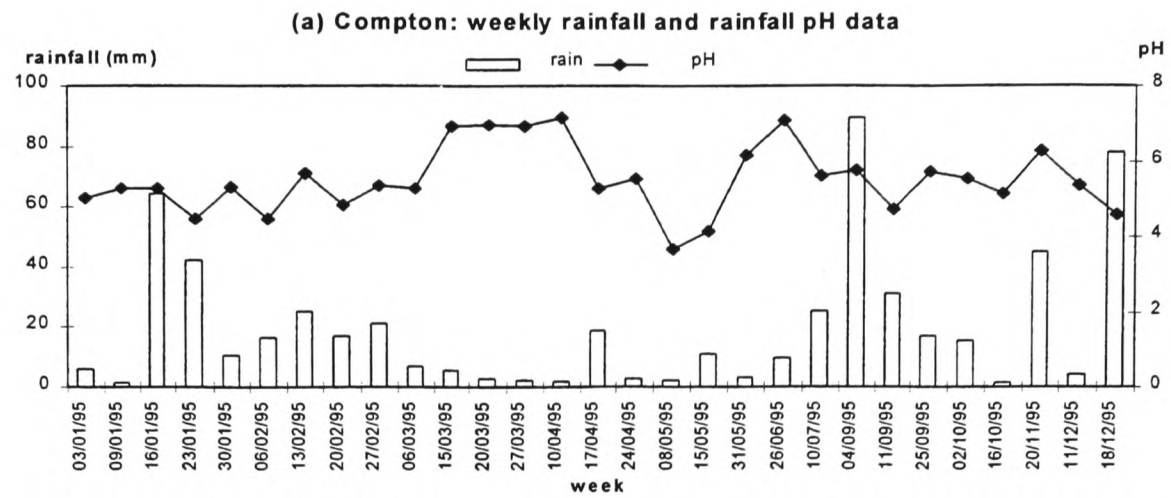
Figure 5.1 (a), (b) and (c) Weekly (1995), yearly (1986-1995) and monthly (1995) rainfall and rainfall pH at Compton (Clark, 1996), (d) Hong Kong monthly rainfall in 1996 (Hong Kong Observatory, 1997).

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Table 5.1 Correlation between rainfall compositions at Compton, Thames region (Clark, 1996)

	pH	SO$_4$	NO$_3$	NH$_4$	Na$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	K$^+$	nssSO$_4$	cond	H$^+$
SO$_4$	0.1 ***											
NO$_3$	-0.3 ****	0.7 *										
NH$_4$	0.1 ****	0.9	0.8 *									
Na$^+$	0.1 ****	0.5	0.4	0.6								
Mg^{2+}	0.2 ****	0.4 ****	0.3 *	0.4 ***	1.0 ***							
Ca^{2+}	0.4 **	0.6	0.5	0.5	0.3	0.2 *						
Cl	0.0 ****	0.6	0.4 **	0.6	0.9	0.9 ***	0.4					
K$^+$	0.2	0.6 ***	0.3 **	0.5 ***	0.5 ***	0.4 ****	0.7 **	0.7 ***				
nssSO$_4$	0.1 ****	1.0	0.7	0.9	0.5	0.3 ***	0.6	0.5	0.6 ***			
cond	0.0 ****	0.9 **	0.9	0.9 **	0.7 **	0.6 *	0.7	0.8 ***	0.7 ***	0.9 **		
H$^+$	-0.6	0.3 ****	0.8 **	0.4 ****	0.1 ***	0.0	0.1 **	0.1 ***	-0.1	0.3 ***	0.5 **	
rain	-0.1 **	-0.5 ****	-0.4 ***	-0.6 ****	-0.4 ***	-0.3 *	-0.3 **	-0.4 ****	-0.4 *	-0.5 ****	-0.5 ***	-0.1

SO$_4$ - sulphate; NO$_3$ - nitrate; NH$_4$ - ammonium; Na$^+$ - sodium; Mg^{2+} - magnesium; Ca^{2+} - calcium;

K$^+$ - potassium; nssSO$_4$ - non sea salt sulphate; cond - conductivity; rain - rainfall

Signigicant difference at *: $p < 0.05$, **: $p < 0.01$ and ***: $p < 0.001$, according to Student's t test.

In winter, although most anthropogenic emissions (e.g. SO_2) and the atmospheric stability (e.g. limited dispersion and thermal inversion) are at maximum, the pH of rainfall in London according to the Compton results does not appear to be much lower than in other seasons (Figure 5.1). This may be explained by the relative abundance of rainfall in this season which may attenuate the effect of the acidity in the rain. A seasonal survey of pH of rainfall at Padova, northern Italy found that the highest acidity occurred in autumn and none of acid impact was found in winter (Camuffo and Bernardi, 1988) while in area of Valley, Italy, the low at pH rainfall was found in winter (Morselli et. al., 1988). The amount of rainfall will thus also be an important factor determining the pH of rainfall.

Camuffo (1984) concluded that more attention should be paid to the very beginning of rainfall, which is more acidic and that a short drizzle appears to be much more dangerous, as it is both acidic in itself and it activates the dry deposition which has occurred previously.

The Review Group on Acid Rain (1997) has reported on wet deposition in urban areas, primarily on results from the Greater Manchester Acid Deposition Survey. Whilst the mean urban network values are similar to those predicted from national network data, some effects from the urban environment are apparent. Lowest hydrogen concentrations were typically found in the city centre and are though to be result of neutralisation by calcium compounds related to calcium sources in the city.

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5.2 Theoretical Model for the Risk Assessment of Road Dust

There is no simple assessment method for dealing with diffuse sources such as heavy metal in urban dust. A risk model for the concentration of heavy metals in dust is used to consider direct pathways, although it requires the use of six to eight parameters to describe processes which affect the complex behaviour of metals in the urban street environment.

5.2.1 Dust load during dry weather and wet weather

Clearly the potential risk of contamination of the soil next to the road depends on the amount of metal in dust and the amount of dust present. The accumulated dust on the road should be an important consideration, because it determines how much metal can be washed off or dissolved in storm-water. However, the experiments were performed in laboratory conditions which do not directly relate to all the factors which may influence metal release in the real world. Some of the other factors which affect metal exposure are discussed in this section. Measurements of the amount of accumulated dust on the road surface were not carried out in this study because the amount of dust accumulated is likely to be a very variable quantity which depends on meteorological factors (such as the time since the last rainfall, wind speed), passing traffic and the local environment. In this study, the accumulation of urban street dust was assessed using a theoretical model according to the probabilities of dry and wet weather conditions.

One expects the dust loading to vary during dry and wet weather as shown in Figure 5.2. During a dry period the quantity of dust will increase, tending to reach a limit representing a balance between the deposition and the removal of dust mainly caused by the re-suspension of dust by road transport vehicles, illustrated qualitatively in Figure 5.2.

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During a wet period the dust loading will be rapidly depleted (see Figure 5.2). As a result of these variations, measurements of dust loading are likely to be strongly associated with the time since the previous rain. The metal loading on the street is given by the product of metal content in dust and the dust loading. However no environmental quality standards in terms of the maximum permissible metal loading of paved surfaces, such as streets, has been set by regulatory authorities. Possibly the closest relevant environmental standard relates to maximum permissible metal contents in soils.

dry period   wet and dry periods
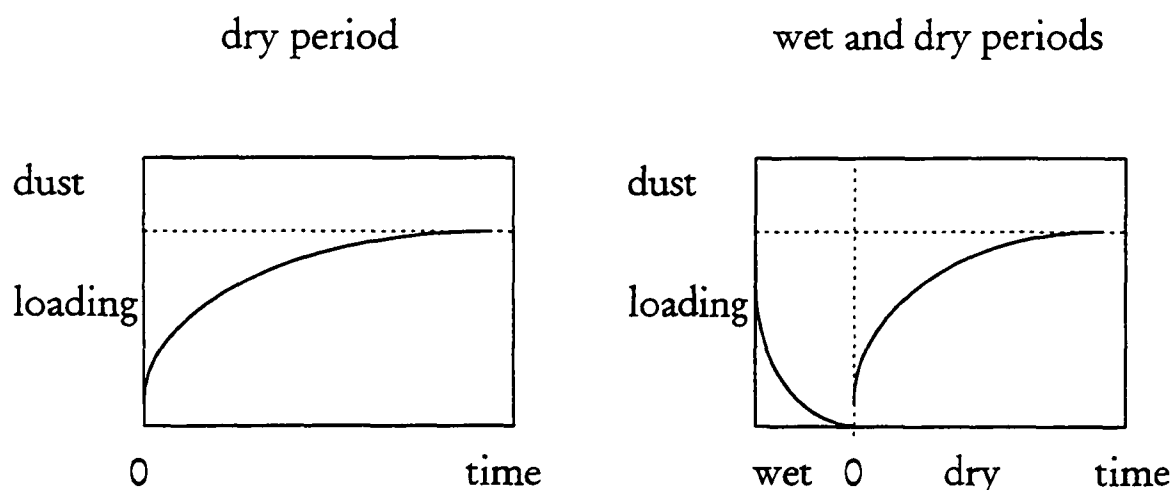
Figure 5.2 The conceptual model of dust loading during dry and wet weather.

Contamination of soils can occur by the direct impact from polluting sources. In the context of this study there are two pathways by which road dust can influence soils as follows:

1. direct deposition of dust onto soil from the atmosphere in the same way as dust is deposited onto the road,

2. surface runoff of rainwater from a road.

One issue raised is whether the two routes for contamination (1) direct deposition or (2) surface runoff could lead to exceedences of the soil metal concentration criteria.

Although most water in urban areas, such as London is designed to runoff to the gutter and then to a combined sewage and drainage system to sewage works for treatment, in exceptional conditions such as during heavy rain or where there is no drainage system, runoff could drain to land. In more rural areas runoff may drain to soakaways but this is not discussed further in this thesis.

In soils that are not exposed to other polluting sources or natural geological enrichment of heavy metals in the region one expects the concentrations of heavy metals to be lower than in dust because of the presence of organic material mixed in the soil.

In the next section a model is constructed which allows us to estimate dust accumulation given the chemical composition. From this the metal content of the soil neighbouring a road which has an inefficient drainage system can be estimated.

5.2.2 Theoretical model for dust accumulation in dry and wet weather

A simple model of the dust accumulation can be constructed taking into account the stochastic behaviour of rainfall (Hall and Hamilton, 1991). In dry conditions material is assumed to deposit at a constant rate D ($g\ m^{-2}\ s^{-1}$). In addition dust is removed by vehicle induced re-suspension according to $- k_d P$, where P ($g\ m^{-2}$) is the accumulated dust on the road surface and k_d is the removal rate (s^{-1}) in dry conditions which is proportional to the flow of traffic.

In dry conditions P satisfies

$$\frac{dP}{dt} = D - k_d P \qquad (5.1)$$

If P = 0 at time t = 0, this has the solution:

$$P = \frac{D}{k_d}\left(1 - \exp(-k_d t)\right) \qquad (5.2)$$

representing the build up of dust to its maximum value D/k_d over a time scale of order $1/k_d$, where k_d describes the removal of dust by resuspension generally thought to be associated with the moving traffic.

In wet conditions P satisfies

$$\frac{dP}{dt} = -k_w P \qquad (5.3)$$

where k_w is the removal rate in wet conditions, $k_w >> k_d$ so that P is rapidly reduced during wet periods.

If it assumes that wet and dry periods occur at random, p_d can be define to be the probability that it is dry at any instant and $p_w = 1 - p_d$ to be the probability that it is wet. Let $P_d(t)$ be the mean accumulated dust after time t assuming that this lies in a dry period. Similarly $P_w(t)$ is the mean accumulated dust after time t assuming that this lies in a wet period. Then the mean accumulated dust at time t+dt in a dry period is given by

$$P_d(t + dt) = P_d(t) + Ddt - \left(k_d + \frac{1}{t_d}\right)dtP_d(t) + \frac{dt}{t_w}P_w(t) \qquad (5.4)$$

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where t_d and t_w are the mean duration of dry and wet periods, respectively and

$$P_w(t + dt) = P_w(t) - \left(k_w + \frac{1}{t_w}\right)dt P_w(t) + \frac{dt}{t_d}P_d(t) \tag{5.5}$$

is the mean accumulated dust at time $t+dt$ in a wet period.

Thus,

$$\frac{dP_d}{dt} = D - \left(k_d + \frac{1}{t_d}\right)P_d + \frac{1}{t_w}P_w \tag{5.6}$$

$$\frac{dP_w}{dt} = 0 - \left(k_w + \frac{1}{t_w}\right)P_w + \frac{1}{t_d}P_d \tag{5.7}$$

or

$$\left(\frac{d}{dt} + k_d + \frac{1}{t_d}\right)P_d - \frac{1}{t_w}P_w = D \tag{5.8}$$

$$-\frac{1}{t_d}P_d + \left(\frac{d}{dt} + k_w + \frac{1}{t_w}\right)P_w = 0 \tag{5.9}$$

These equations can be solved using Laplace transforms in the following way. Taking Laplace transforms

$$\overline{P_d} = \int_0^\infty \exp(-pt)P_d \, dt$$

$$\overline{P_w} = \int_0^\infty \exp(-pt)P_w \, dt$$

Then equation (5.8) and (5.9) can be written as

$$\begin{pmatrix} p + k_d + \dfrac{1}{t_d} & -\dfrac{1}{t_w} \\[2mm] -\dfrac{1}{t_d} & p + k_w + \dfrac{1}{t_w} \end{pmatrix} \begin{pmatrix} \overline{P_d} \\[1mm] \overline{P_w} \end{pmatrix} = \begin{pmatrix} D \\ P \\ 0 \end{pmatrix} \qquad (5.10)$$

or

$$\begin{pmatrix} \overline{P_d} \\[1mm] \overline{P_w} \end{pmatrix} = \begin{pmatrix} p + k_w + \dfrac{1}{t_w} & \dfrac{1}{t_w} \\[2mm] \dfrac{1}{t_d} & p + k_d + \dfrac{1}{t_d} \end{pmatrix} \begin{pmatrix} D \\ p \\ 0 \end{pmatrix} \dfrac{1}{(p - p_1)(p - p_2)} \qquad (5.11)$$

where p_1 and p_2 are the roots of

$$p^2 + p\left(k_d + k_w + \frac{1}{t_d} + \frac{1}{t_w} \right) + \left(k_d + \frac{1}{t_d} \right)\left(k_w + \frac{1}{t_w} \right) - \frac{1}{t_d t_w} = 0 \qquad (5.12)$$

$$p_{1,2} = -\frac{1}{2}\left(k_d + k_w + \frac{1}{t_d} + \frac{1}{t_w} \right)$$
$$\pm \frac{1}{2}\sqrt{\left(kd + kw + \frac{1}{td} + \frac{1}{tw} \right)^2 - 4\left(\left(k_d + \frac{1}{t_d} \right)\left(k_w + \frac{1}{t_w} \right) - \frac{1}{t_d t_w} \right)} \qquad (5.13)$$

Equation (5.11) can be written as

$$\begin{pmatrix} \overline{P_d} \\[1mm] \overline{P_w} \end{pmatrix} = \begin{pmatrix} D(p + k_w + \dfrac{1}{t_w}) \\[2mm] \dfrac{D}{t_d} \end{pmatrix} \dfrac{1}{p(p - p_1)(p - p_2)} \qquad (5.14)$$

Expressing this equation in terms of partial fraction one obtains an expression for the mean dust loading during wet periods:

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$$\overline{P_w} = \frac{D}{t_d} \frac{1}{(p_1 - p_2)} \left(\frac{1}{(p - p_1)p_1} - \frac{1}{(p - p_2)p_2} \right) + \frac{D}{t_d} \frac{1}{p_1 p_2 p} \qquad (5.15)$$

Inverting the Laplace transform

$$P_w(t) = \frac{D}{t_d} \left[\frac{\left(\frac{1}{p_1} \exp\!\left(p_1 t \right) - \frac{1}{p_2} \exp\!\left(p_2 t \right) \right)}{\left(p_1 - p_2 \right)} + \frac{1}{p_1 p_2} \right] \qquad (5.16)$$

Equation (5.16) gives the mean accumulated dust $P_w(t)$ after time t, assuming that this lies in a wet period. The mean dust loading during dry periods is obtained by expressing the Laplace transform in terms of partial fraction and inverting

$$\overline{P_d} = D(k_w + \frac{1}{t_w}) \frac{1}{p(p - p_1)(p - p_2)} + \frac{D}{(p - p_1)(p - p_2)} \qquad (5.17)$$

Since

$$\frac{1}{p(p - p_1)(p - p_2)} = \frac{1}{p_1 p_2 p} + \frac{1}{p_1 (p_1 - p_2)(p - p_1)} + \frac{1}{p_2 (p_2 - p_1)(p - p_2)} \qquad (5.18)$$

Inverting the Laplace transform one obtains

$$P_d(t) = D \left(k_w + \frac{1}{t_w} \right) \left(\frac{1}{p_1 p_2} + \frac{\frac{1}{p_1} \exp(p_1 t) - \frac{1}{p_2} \exp(p_2 t)}{\left(p_1 - p_2 \right)} \right)$$
$$+ D \left(\frac{\exp(p_1 t) - \exp(p_2 t)}{p_1 - p_2} \right) \qquad (5.19)$$

Equation (5.19) gives the mean accumulated dust $P_d(t)$ after time t, assuming that this lies in a dry period. The value t is the time since the process of dust accumulation and removal began (see Figure 5.2). One is not really interested in the time dependence near the start of dust accumulation. Of more interest is the average dust loading after many periods of intermittent rain and dry weather. The roots p_1 and p_2 are negative, so that the asymptotic limits of these expressions can be considered. As t $\rightarrow\infty$, that is long after the start of the accumulation process, the mean dust loading in a wet period (equation (5.16)) becomes:

$$P_w \rightarrow \frac{D}{t_d p_1 p_2} \tag{5.20}$$

and the mean dust loading in a dry period (equation (5.19)) becomes:

$$P_d \rightarrow \left(k_w + \frac{1}{t_w}\right)\frac{D}{p_1 p_2} \tag{5.21}$$

where

$$p_1 p_2 = \left(k_d + \frac{1}{t_d}\right)\left(k_w + \frac{1}{t_w}\right) - \frac{1}{t_d t_w} \tag{5.22}$$

The surface runoff $k_w P_w$, which equals the runoff per unit area of paved surface during wet periods, is given by substituting for P_w given by equation (5.20). The surface runoff is thus as follows:

$$k_w P_w = \frac{k_w D}{\left(k_d t_d + 1\right)\left(k_w + \frac{1}{t_w}\right) - \frac{1}{t_w}} = \frac{D}{1 + k_d t_d\left(1 + \frac{1}{k_w t_w}\right)} \tag{5.23}$$

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Equation (5.23) represents an equilibrium between the deposition of dust onto the road and runoff of dust from the road. From equation (5.23) it may be seen that, on average, part of the dust deposition on the road surface is removed by runoff either to the drainage system or onto the surrounding soil. The rest of the deposition is re-suspended from the road by the movement of traffic and dispersed in the urban atmosphere.

The average deposition of dust particles to an unit area of the road surface, taken to equal D, is the sum of particles associated with vehicle emissions and the deposition of particles from the atmosphere. From equation (5.23) the runoff fraction (F_r) is seen to be

$$F_r = \frac{1}{1 + k_d t_d \left(1 + \dfrac{1}{k_w t_w}\right)} \qquad (5.24)$$

The fraction of dust F_s re-suspended is

$$F_s = \frac{k_d t_d \left(1 + \dfrac{1}{k_w t_w}\right)}{1 + k_d t_d \left(1 + \dfrac{1}{k_w t_w}\right)} \qquad (5.25)$$

and $F_r + F_s = 1$. It is apparent that the runoff fraction and the re-suspended dust fraction depends on the following parameters, the mean duration of wet and dry periods (t_w and t_d) and the rate of removal in dry and wet weather (k_w and k_d) although the values of these are not known to any great accuracy. If the rate of removal in dry weather was zero ($k_d = 0$) then the runoff and deposition would be equal as expected and all particles deposited on the road would eventually be washed off. If the rate of removal in dry weather was zero ($k_d = 0$), this would represent the situation when there is no road sweeping or no moving cars.

If the rate of removal in rain was very fast, then k_w would be very large and the surface runoff given by equation (5.23) becomes:

$$k_w P_w \rightarrow \frac{D}{\left(1 + k_d t_d\right)} \qquad (5.26)$$

The rate of removal by re-suspension then just depends on the rate of removal in dry weather k_d and the mean duration of dry weather t_d.

Although the parameters in this model of runoff and re-suspension of dust are not known with any accuracy, the model does provide a conceptual framework to analyse the mechanisms by which soil adjacent to roads may become contaminated.

5.2.3 Theoretical model of metal content of soil adjacent to a road

The starting point is an approximate estimate of the amount of Cd, Cu, Pb and Zn emitted from road transport as airborne dust. Salway *et al.* (1996) have made an estimate of the emissions of Cd, Cu, Pb and Zn associated with road transport in the UK. Their estimates suggest that 0.4, 0.6, 1295 and 242 tonnes of Cd, Cu, Pb and Zn, respectively, are emitted from road transport in the UK each year though it is not known whether these figures accurately reflect particles re-suspended from road surfaces. Clearly, in recent years the figure for Pb will have decreased substantially because of the phase-out of petrol lead and the control of lead-bearing paint for interior use. Taking the total distance travelled by motor vehicles in the UK to be 440×10^9 vehicle kilometres per year (Department of Transport, 1997) an estimate of the vehicle source strengths for Cd, Cu, Pb and Zn in μg km^{-1} can be made. The emission factors (E) are shown in Table 5.2.

Table 5.2 Estimate of the emission factors (μg km^{-1}vehicle^{-1}) of Cd, Cu, Pb and Zn from road transport (data calculated from Salway *et al.*, 1996).

Heavy Metal	E (μg km^{-1}vehicle^{-1})
Cd	0.9
Cu	1.4
Pb	2930
Zn	548

Thus for a road carrying a traffic flow of 20,000 vehicles per day, which corresponds to the London roadside site where dust samples were collected, the annual emission figures for Cd, Cu, Pb and Zn are 6.6, 9.9, 21388 and 3997 g km^{-1} per year.

An alternative estimate of road dust emission factors can be made from measurements of runoff composition undertaken by Colwill *et al.*, (1984, 1985). These authors found that for a motorway carriageway carrying about 32,500 vehicles per day the amount of Zn in runoff was about 10 kg km^{-1} year^{-1}. The amount of Pb in runoff measured by Colwill *et al.* (1984, 1985) was found to be 5 kg km^{-1} year^{-1} but it is now likely to be considerably less due to the widespread use of unleaded petrol. These values are equivalent to an emission factor for Zn of 843 μg km^{-1} vehicle^{-1} and an emission factor for Pb of 422 μg km^{-1} vehicle^{-1}. These values are comparable to the earlier estimates accepting that both are based on rather crude assumptions.

Colwill *et al.*, (1984) also give a value for the total solids in runoff, in the absence of road salting of 2400 kg km^{-1} year^{-1} which is equivalent to 0.2 g km^{-1} vehicle^{-1}. The proportions of Cd, Cu, Pb and Zn found in urban road dust from London (see Table 4.5) are 9$\pm$2, 207$\pm$105, 1422$\pm$780, 2708$\pm$1178 μg g^{-1}, respectively. These values correspond to the emission factors shown in Table 5.3.

Table 5.3 Estimate of the emission factors (μg km^{-1}vehicle^{-1}) of Cd, Cu, Pb and Zn in runoff (data calculated from Colwill *et al.*, 1984 and the empirical chemical data in Chapter 4).

Heavy Metal	E (μg km^{-1}vehicle^{-1})
Cd	1.8± 0.4
Cu	41.4± 21.0
Pb	284.4± 156.0
Zn	441.6± 235.6

These emission factors are substantially different from some of those estimated earlier in Table 5.2 which reflects the different assumptions made. In the later risk assessment upper bounds on these estimates will be used in order to incorporate a margin of safety.

Colwill *et al.*, (1984) note that for a drainage system such as a sedimentation tank about 50% of the solids are removed, while about 80% of the solids are removed from drainage passing through a lagoon.

In the following section an estimate of the contamination of soil next to roads is made using upper bounds of the emission factors in Table 5.3 and estimates of the fraction of particles associated with runoff and resuspension.

5.2.3.1 Assessment of metal concentration in soil arising from road surface runoff

As this is an assessment of risk a worst case scenario assumption is made that runoff water does not flow into a drainage system but flows directly onto the land next to the road.

$$v_g\, C_{urban} \Bigg\downarrow \qquad \Bigg\downarrow EN/W$$

```
 ┌─────────────┐
 │  road       │
 └─────────────┘
 ◄────W────►
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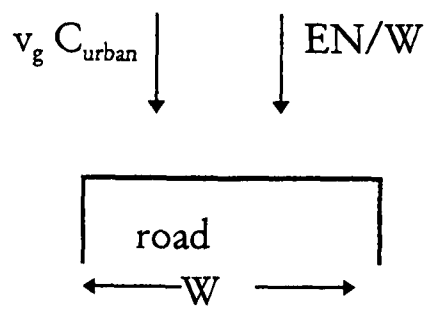
Figure 5.3 The conceptual model of the deposition rate of particles from the vehicles and the urban atmosphere on to a road.

The deposition rate of particles onto the road ($g\ m^{-2}s^{-1}$) is taken to be the sum of particles emitted per vehicle on the road and the deposition rate of particles from the rest of the urban atmosphere (see Figure 5.3) and the deposition rate is given as follows:

$$D = \frac{E \cdot N}{W} + v_g C_{urban} \qquad (5.27)$$

where

E is the emission factor ($\mu g\ m^{-1} vehicle^{-1}$),

N is the number of vehicles per second,

W is the width (m) of the road;

v_g is the deposition velocity ($m\ s^{-1}$) of urban dust particle and

C_{urban} is the concentration ($\mu g\ m^{-3}$) of dust particles in the urban atmosphere (see Figure 5.3).

As a first approximation the second term in equation (5.27), $v_g C_{urban}$, is neglected as it is assumed that the contribution from vehicles on the road is the dominant factor.

Figure 5.4 shows the assumed processes affecting the metal concentration in the soil next to roads. If the runoff is spread evenly over a width L (m) of land at the side of the road, the contamination entering the soil by runoff (R_r) is given by

$$R_r = \frac{E \cdot N}{L} \cdot F_r \qquad (5.28)$$

where F_r given by equation (5.24) is the runoff fraction, and it is assumed that R_r is zero for distances from the road greater than L.

Typical values of t_d, t_w, k_d and k_w for London are 100 h, 10 h, 1/200 h^{-1} and 1 h^{-1}, respectively, so that F_r is equal to 20/31. Assuming a typical two lane urban road carrying 20,000 vehicles per day such as the study site LDR, and the runoff is spread evenly over 15 m of land (L=15), then R_r can be calculated using the emission factors in Tables 5.2 and 5.3. The concentrations of metal ($\mu g\ l^{-1}$) discharge from the runoff therefore can be calculated using R_r and the yearly rainfall data which is assumed to equal 0.5 m per year in London (see Figure 5.1). The calculated concentrations of metal in runoff according to equation (5.28) and yearly rainfall data are compared to USEPA and Ohio EPA surface water discharge criteria (Sansalone and Bucherger, 1998) and the results are shown in Table 5.4.

It is accepted that accurate values for some these parameters are not known e.g. for k_d and k_w. The values chosen appear plausible and are a starting point for a sensitivity analysis. The introduction of these parameters emphasised the kind of measurements that must be made if purely empirical approaches were to be adopted, linking road dust to exposure.

Table 5.4 Calculated metal concentration in runoff discharge versus EPA surface water discharge criteria.

| | Calculated runoff concentration (μg l^{-1}) | | Surface water discharge criteria (μg l^{-1}) | |
	from traffic emission factor	from runoff emission factor	USEPA	Ohio EPA
Cd	0.5	0.9	3.7	5.6
Cu	1	20	17	18
Pb	1460	138	65	82
Zn	243	215	110	120

The results presented in Table 5.4 indicate that the calculated Pb and Zn concentrations in the runoff discharge using both the traffic and runoff emission factors (Table 5.2 and Table 5.3, respectively) and the Cu concentration using the runoff emission factors (Table 5.3) exceed USEPA and Ohio EPA water quality criteria. It is worth noting that the USEPA discharge criteria are based on the dissolved fraction mass of metal while Ohio EPA criteria are based on the total extractable metal mass. Although the equation (5.28) is based on very simple parameters, such as traffic flow, emission factors, local factors and meteorological conditions, it does provide a means to calculate the metal concentration in possible local conditions and to test whether metal concentration in the runoff discharge exceeds the discharge criteria. In a later section, the parameter, R_r will incorporate the partition coefficient and other parameters to evaluate the metal concentration in the soil next to a road, taking into account metal mobility.

5.2.3.2 Metal concentration in soil arising from resuspension

The amount of contamination entering the soil by re-suspension (R_s) depends on the distance from the road, x, (see Figure 5.4) and is given by

$$R_s = E \cdot N \frac{v_g}{h(x)u} \cdot F_s \qquad (5.29)$$

where v_g is the deposition velocity (m s^{-1}) of re-suspended dust particles, u is the wind speed (m s^{-1}) and h(x) is the depth (m) of the dust cloud and x is the distance from the road.
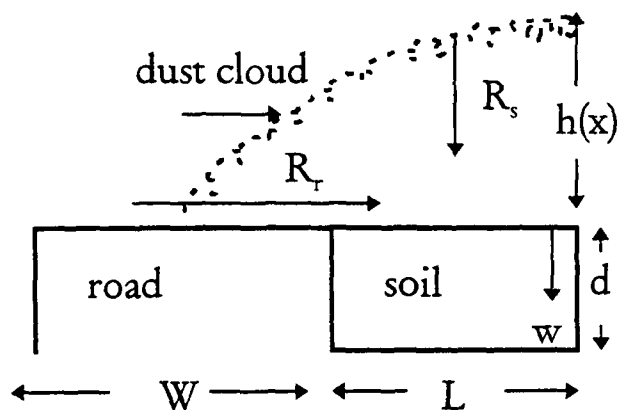
Figure 5.4 The system of road runoff to soil near the road.

It is assumed that the movement of vehicles mixes the particles in the atmosphere and so to a first approximation

$$h(x) = 0.1\left(\frac{W}{2} + x\right) \qquad (5.30)$$

$R_r + R_s$ where R_r is given by equation (5.28) and R_s is given by equation (5.29), is the total amount of material entering the soil next to the road. The contamination of the soil depends on the depth of the soil, taken to be d, and the rate of percolation of water through the soil, taken to be w (m s^{-1}).

It is worth noting that some of the dust samples described in earlier chapters were collected in a car park with no obvious drainage system. Water appeared to collect on surrounding areas which were sufficiently porous to take rainwater away. One would expect the fraction of material in runoff and the fraction of re-suspension in a car park to be different to that along a

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road and to depend strongly on local conditions. There is no evidence that the mechanisms by which the dust is removed from the road surface such as resuspension have any strong influence on the chemical form of the particles.

5.2.3.3 Metal concentration in soil subject to leaching

It is assumed, as a first approximation, that the concentration of metal in the soil is in equilibrium with the concentrations of metal in soil water, so that

$$C_s = k_{sw} C_w \tag{5.31}$$

where k_{sw} is a partition coefficient between metal in the soil and the metal in the percolating water. This assumption is thought to apply if the percolation of water through the soil is every slow compared with the time scales of the chemical reactions and the time taken to reach equilibrium.

Heavy metals are removed from the soil by the percolation of water. If this occurs at a velocity w (m s^{-1}) then one can write down an equation relating the overall loss to the loss by percolation, namely

$$k_s d \left(\rho_s C_s + \theta C_w \right) = w \theta C_w \tag{5.32}$$

where θ (l l^{-1}) is the water content of the soil, ρ_s is the density of soil (kg m^{-3}) and k_s (s^{-1}) describes the rate of removal of metal from the soil.

$$k_s = \frac{w\theta C_w}{\left(\rho_s C_s + \theta C_w \right) d} = \frac{w\theta}{\left(\rho_s K_{sw} + \theta \right) d} = \frac{w}{\left(1 + \frac{\rho_s k_{sw}}{\theta} \right) d} \tag{5.33}$$

The concentration of the metal in the soil is given by

$$C_s = \frac{\left(R_r + R_s \right)}{k_s \rho_s d} = \frac{\left(R_r + R_s \right)\left(1 + \frac{\rho_s k_{sw}}{\theta} \right)}{w \rho_s} \tag{5.34}$$

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where R_r and R_s are given by equation (5.28) and (5.29), respectively.

The concentration of metal in the soil given by the runoff model described by equation (5.34) depends on a number of physical and chemical parameters, many of which are only known approximately. It appears to be based on a rather speculative model. However the model does illustrate the role of processes which may influence heavy metal concentrations in the soil next to a road. Strictly speaking the coefficient k_{sw} discussed in Chapter 4 refers to the separation of metal between liquid and solid phases when the contact liquid is an artificial solution. In reality one should be considering the separation of particles in soil and soil water which will be affected by weathering processes. However as a first approximation in the risk assessment they are assumed to be the same. It may argued that weathering is likely to reduce the acidity of percolating water and therefore this assumption will lead to an overestimate of the rate of removal of metal from the soil.

The partition coefficient, k_{sw}, depends on the metal under consideration and should be based on the measured values described in Chapter 4. Moreover, k_{sw} does not fully describe the complex processes describing the leaching of the metal from soil into water. Sequential extraction procedures showed that this is a complicated process depending on the form that the metal is held in the dust particles but sequential extraction does not lead to a practical assessment method.

Equation (5.34) shows the chemical and physical parameters and processes that can affect the concentration of heavy metal in soil. The equation provides a framework for assessing the potential risk of metal release from dust. The risk model is dependent on many local factors including

meteorology. This thesis concentrates on the main chemical factor k_{sw}, the partition coefficient.

For each particular metal in the dust it is necessary to choose a representative value of k_{sw} based on the measurements. If k_{sw} is large then the metal is only slowly removed by the percolating water. The factor $(R_s + R_r)$ represents the sum of the runoff and the attenuation of the deposition arising from the resuspension of deposited matter which is blown away from the immediate neighbourhood of the road.

5.2.4 Statistical model of dust deposition to roads

The derivation of the above equations for dust accumulation on a road was based on the following model of rainfall duration. An alternative derivative is described in this Section. Fisher (1983) developed a long-range transport model of atmospheric pollution. The principles of this model can also be applied to road dust deposition. Within this context one can let functions $G_{DD}(t)$ and $G_{WD}(t)$ have the following meanings :

$G_{DD}(t)$ is the probability that a particle deposited on the road in dry conditions at time $t = 0$ remains on the road until dry conditions at time t,

$G_{WD}(t)$ is the probability that a particle deposited on the road in dry conditions at time $t = 0$ remain on the road until wet condition at time t.

The equation satisfied by $G_{DD}(p)$ and $G_{WD}(p)$, etc. can be written in matrix form as follows:

$$
\begin{bmatrix} p + k_d + t_d^{-1} & -t_w^{-1} \\ -t_d^{-1} & p + k_w + t_w^{-1} \end{bmatrix} \begin{pmatrix} G_{DD}(p) \\ G_{WD}(p) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{5.36}
$$

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where k_d is the removal rate of dust in dry conditions, k_w is the removal rate in wet conditions and the Laplace transforms $\int_0^\infty G \exp(-pt)dt$ have been taken.

During dry conditions the deposition rate is D, a constant. The particle loading at time t in dry conditions is

$$P_d(t) = \int_0^t G_{DD}(t - t')Ddt' \tag{5.37}$$

(At time t', D is the deposition rate and $G_{DD}(t-t')$ is the fraction of this deposition surviving until time t. The integral sums over all previous conditions).

The particle loading in wet conditions at time t is

$$P_w(t) = \int_0^t G_{WD}(t - t')Ddt' \tag{5.38}$$

Taking Laplace transforms,

$$\overline{P_d} = G_{DD}\frac{D}{p} \text{ and } \overline{P_w} = G_{WD}\frac{D}{p} \text{ from the convolution theorem.}$$

Thus

$$\begin{pmatrix} p + k_d + t_d^{-1} & -t_w^{-1} \\ -t_d^{-1} & p + k_w + t_w^{-1} \end{pmatrix} \begin{pmatrix} \overline{P_d} \\ \overline{P_w} \end{pmatrix} = \begin{pmatrix} \dfrac{D}{p} \\ 0 \end{pmatrix} \tag{5.39}$$

which is similar to equation (5.10) described earlier, for the accumulated dust in dry and wet periods.

5.2.5 Sensitivity of soil concentration to meteorological influence

One can compare the partition coefficient between soil and water commonly applied in environmental risk assessments with the values that would be derived from the chemical analyses in earlier sections (Chapter 4). This

would show that an assessment of the contamination of soil adjacent to a road with improper drainage can lead to widely differing assessments depending on the value for k_{sw}.

The soil contamination would also depend on the rain climatology of the region according to the values of t_d and t_w that apply (the mean duration of dry and wet periods, respectively). These factors influence the fraction of material which would be included in runoff and the fraction likely to be re-suspended. In Hong Kong for example, the nature of rainfall and runoff is very seasonal (see Figure 5.1). Hong Kong usually experiences periods of heavy rain between April and September. During this season one expects the term $k_w t_w$ to be large, so that the fraction re-suspended arising from resuspension is given approximately by equation (5.26). During the remaining months $k_w t_w$ will be small and most of dust will be re-suspended.

In London, by contrast, with a more evenly distributed rainfall pattern throughout the seasons, the fractions re-suspended and the fraction of metal included in runoff will be more comparable.

Typical values of the removal rate in dry and wet weather and the mean duration of dry and wet weather for London are $t_d \cong 100$ h, $t_w \cong 10$ h, $k_d \cong 1/200$ h^{-1}, $k_w \cong 1$ h^{-1}, so that F_s and F_r are equal to 11/31 and 20/31, respectively. Hence about 1/3 of dust deposited is estimated to be re-suspended and about 2/3 is estimated to be included in runoff.

This suggests that the climatology of different regions of the world affects the heavy metal exposure routes (by the fraction re-suspended and the fraction of metal in runoff) but it does not affect the mechanisms of exposure, since differences in the values of k_{sw} for a particular metal do not show systematic differences in different locations.

Earlier sections showed that k_{sw} cannot be determined from the total metal content of particles in soil, rather it depends on the pH and other factors associated with the water in the soil. For some metals consideration of total metal content would lead to a large overestimate of the metal removed by the percolating water.

Most environmental risk assessments involving metal contamination assume a single value for a given metal for k_{sw} which is the ratio of the concentration of metal in particle form to the concentration of metal dissolved in soil water. This is shown in this chapter to be the key parameter but to depend on coupled processes. In the two reaction kinetic model described in Chapter 4 Section 4.3.2.1, k_{sw} corresponds to the ratio between metal in dust and metal in solution (equation (4.9)) when equilibrium has been reached and is high for metals which tend to remain in solid form. In the EPA's river model, the partition coefficient, k_{sw}, depends on the amount of suspended solid in the river where the partition coefficient decreases as the suspended solid concentration decreases (Ambrose *et al.*, 1988). Values for k_{sw} available from the literature and which are used in environmental risk assessment for the EPA's river model are 6.5 ml g^{-1} for Cd, 35 ml g^{-1} for Cu and 900 ml g^{-1} for Pb. These fixed values do not represent the full range of variation that can occur for this parameter depending on pH. For Cd, they would correspond to pH 1 and 2), for Cu pH $\cong$ 2 and for Pb, pH $\cong$ 4 (see Tables 4.11-4.14). If these values are used to estimate the metal released, they will lead to overestimates of metal concentrations in the percolating water at pH 4 which is most likely to be apply under acid rain condition. It will also underestimate the metal left in the soil or sediment though some of this will not be available for uptake because it is not in a soluble form.

5.3 Application of Runoff Model to Risk Assessment Model

The theoretical runoff model described by equation (5.34) has been used to predict the level of heavy metal in soil next to a road. The runoff model incorporates the road transport heavy metal emission factors, meteorological data, soil/dust physical and chemical properties to calculate the concentration of heavy metal in soil under the assumption of no drainage system is connected to the road and the road surface runoff runs directly onto the surrounding land.

Values for the main parameters used in the runoff model are shown in Table 5.5 and correspond to a road carrying 20,000 vehicles per day, typical of many two lane routes in London.

Table 5.5 The parameters in the runoff model (equation 5.34).

	Parameters	Unit	Values
t_d	mean duration of dry period	h	100
t_w	mean duration of wet period	h	10
k_d	dust remove rate in dry weather	h^{-1}	1/200
k_w	dust remove rate in wet weather	h^{-1}	1
ρ_s	soil density	$kg\ l^{-1}$	1.3
θ	soil moisture	$l\ l^{-1}$	0.3
N	no of vehicles per second	vehicles s^{-1}	0.23
W	width of the road	m	15
L	width of the land	m	15
u	wind speed	$m\ s^{-1}$	3
w	rainfall velocity	$m\ s^{-1}$	1.6 E(-8)
v_g	deposition velocity	$m\ s^{-1}$	0.01

Table 5.6 The partition coefficients of Cd, Cu, Pb and Zn in dust at different pH solutions.

pH	Partition coefficients (l/kg)			
	$k_{sw}(Cd)$	$k_{sw}(Cu)$	$k_{sw}(Pb)$	$k_{sw}(Zn)$
2	14	37	15	10
3	22	82	55	17
4	35	180	202	31
5	57	396	747	56
6	92	872	2764	100

The emission factors of Cd, Cu, Pb and Zn are taken to be 1×10^{-9}, 1.4×10^{-9}, 3×10^{-6} and 5×10^{-7} g m^{-1} vehicle^{-1} (Table 5.2), respectively, and these values were calculated from the total of Cd, Cu, Pb and Zn emission associated with road transport in UK (Salway *et al.*, 1996). Although the runoff model describing contamination of roadside soil contains a number of parameters which can not be accurately quantified, a risk assessment was undertaken in which typical values have been assumed.

The partition coefficients for Cd, Cu, Pb and Zn between pH 2 to 6 are calculated using linear regression equations in Chapter 4 Table 4.10. The partition coefficients of Cd, Cu, Pb and Zn in London road dust are applied in this model and the values are shown in Table 5.6.

The results showing the concentrations of Cd, Cu, Pb and Zn in soil according to equation (5.34) at distances close to the road are shown in Figure 5.5. These metal concentrations are produced by the contribution from the nearby road alone. The concentrations of Cd, Cu, Pb and Zn in soil are strongly dependent on the partition coefficients at different pH. The influence of the distance between soil and road is relatively small when compared to the partition coefficients. This implies that the metal

concentrations in soil directly next to a road was mainly derived from the road surface runoff whereas the dry deposition of re-suspended dust does not show large influence in the immediate vicinity of the road. The greater k_{sw} the greater is the fraction in particulate form. The greater the fraction in the particulate form the lower the amount removed by drainage and hence the higher the amount of metal remaining in the soil. Therefore, the solid-bound metal in dust tends to accumulate in the soil and this may pose a contamination risk on soil or terrestrial environment near a road. On the other hand, when k_{sw} is small the dissolved form of metals will tend to dissolve in the runoff and percolate through the soil. It may then be adsorbed elsewhere by the soil or run into the aquatic environment. The dissolved metal may pose a potential contamination risk to the aquatic environment as well as in the soil.

There are three components to the concentration of metal in the soil next to a road including:

1) some of the metal is washed directly onto the soil by road surface runoff;

2) some of the metal is re-suspended from the road, carried by the wind and then deposited onto the soil;

3) some of metal arises from other sources in the urban area producing a background urban airborne concentration some of which is deposited to the soil.

The first two components represent the local influence of road and are estimated using the runoff model described by equation (5.34). In this study, the third component, the urban background dust contribution, has not be included in the calculation.

In the broader picture the re-suspended dust fraction eventually contributes to the general urban airborne particle concentration which is made up of contributions from vehicles on roads in the whole urban area. This latter contribution, which could be considered to be the urban background dust contribution, is neglected in this calculation.

The concentrations of Cd, Cu, Pb and Zn estimated by the runoff model using equation (5.34) are compared with the Trigger Concentration Guidance from the ICRCL for contaminated soil (see Table 3.9 in Chapter 3) which are 15 mg kg^{-1} for Cd, 130 mg kg^{-1} for Cu, 2000 mg kg^{-1} for Pb and 300 mg kg^{-1} for Zn. The preliminary results (see Figure 5.5) suggest that there is no risk of the Guideline values being exceeded from the effect of road transport alone apart from the case of Pb at a pH of 5 and 6. The possibility arises for Pb because of the high emission rate from the traffic (which has reduced in recent year and will be further reduced when Pb in petrol is phased out at the end of 1999) and because of the high partition coefficient for Pb which means that it is not washed out of the soil as rapidly as the other metals.

The calculated concentration of Cd, Cu, Zn are much lower that the background levels of Dutch Criteria Index category A for soil which are 1 mg kg^{-1} for Cd, 50 mg kg^{-1} for Cu, 200 mg kg^{-1} for Zn.

An extremely high calculated Pb concentrations (ca. 4800 and 18000 μg g^{-1}) in soil were obtained using k$_{sw}$ at pH 5 and 6, respectively. The model may not apply in these conditions, since when high partition coefficients are used in the calculation there is very little removal by leaching and concentrations would build up in time within the soil.
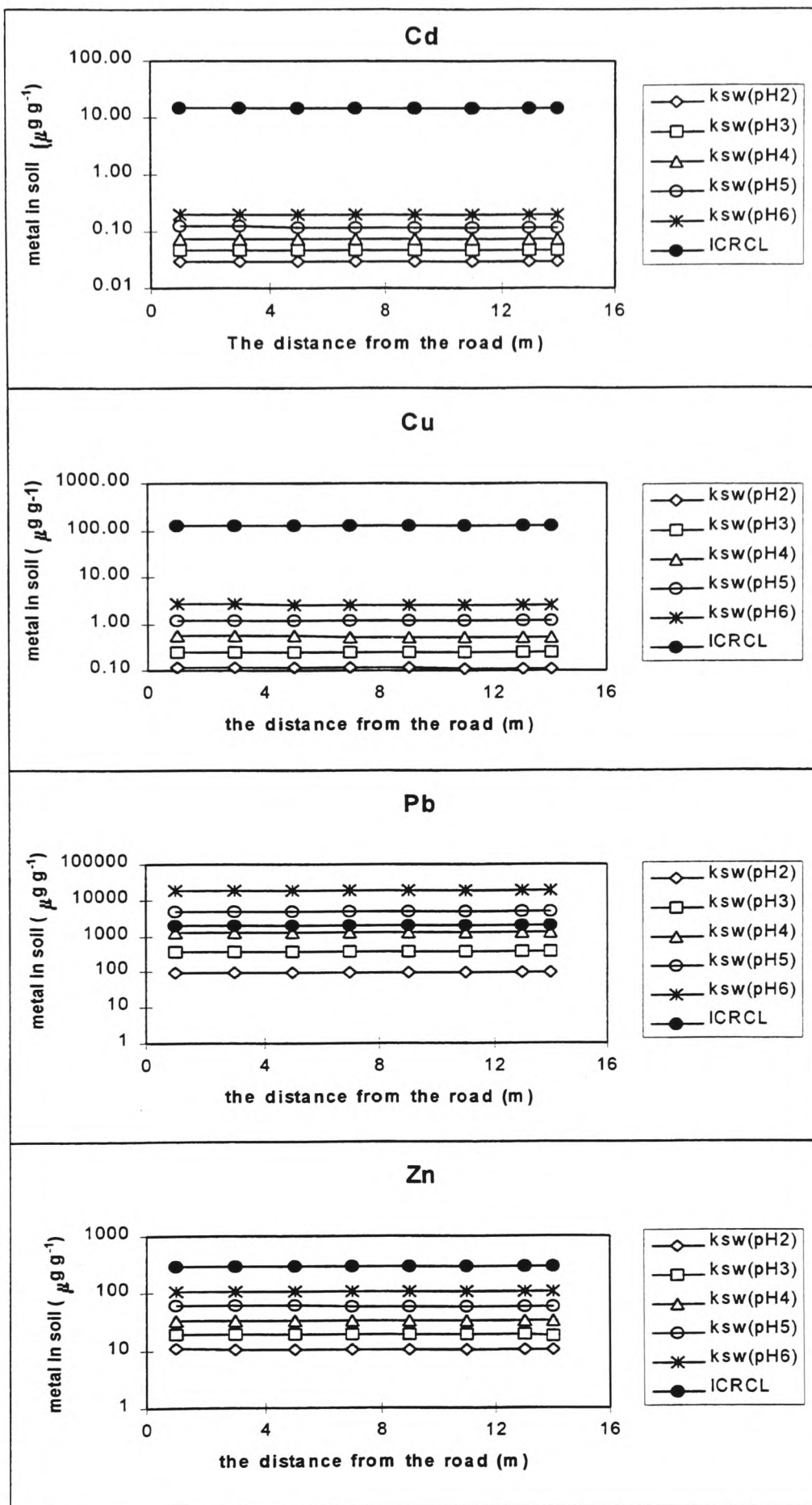
Figure 5.5 The calculated metal concentration in soil using emission factors from road transport (in Table 5.2).

Results using alternative estimates emission factors are showed in Table 5.3 which are calculated using the total solid in highway runoff (Colwill *et al.*, 1984) and the proportions of Cd, Cu, Pb and Zn found in the dust according to the experimental study in Chapter 4. This is equivalent to 1.8×10^{-9} g m^{-1} vehicle^{-1} for Cd, 4.14×10^{-8} g m^{-1} vehicle^{-1} for Cu, 2.84×10^{-7} g m^{-1} vehicle^{-1} for Pb and 4.42×10^{-7} g m^{-1} vehicle^{-1} for Zn. The estimated concentrations of Cd, Cu, Pb and Zn are shows in Figure 5.6 and are somewhat different to the value presented in Figure 5.5. The concentrations of Cd, Cu, Pb and Zn of soil present in Figure 5.6 apparently show no exceedence of the Trigger Concentration Guidance from the ICRCL for contaminated soil. Hence emission factors are an important parameter which decide the strength of the metal input to the natural environment. Figure 5.5 and 5.6 clearly show that the soil concentration is very sensitive to the acidity of the runoff water, which may change as the water percolates through the soil.

It is important to understand the model's sensitivity to the key input parameters apart from the meteorological influences which were discussed in Section 5.2.5. According to the sensitivity test the information can provide information on which parameters are most important to specify accurately. The sensitivity test was carried out by selecting a base value and then varying it by taking three times its value and one-third of its base value. The dependence of soil concentration was simulated by varying the partition coefficient (k_{sw}), the emission factor (E), the traffic flow (N), the deposition velocity (v_g), the wind speed (u), the soil density (ρ_s), the soil moisture (θ), the width of the road (W), the width of the land (L) and the rainfall velocity (w). Only the Pb concentration in the soil were studied in this analysis. The base values using in the sensitivity test are presented in Table 5.7 and the

results of the sensitivity test are shown in Figure 5.7. The Pb concentration in soil shows little difference when the deposition velocity, wind speed, soil density or the width of the road were varied (see Figure 5.7). When the width of the land, the soil moisture and the rainfall velocity were varied, the soil Pb levels are inversely proportional to the change in the magnitude of the parameters. These showed that the width of the land, the soil moisture and the rainfall velocity act as attenuation factors when the runoff flows onto wider width of land, with higher soil moisture and higher rainfall rate. On the other hand if the runoff runs onto narrower strip of land, with lower soil moisture and lower rainfall rate, then higher levels of heavy metal will accumulate in the soil. The concentration of Pb in soil shows increasing sensitivity to the partition coefficient, emission factor and traffic flow by a factor of three when using three times the base case.
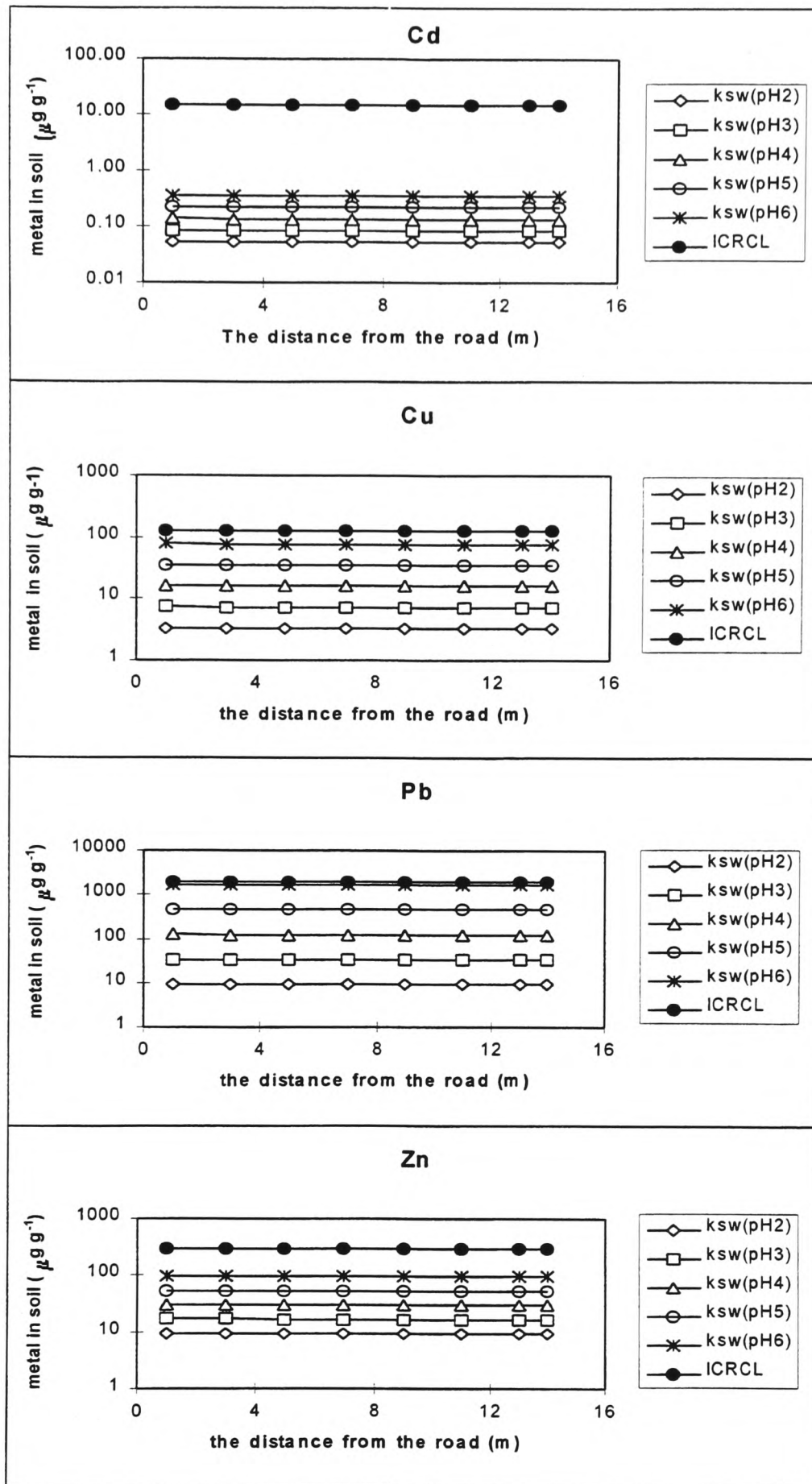
Figure 5.6 The calculated metal concentrations in soil using emission factors

in runoff and experimental data (in Table 5.3).

Table 5.7 The base values for sensitivity test

Parameters	Unit	Base values
t_d	h	100
t_w	h	10
k_d	h^{-1}	0.005
k_w	h^{-1}	1
ρ_s	$kg\ l^{-1}$	1.3
θ	$l\ l^{-1}$	0.3
N	vehicle s^{-1}	0.231481
W	m	15
L	m	15
u	$m\ s^{-1}$	3
w	$m\ s^{-1}$	1.59×10^{-8}
v_g	$m\ s^{-1}$	0.01
$k_{sw}(Pb)$	$ml\ g^{-1}$	202
E(Pb)	$g\ m^{-1}vehicle^{-1}$	2.84×10^{-7}
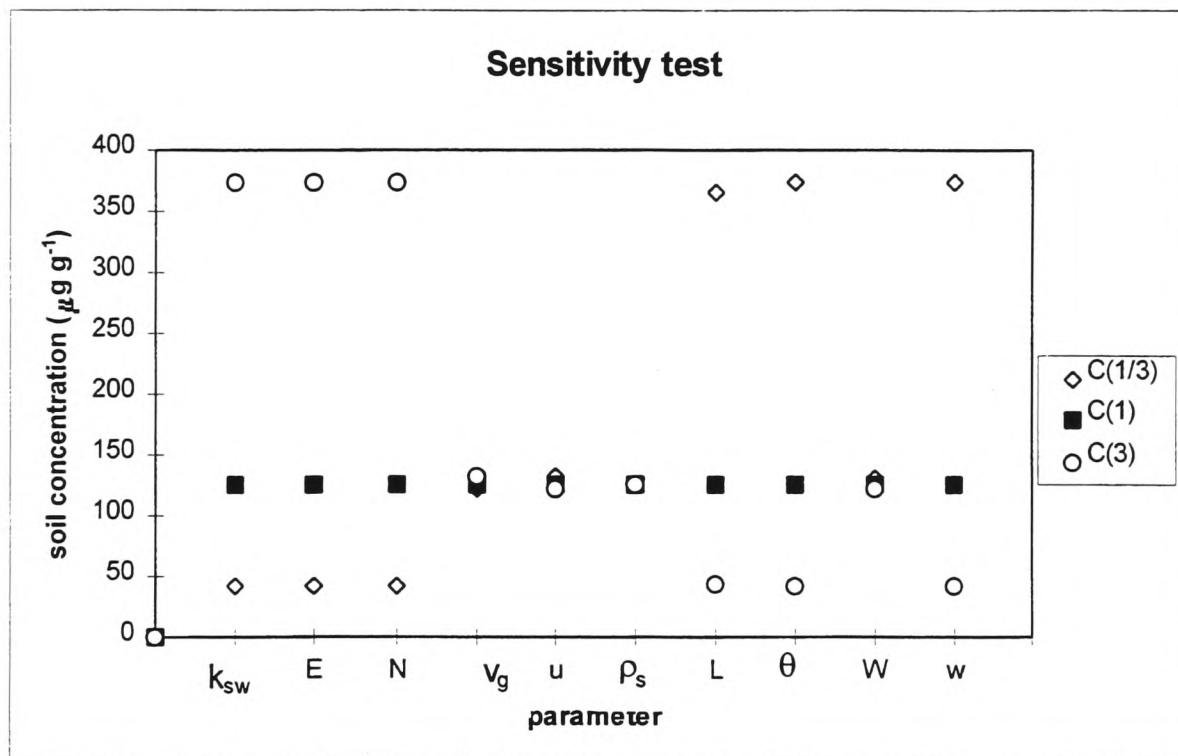
Note: C(1), C(1/3) and C(3) are the soil concentration are calculated using the base values, one-third of the base values and the three times of base values.

Figure 5.7 Sensitivity test of soil concentrations varied with different parameters.

5.4 Summary

It may be seen that the risk of exposure is very sensitive to the distribution between the dissolved and particulate forms of the metal, which is of equal importance as the source strength of the metals.

Application of a theoretical model to a typical two lane road in London for assessing the potential risk of Cd, Cu, Pb and Zn in urban road dust on soil suggests that only Pb in road dust may exceed the ICRCL Guideline value. This may be an overestimate because the lead in petrol will be progressively phased out within the recent year. The assessment using the theoretical model shows that the risk of exposure is very sensitive to the partitioning of metal between the dissolved and particulate forms of the metal as well as emission factors and traffic flow. Higher levels of rainfall, high moisture of soil and a greater width of land, next to the road, may act as attenuation factors when road surface runoff flows directly onto adjacent land.

If the metal remains in the soil further exposure could take place by the ingestion of soil from unwashed vegetation. The uptake of metal is then dependent on conditions to which the soil is exposed in the gut. It is therefore interesting to compare the partitioning between particulates and dissolved metal in this situation and this is the topic of Chapter 6.

IN VITRO METAL RELEASE UNDER SIMULATED GASTRIC
CONDITIONS: SIMULATION OF CHILDREN EXPOSURE
UNDER HAND TO MOUTH ACTIVITY

6.1 Introduction

This chapter and Chapter 7 consider two alternative empirical ways by which human health may be threatened by heavy metals in dust. As part of the risk assessment of metal-rich street dust in the urban environment, this chapter considers one of the typical human exposure pathways — dust/soil ingestion by the vulnerable urban pediatric population. Although direct soil ingestion by humans may not be an obvious exposure mechanism, it has been proven to be one of the dominant pathways for Pb in urban areas (Davies *et al.*, 1990) and former smelters and mining towns (Cotter-Howells and Thornton, 1991) and for As near Cu smelters (Polissar *et al.*, 1990).

This study focuses on the solubility of metal bearing urban street dust under different simulated gastric conditions and the metal release kinetics of urban dust under simulated *in vitro* gastric conditions. These results will be applied to quantify the importance of the dust ingestion pathway by human for risk assessments. This chapter focuses on four heavy metals, Cd, Cu, Pb and Zn. The objectives are: (1) to investigate the influence of the particle size of dust particles and pH on metal release under *in vitro* simulated gastric conditions, (2) to determine the rates of metal release under simulated gastric conditions and (3) to analyse the relationship between metal release kinetics and geochemical speciation.

6.1.1 Dust ingestion

Despite the acknowledged importance of the ingestion of dust and soil a route of exposure of metal contaminants to the urban pediatric population, little is known about the bioavailability of these contaminants. Of order 30% or more of ingested soil/dust Pb has been estimated to be bioavailable for children (USEPA, 94), based on toxicological studies using pure Pb salts. However using pure Pb salts as an analogue for Pb bearing soils and dust in toxicological studies leads to an overestimate of the bioavailability, as solid phase of Pb in soil and dust are much less soluble (Davis *et al.*, 1992; Gasser *et al.*, 1996).

The highly acidic condition in the human stomach may influence the metal release and bioavailability of solid bound particles. On the other hand, the solubility of metals in the gastrointestinal (GI) tract will be highest in the stomach because of the high acidity of gastric fluid (Gasser *et al.*, 1996). Therefore, the pH (acidity) and biochemical matrix in the gastrointestinal fluid both have a strong influence on metal absorption.

This chapter consider the children who have been described as either the average child playing in a *"normal dirty way"* (Duggan *et al.* 1985) or the USEPA's approach, the *"most-exposed, most-susceptible individuals"* (Wixson and Davies, 1993). The most exposed individuals are those who have less care, are regularly exposed to the metal-rich media and are more likely to exhibit pica (hand to mouth) behaviour. These children are poorly nourished and would therefore ingest more soil and dust and hence absorb more metal from soil and dust than well cared for and well nourished children (Wixson and Davies, 1993).

The biological availability (or simply, bioavailability) of environmental pollutants is a simple parameter for assessing potential human risks

associated with environmental contaminants which are deliverable or delivered to target organs. The bioavailability is the degree to which a contaminant in a potential source is free for uptake such as movement into or onto the organism. There are various definitions of bioavailability depending on the purpose of study. Firsov and Piotrovskii (1986) defined the biological availability for a drug as,

"the fraction (nutrient, drug or human environmental toxicant) of a

substance entering the systemic circulation (extent of systemic

absorption) and the rate at which entry occurs".

The bioavailability of environmental Pb has been defined as *"the biological aspects of Pb uptake from body compartment, the biophysico-chemical behaviour of different Pb species in body compartment, interactive relationships and toxico-kinetics of Pb in human body"* (Mushak, 1991) and *"a fraction which can be absorbed into bloodstream by animal species ingesting the diet"* (Wixson and Davies, 1993). The bioavailability of Cd, Cu, Pb and Zn of urban dust from the GI tract to the blood stream is governed by the dissolved metal species fraction of the total metal. The fraction of dissolved metal may further be transported across a biological membrane by passive diffusion, facilitated diffusion, active transport, pincytosis, or ionic or electrochemical diffusion to bloodstream and soft tissue (Selen, 1991).

6.1.2 The absorption of metals in the gastrointestinal system

The GI tract mainly comprises the oesophagus, stomach, small intestine (the duodenum, jejunum and ileum) and the colon (Hrudey *et al.*, 1996). The small intestine is the main absorptive site through which heavy metal are transported into the blood, while the stomach plays a special role in the uptake via transformations of metal-bearing media or form-specific metal ions to potentially more soluble and mobile forms (Mushake, 1991). Gastric

acidity may accelerate the dissolution of metals from solid media. The hydrochloric acid (HCl) in the stomach is essential for the conversion of inactive pepsinogen to the enzyme pepsin and it also kills the bacteria in the stomach, thereby reducing the number of organisms reaching the intestine (Beaumont, 1955). The HCl and pepsin govern the digestion of protein. The pH of gastric fluid in the stomach at higher rates of secretion may be less than 1 and in a empty stomach the pH is usually less than 2 (Johnson, 1991). After leaving the stomach, the gastric fluid is neutralised in the duodenum (pH $\cong$ 7) by means of bicarbonate and other agents from the pancreas (Vick, 1984). Therefore, the highest solubility of metals in the GI tract is likely to be in the stomach because of the high acidity of gastric fluid (pH = 1-2).

Gastrointestinal absorption is the main mechanism by which metal enters human body, to be transported around the bloodstream (Mushake, 1991). The average uptake of heavy metal by this route has been calculated as being around 10-20%. Young children have been shown to have higher absorption of Pb (40-50%) than adults (10-15%), but absorption is influenced by the food in the stomach and the nutrient status of individuals (Mushake, 1991). Cadmium and Pb are absorbed by pulmonary or gastrointestinal absorption, firstly transported in the bloodstream to soft tissues where they have a short half-life, and then transported to the reservoir of the bone where they have a long half-life.

There are many factors that influence the absorption of metals in soil/dust ingestion by children. For instance, the physical and chemical properties of dust particles, the nutrient status, the ages of children and the amount of food in the stomach can substantially affect to what extent metal-bearing dust is absorbed (Wixson and Davies, 1993).

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The solubility of metals in dust depends on the nature of the metal-bound dust itself and the composition of the solution. Chemical speciation of metal-bound dust/soil has to be thoroughly understood in order to simulate metal release kinetics in the human GI tract. The dissolution kinetics of Pb under gastric conditions in soil, smelter and waste impacted materials have been studied by Ruby *et al.*, (1992) and Gasser *et al.*, (1996). These kinetic approaches provide a powerful technique that integrates several important factors governing metal release, including particle size, chemical speciation and pH.

6.1.3 National guidelines on Pb exposure

Standards for toxic metals in dust fall-out have been issued in some countries including Switzerland, Germany and Yugoslavia in order to prevent excessive accumulation of toxic metals in soil (Ewers, 1991). Since Pb in surface dust represents an important source of Pb exposure for young children, the necessity of standards for Pb in dust or dust fall-out has been emphasised (Duggan, 1983; Brunekreef *et al.* 1983) and it has been proposed that 1000 μg g^{-1} may be an appropriate for Pb in dust standard to prevent increased exposure of children (Laxen *et al.* 1987; Ewers *et al.* 1988). Exposure limits of Pb for the general population have also been proposed for Pb. The recommendations refer either to the blood Pb (PbB) level which should not be exceeded by a given proportion of the general population or to maximum tolerable PbB in individuals, mainly children. The European Commission Council Directive on Biological Screening of the Population for Pb (77/312/EEC) proposed, the following guidelines:

- 50 % of an investigated population group should have PbB < 20 μg dl^{-1},

- 90 % of an investigated population group should have PbB < 30 μg dl^{-1},

- 98 % of an investigated population group should have PbB < 35 μg dl^{-1}.

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Actions have to be taken to trace and reduce the source of exposure if these values rise beyond reference levels. More stringent guidelines set by the Dutch Ministry of Public Health based on a survey of PbB in pre-school children (Brunekreef *et al*. 1983) recommend that:

- 50 % of investigated pre-school children have PbB < 20 μg dl^{-1},

- 90 % of investigated pre-school children have PbB < 25 μg dl^{-1},

- 98 % of investigated pre-school children have PbB < 30 μg dl^{-1}

The individual action levels of PbB level range from 20 to 30 μg dl^{-1} in various countries. These levels are associated with actions to trace and reduce the sources of exposure on an individual basis (Ewers, 1991). The West German Federal Health Agency proposed the use of categorical limits (see Table 6.1) as a basis for the assessment of Cd and Pb concentrations in human blood for non-occupationally exposed individuals (Ewers, 1991). In the USA, a Pb level in blood of 10 μg dl^{-1} has been adopted for Pb poisoning by the Centre for Disease Control (CDC) and the USEPA (Burgoon *et al*, 1995).

Table 6.1 Guideline values for the assessment of metal concentrations in human blood by the West-German Federal Health Agency (cited by Ewers, 1991).

Metal	Human blood	Category I ($\mu g\ dl^{-1}$)	Category II ($\mu g\ dl^{-1}$)	Category III ($\mu g\ dl^{-1}$)
Cadmium	- children	<1	1- 3	>3
	- adults	<2	2- 5	>5
Lead	- pregnancy women and children	<15	15- 25	>25
	- adults	<15	15- 35	>35

*Category I: normal range of blood level;

*Category II indicates an increased concentration. Sampling and measurement should be repeated;

*Category III indicates a significantly increased concentration. The adverse health effects cannot be excluded. If increased exposure persists for a long period, the source of the exposure should be identified and eliminated or reduced.

6.2 Materials and Methods

6.2.1 Sample collection and chemical characterisation

Two batches of dust samples, one collected in September 1995 in London and the other collected in March 1996 in Hong Kong, were used for the study of *in vitro* metal release under simulated gastric conditions. The background soil samples collected at the Hong Kong and London sites were also used. The sampling details and methods of chemical characterisation have been discussed in Chapter 4.

6.2.2 In vitro, dilute acid extraction under simulated gastric conditions

Dust samples were treated with diluted acid to simulate gastric conditions. Each dust sample was conducted in triplicate. Two methods were used, one using diluted HCl solution, the other using 1% saline pepsin HCl solution. Pepsin is an important enzyme for digestion in the stomach.

Method 1: Solutions of pH 1.0, 1.6 and 1.8 saline (0.015 M NaCl) hydrochloric acid were prepared. Half gram of dust was mixed with 50 ml saline (0.015 M NaCl) HCl at pH 1.0, 1.6 and 1.8 in an orbital shaker for 8 hours, and then centrifuged for 30 minutes.

Method 2: Solutions of pH 1.0, 1.6 and 1.8 saline (0.015 M NaCl) hydrochloric acid with 1% of saline pepsin solution were prepared. Half gram of dust sample was mixed with 50 ml 1% saline pepsin (0.015 M NaCl) HCl at pH 1.0, 1.6 and 1.8 in an orbital shaker for 8 hours, and then centrifuged for 30 minutes.

The Cd, Cu, Pb and Zn contents in the supernatant were measured using a flame atomic absorption spectrophotometer and anodic stripping voltameter (TraceLab^{TM} Radiometer, Copenhagen).

6.2.3 In vitro, kinetic analyses of metal release under simulated gastric condition

Method 1: Solutions of pH 1.0, 1.6 and 1.8 saline (0.015 M NaCl) hydrochloric acid with 1% of saline pepsin solution were prepared. 2.5 g of dust sample was mixed with 250 ml 1% saline pepsin (0.015 M NaCl) HCl solution at constant pH = 1.0, 1.6 and 1.8 in an orbital shaker water bath at 37°C. pH was checked frequently and adjusted using HCl or NaOH to maintain the constant pH. Seventeen 10 ml portions of the sample solution were withdrawn during 4 hours and the eighteenth 10ml portion was taken after another 20 hours.

Method 2: Solutions of pH 1.0, 1.6 and 1.8 saline (0.015 M NaCl) hydrochloric acid were prepared. 2.5 g of dust was mixed with 250 ml saline (0.015 M NaCl) HCl solution at constant pH = 1.0, 1.6 and 1.8 in an orbital shaker water bath at 37 C. Seventeen 10 ml sample solution samples were

withdrawn during the first 4 hours and the eighteenth was taken after another 20 hours.

All collected solution samples were filtered through a 0.22 μm membrane filter and then the Cd, Cu, Pb and Zn concentrations were determined using a flame atomic absorption spectrophotometer and anodic stripping voltameter (TraceLab™ Radiometer, Copenhagen).

6.3 Results

6.3.1 In vitro, dilute acid extraction under simulated gastric conditions

The results of metal extraction from dust and soil samples at pH 1.0, 1.6 and 1.8 diluted acid after 8 h are shown in Tables 6.2 to 6.5 and Figure 6.1.

Metals released from the dust and soil samples were highly dependent on pH. Significant differences ($p < 0.001$) were found among extraction solution at pH 1.0, 1.6 and 1.8. In general, the lower the pH, the higher amount of metal release.

Higher percentages of Cd were released from the LDC and LDR dust samples than the other samples, while higher percentages of Cu were released from the LDR, HDR and HDC dust samples (see Figure 6.1). Road dust from LDR and HDR sites have relatively higher percentages of Pb and Zn release under pH 1 extraction solution when compared to car park dust from LDC and HDC sites and soil from LSB and HSB sites. Among the four metals, Cd had the highest percentage of release in London dust samples while Zn at pH 1.0 had the highest percentage release in Hong Kong dust samples. In comparison with the dust samples, the background soil sample had a lower percentage of metal release.

There are no significant differences in the patterns of metal release between having 1% of pepsin and without pepsin in the extraction solution with the exception that, under the pH 1.8 extraction solution, Zn and Pb release from the dust samples has been significantly ($p < 0.05$) accelerated by having 1% of pepsin.

No significant difference in metal release from the dust samples was found among the three selected particle size ranges ($< 125\mu m$, 125-250 μm and 250-500μm) although several researchers (e.g. Van Borm *et al.*, 1988 and Spittler and Feder, 1979) observed that the smaller the particles, the higher the relative concentrations.

Table 6.6 shows the significant correlation coefficients between different metals under simulated gastric conditions at pH 1.0, 1.6 and 1.8. Significant positive correlations for Pb (pH 1.6)/ Zn (pH 1.6) were found both in acidic solutions with and without pepsin. Where the correlation coefficient is not significant ($| r | < 0.5$; $p > 0.05$), the coefficient is not shown in Table 6.6. The rather scattered pattern of significant correlations suggests that a simple interpretation is not easy to find.

Table 6.2 Concentrations (arithmetic mean ± sd, µg g⁻¹) of Cd released under different simulated gastric conditions after 8 hours.

	solution	pH 1.0	Cd (µg g-1) pH 1.6	pH 1.8
LDC1	HCl	1.5 ± 0.8	0.7 ± 0.2	0.5 ± 0.2
	HCl+ pepsin	6.2 ± 0.8	3.1 ± 1.2	2.1 ± 0.9
LDC2	HCl	4.3 ± 1.3	1.9 ± 1.4	4.9 ± 1.6
	HCl+ pepsin	5.7 ± 0.4	3.5 ± 0.4	2.3 ± 0.5
LDC3	HCl	3.0 ± 0.3	5.2 ± 0.8	4.6 ± 1.9
	HCl+ pepsin	4.5 ± 0.2	2.4 ± 0.7	0.8 ± 0.4
LDR1	HCl	7.7 ± 1.3	0.2 ± 0.1	0.1 ± 0.1
	HCl+ pepsin	4.0 ± 0.3	1.8 ± 0.2	1.6 ± 0.5
LDR2	HCl	4.5 ± 0.8	0.5 ± 0.3	0.5 ± 0.0
	HCl+ pepsin	1.7 ± 0.4	1.1 ± 0.2	1.4 ± 0.4
LDR3	HCl	5.5 ± 4.4	0.5 ± 0.0	0.4 ± 0.1
	HCl+ pepsin	0.8 ± 0.2	0.9 ± 0.2	0.7 ± 0.1
HDC1	HCl	1.0 ± 0.8	0.6 ± 0.1	0.5 ± 0.1
	HCl+ pepsin	1.1 ± 0.2	0.8 ± 0.3	0.7 ± 0.1
HDC2	HCl	1.0 ± 0.6	0.8 ± 0.2	1.6 ± 1.2
	HCl+ pepsin	1.0 ± 0.1	0.4 ± 0.1	0.7 ± 0.1
HDC3	HCl	2.3 ± 0.4	0.3 ± 0.0	0.2 ± 0.1
	HCl+ pepsin	0.9 ± 0.2	0.4 ± 0.2	0.1 ± 0.2
HDR1	HCl	0.8 ± 0.9	0.3 ± 0.2	0.5 ± 0.1
	HCl+ pepsin	2.5 ± 0.3	1.4 ± 0.1	1.3 ± 0.6
HDR2	HCl	1.4 ± 0.5	1.3 ± 0.2	0.3 ± 0.0
	HCl+ pepsin	1.6 ± 0.3	0.6 ± 0.0	0.5 ± 0.4
HDR3	HCl	1.3 ± 0.4	1.2 ± 0.1	0.9 ± 0.7
	HCl+ pepsin	0.6 ± 0.2	0.6 ± 0.1	0.9 ± 0.4
HSB	HCl	0.7 ± 0.2	0.9 ± 0.1	0.7 ± 0.1
	HCl+ pepsin	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
LSB	HCl	0.1 ± 0.9	0.4 ± 0.3	0.2 ± 0.4
	HCl+ pepsin	0.5 ± 0.7	0.0 ± 0.0	0.0 ± 0.0

HDR1, HDR2, HDR3, (HDC1, HDC2, HDC3): Hong Kong road dust, (Hong Kong car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.
LDR1, LDR2, LDR3, (LDC1, LDC2, LDC3) : London road dust, (London car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.

Table 6.3 Concentrations (arithmetic mean ± sd, μg g^{-1}) of Cu released under different simulated gastric conditions after 8 hours..

| | solution | Cu (μg g-1) | | |
		pH 1.0	pH 1.6	pH 1.8
LDC1	HCl	34.5 ± 7.9	16.5 ± 0.5	25.4 ± 3.3
	HCl+ pepsin	74.2 ± 11.6	19.4 ± 1.8	22.6 ± 13.0
LDC2	HCl	45.8 ± 14.4	15.8 ± 2.0	11.3 ± 2.2
	HCl+ pepsin	64.4 ± 6.8	28.9 ± 1.2	28.4 ± 15.9
LDC3	HCl	39.6 ± 27.7	6.5 ± 1.3	7.8 ± 3.3
	HCl+ pepsin	57.1 ± 5.6	11.8 ± 3.1	5.4 ± 0.7
LDR1	HCl	122.6 ± 60.6	6.5 ± 2.4	4.1 ± 4.4
	HCl+ pepsin	201.3 ± 36.2	37.8 ± 1.1	11.8 ± 12.3
LDR2	HCl	77.5 ± 90.1	5.6 ± 2.2	12.2 ± 2.3
	HCl+ pepsin	105.1 ± 10.3	33.0 ± 7.6	14.7 ± 9.5
LDR3	HCl	191.7 ± 30.3	29.0 ± 2.6	8.5 ± 1.6
	HCl+ pepsin	39.5 ± 14.8	22.1 ± 2.6	11.5 ± 3.6
HDC1	HCl	79.8 ± 3.9	46.2 ± 10.5	11.6 ± 1.4
	HCl+ pepsin	37.0 ± 2.0	12.5 ± 2.8	16.2 ± 5.2
HDC2	HCl	78.3 ± 15.3	46.3 ± 5.9	12.7 ± 3.5
	HCl+ pepsin	45.1 ± 7.6	10.9 ± 3.8	8.4 ± 3.9
HDC3	HCl	120.1 ± 23.5	48.0 ± 3.9	7.2 ± 3.0
	HCl+ pepsin	34.3 ± 2.6	9.3 ± 3.4	8.6 ± 1.4
HDR1	HCl	262.1 ± 16.7	15.5 ± 3.1	8.0 ± 1.0
	HCl+ pepsin	145.2 ± 5.7	49.1 ± 9.3	31.4 ± 18.1
HDR2	HCl	177.9 ± 25.3	20.6 ± 10.8	9.5 ± 7.6
	HCl+ pepsin	90.1 ± 15.7	24.3 ± 6.4	19.2 ± 3.9
HDR3	HCl	146.8 ± 42.9	46.3 ± 7.9	9.0 ± 2.7
	HCl+ pepsin	39.7 ± 4.4	21.1 ± 6.9	14.7 ± 1.0
HSB	HCl	14.0 ± 2.8	11.0 ± 8.2	11.0 ± 3.6
	HCl+ pepsin	5.2 ± 2.6	2.9 ± 0.8	1.4 ± 1.2
LSB	HCl	8.6 ± 0.2	7.1 ± 1.6	2.7 ± 1.7
	HCl+ pepsin	9.3 ± 1.0	2.9 ± 0.8	2.3 ± 1.4

HDR1, HDR2, HDR3, (HDC1, HDC2, HDC3): Hong Kong road dust, (Hong Kong car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.
LDR1, LDR2, LDR3, (LDC1, LDC2, LDC3) : London road dust, (London car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.

Table 6.4 Concentrations (arithmetic mean $\pm$ sd, μg g^{-1}) of Pb released under different simulated gastric conditions after 8 hours.

	solution	Pb (μg g-1) pH 1.0	pH 1.6	pH 1.8
LDC1	HCl	247.8 $\pm$ 1.7	5.1 $\pm$ 0.2	3.5 $\pm$ 0.1
	HCl+ pepsin	497.6 $\pm$ 63.5	53.7 $\pm$ 23.0	20.1 $\pm$ 9.2
LDC2	HCl	200.7 $\pm$ 63.9	3.3 $\pm$ 1.8	3.6 $\pm$ 0.2
	HCl+ pepsin	421.0 $\pm$ 9.2	72.3 $\pm$ 3.9	27.5 $\pm$ 5.4
LDC3	HCl	71.2 $\pm$ 57.5	2.6 $\pm$ 0.3	2.4 $\pm$ 0.4
	HCl+ pepsin	226.8 $\pm$ 72.0	32.4 $\pm$ 10.7	10.3 $\pm$ 0.7
LDR1	HCl	1123.7 $\pm$ 35.9	0.8 $\pm$ 0.4	1.4 $\pm$ 1.3
	HCl+ pepsin	1010.5 $\pm$ 58.0	77.2 $\pm$ 10.8	28.0 $\pm$ 7.1
LDR2	HCl	885.2 $\pm$ 397.1	0.8 $\pm$ 0.5	0.8 $\pm$ 0.2
	HCl+ pepsin	558.5 $\pm$ 21.8	71.4 $\pm$ 20.4	35.4 $\pm$ 3.1
LDR3	HCl	481.2 $\pm$ 73.4	69.5 $\pm$ 24.5	0.7 $\pm$ 0.4
	HCl+ pepsin	273.6 $\pm$ 26.9	66.5 $\pm$ 19.7	36.4 $\pm$ 9.8
HDC1	HCl	122.4 $\pm$ 0.8	86.9 $\pm$ 6.3	0.7 $\pm$ 0.2
	HCl+ pepsin	79.5 $\pm$ 2.4	33.3 $\pm$ 0.1	25.3 $\pm$ 1.6
HDC2	HCl	87.2 $\pm$ 5.8	69.3 $\pm$ 8.1	0.8 $\pm$ 0.1
	HCl+ pepsin	64.2 $\pm$ 4.4	27.1 $\pm$ 2.4	16.8 $\pm$ 0.8
HDC3	HCl	64.0 $\pm$ 37.9	50.3 $\pm$ 5.3	0.3 $\pm$ 0.0
	HCl+ pepsin	43.0 $\pm$ 4.3	17.3 $\pm$ 1.2	12.3 $\pm$ 2.2
HDR1	HCl	557.6 $\pm$ 84.4	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1
	HCl+ pepsin	357.5 $\pm$ 1.6	42.1 $\pm$ 5.3	26.7 $\pm$ 2.5
HDR2	HCl	386.9 $\pm$ 32.5	3.5 $\pm$ 1.6	0.1 $\pm$ 0.1
	HCl+ pepsin	191.0 $\pm$ 8.5	29.0 $\pm$ 2.5	16.4 $\pm$ 1.9
HDR3	HCl	200.6 $\pm$ 49.9	133.9 $\pm$ 39.1	0.7 $\pm$ 0.6
	HCl+ pepsin	109.0 $\pm$ 17.5	30.8 $\pm$ 8.2	16.0 $\pm$ 4.5
HSB	HCl	9.0 $\pm$ 0.4	7.6 $\pm$ 0.9	0.9 $\pm$ 0.3
	HCl+ pepsin	14.0 $\pm$ 5.1	5.8 $\pm$ 1.9	5.3 $\pm$ 1.9
LSB	HCl	40.8 $\pm$ 29.6	28.1 $\pm$ 5.2	9.5 $\pm$ 13.5
	HCl+ pepsin	54.8 $\pm$ 1.7	13.1 $\pm$ 1.8	7.4 $\pm$ 3.3

HDR1, HDR2, HDR3, (HDC1, HDC2, HDC3): Hong Kong road dust, (Hong Kong car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.
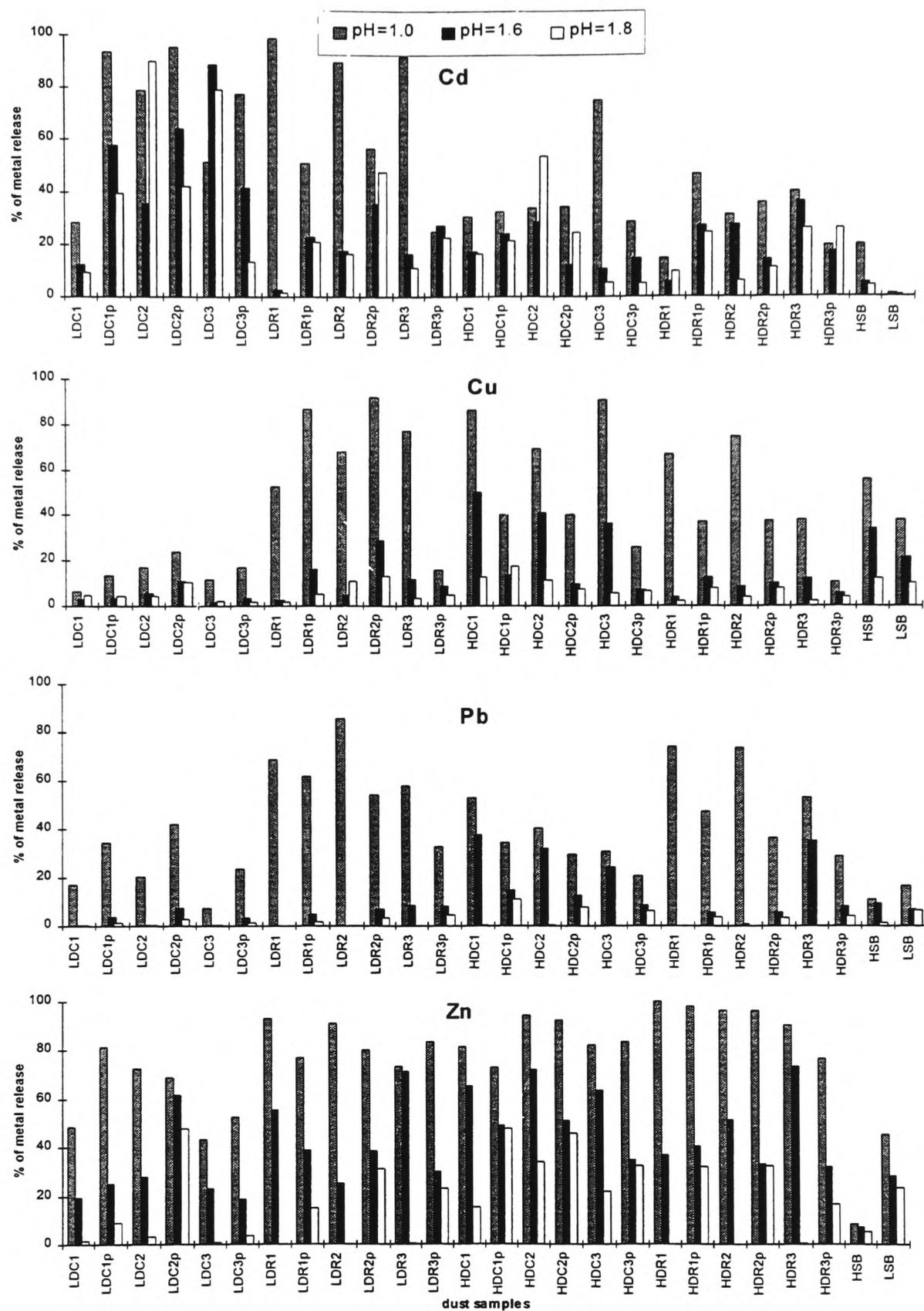LDR1, LDR2, LDR3, (LDC1, LDC2, LDC3) : London road dust, (London car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.

Table 6.5 Concentrations (arithmetic mean ± sd, µg g^{-1}) of Zn released under different simulated gastric conditions after 8 hours.

	solution	pH 1.0	Zn (µg g-1) pH 1.6	pH 1.8
LDC1	HCl	1212.7 ± 22.9	485.8 ± 38.8	36.7 ± 1.1
	HCl+ pepsin	2023.4 ± 74.3	625.3 ± 330.2	220.9 ± 265.5
LDC2	HCl	1290.5 ± 52.1	495.7 ± 104.5	54.3 ± 0.9
	HCl+ pepsin	1224.4 ± 931.9	1090.5 ± 1.7	849.0 ± 304.7
LDC3	HCl	721.5 ± 38.7	387.2 ± 7.9	14.9 ± 1.4
	HCl+ pepsin	874.6 ± 151.2	312.1 ± 53.9	63.5 ± 20.8
LDR1	HCl	2790.6 ± 53.0	1864.3 ± 18.9	3.4 ± 0.8
	HCl+ pepsin	2581.6 ± 154.5	1299.0 ± 202.1	499.1 ± 132.6
LDR2	HCl	1434.9 ± 77.5	483.5 ± 351.3	2.4 ± 0.3
	HCl+ pepsin	1542.5 ± 396.5	737.5 ± 135.4	603.0 ± 25.5
LDR3	HCl	1081.0 ± 305.5	910.9 ± 173.7	4.8 ± 0.9
	HCl+ pepsin	1050.8 ± 372.7	384.6 ± 45.8	298.1 ± 27.7
HDC1	HCl	466.4 ± 17.9	375.1 ± 25.3	88.7 ± 2.5
	HCl+ pepsin	418.0 ± 17.1	281.0 ± 21.7	274.5 ± 6.8
HDC2	HCl	587.7 ± 39.0	448.5 ± 81.4	210.9 ± 48.2
	HCl+ pepsin	575.9 ± 10.1	317.1 ± 9.1	285.2 ± 72.0
HDC3	HCl	473.7 ± 25.4	366.9 ± 14.1	126.7 ± 13.7
	HCl+ pepsin	479.0 ± 33.3	199.6 ± 38.9	185.3 ± 43.4
HDR1	HCl	2394.3 ± 48.3	887.2 ± 20.2	3.3 ± 0.4
	HCl+ pepsin	2346.6 ± 128.5	968.1 ± 203.9	765.9 ± 226.9
HDR2	HCl	1986.4 ± 40.2	1065.0 ± 14.2	4.0 ± 0.4
	HCl+ pepsin	1988.1 ± 80.7	684.7 ± 236.1	670.1 ± 143.7
HDR3	HCl	1560.5 ± 305.5	1270.1 ± 143.6	6.7 ± 1.1
	HCl+ pepsin	1327.6 ± 97.0	552.0 ± 73.9	289.6 ± 21.0
HSB	HCl	13.0 ± 1.3	11.3 ± 0.1	8.3 ± 0.4
	HCl+ pepsin	68.6 ± 16.1	43.0 ± 1.9	35.5 ± 3.1
LSB	HCl	31.9 ± 0.5	30.9 ± 0.4	4.7 ± 0.9
	HCl+ pepsin	71.2 ± 2.0	48.0 ± 5.0	49.7 ± 16.3

HDR1, HDR2, HDR3, (HDC1, HDC2, HDC3): Hong Kong road dust, (Hong Kong car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.
LDR1, LDR2, LDR3, (LDC1, LDC2, LDC3) : London road dust, (London car park dust) 0-125 m, 125-250 m, 250-500 m, respectively.

HDR1, HDR2, HDR3: Hong Kong road dust 0-125 μm, 125-250 μm, 250-500 μm, respectively;
HDC1, HDC2, HDC3: Hong Kong car park dust 0-125 μm, 125-250 μm, 250-500 μm, respectively.
LDR1, LDR2, LDR3: London road dust 0-125 μm, 125-250 μm, 250-500 μm, respectively.
LDC1, LDC2, LDC3: London car park dust 0-125 μm, 125-250 μm, 250-500 μm, respectively.
LSB and HSB are London soil and Hong Kong soil, respectively;
p stands for the saline HCl and 1% pepsin solution, the other is saline HCl solution

Figure 6.1 Percentages of metal release at different simulated gastric conditions after 8 hours.

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Table 6.6 Significant correlation coefficients (n=36, $|r| \geq 0.5$, $p < 0.05$)for the Cd, Cu, Pb and Zn extracted under different acid conditions.

Extracted by saline hydrochloric acid

	Cd (pH 1.8)	Cu (pH 1.0)	Cu (pH 1.6)	Cu (pH 1.8)	Pb (pH 1.0)	Pb (pH 1.6)
Pb (pH 1.8)	0.7*					
Zn (pH 1.0)		0.7**			0.8***	
Zn (pH 1.6)			0.6***			0.8***

Extracted by saline hydrochloric acid plus 1% of pepsin

	Cd (pH 1.8)[P]	C u (pH 1.0)[P]	Cu (pH 1.6)[P]	Cu (pH 1.8)[P]	Pb (pH 1.0)[P]	Pb (pH 1.6)[P]	Pb (pH 1.8)[P]
Pb (pH 1.8)[P]				0.7**			
Zn (pH 1.0)[P]							
Zn (pH 1.6)[P]						0.6***	
Zn (pH 1.8)[P]				0.8***			0.7***

r: correlation coefficient; [P] : pepsin in solution; *:p< 0.05; **:p<0.001; ***: p<0.0001.

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6.3.2 In vitro, kinetic analyses of metal release under simulated gastric condition

Concentrations (μg ml^{-1}) and percentages of metal released from dust samples under simulated gastric conditions are shown in Figures 6.2, 6.3, 6.4 and 6.5. The amounts of metal released from dust samples were affected by the time of leaching and the pH of the extraction solution. In general, the release of Cd, Cu, Pb and Zn from the urban street dust samples followed a fast and a slow release pattern. The majority of metal release rates were much faster within the first 20 minutes, and then slowed down with time and increased pH. The Cd, Cu, Pb and Zn release patterns in Figures 6.4 and 6.5 are similar to the results of the time dependency of these metals release kinetics at pH 1 (see Figures 4.9a and 4.9b) described in Chapter 4 Section 4.3.4.1.

In Figure 6.2, saline HCl solution was used as the extractant to assess the time dependent metal release kinetics from urban street dust. Similar amounts (μg ml^{-1}) of Cd, Cu, Pb and Zn release were found in dust samples from HDC and HDR sites. Dust samples from LDR and LDC sites had a higher amount of Cd and Pb release than from HDR and HDC site dust except Pb at pH 1.8, while higher amounts of Cu and Zn were found in HDR and HDC sites (see Figure 6.2). On the other hand, when dust samples were extracted by 1% pepsin saline HCl solution (Figure 6.3), metal release from LDC and HDC sites generally decreased, while dust samples from LDR and HDR sites did not show much influence due to pepsin. In Figure 6.3, the investigated metals show a higher amount of metal release from the road dust than from the car park dust except in the case of Cd. However, no significant difference ($p < 0.05$) in metal release is found between the saline extractant solution with pepsin and without pepsin.
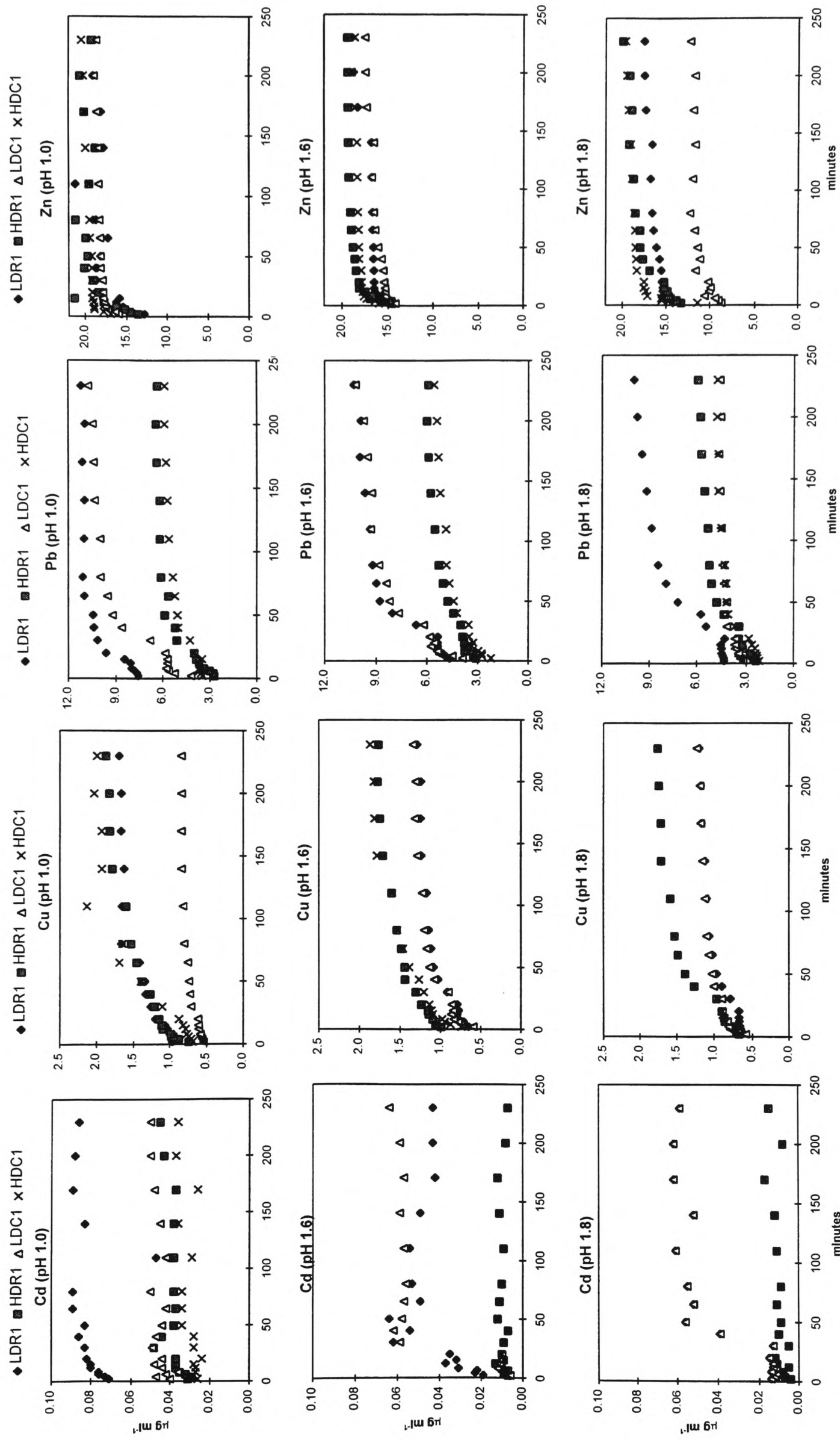
Figure 6.2 Time dependent concentrations (μg ml^{-1}) of metal release under simulated gastric condition at pH 1.0 , 1.6 and 1.8 saline HCl solution in different dust samples.

LDR1 : London road dust < 125 μm; HDR1 : Hong Kong road dust < 125 μm; LDC1 : London car park dust < 125 μm; HDC1 : Hong Kong car park dust < 125 μm

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Figure 6.3 Time dependent concentrations ($\mu g\ ml^{-1}$) of metal release under simulated gastric condition at pH 1.0 , 1.6 and 1.8 saline HCl and 1% pepsin solution in different dust samples.

LDR1: London road dust <125 μm; HDR1; Hong Kong road dust < 125 μm; LDC1 : London car park dust < 125 μm; HDC1 : Hong Kong car park dust < 125 μm

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Percentages of Cd, Cu, Pb and Zn release using pH 1 extraction solution after 4 hours at a temperature of 37 °C were 25-80%, 60-90%, 40- 90% and 65- 99%, respectively (see Figure 6.4 and Figure 6.5).

The results show that metals released from dust using pH 1.0, 1.6 and 1.8 solutions generally followed a fast-slow reaction pattern. The pattern showed a very rapid extraction during the first 20 minutes followed by a much slower extraction rate. A similar release pattern of metals from waste and soil samples at pH 1 solution was found by Casser et al. (1996).

The complexity of diffuse sources of contaminants in urban areas, such as those of metals in urban street dust, which consist of multiple geochemical phases of metals and substantial mixing with other materials, leads to complex surface reactions and release mechanisms.

Previous studies (such as Spark, 1989) have tried to apply simple mathematical equations to the empirical data to describe the complex system on soil and contaminated waste. Effort has been made to use first order, second order, parabolic, polynomial, logarithmic and power equations in these studies. An empirical model consisting of two first order equations is adopted in this study, because it provides the best fit to the metal release data:

$$C = C_1\left(1 - \exp\left(-k_1 t\right)\right) + C_2\left(1 - \exp\left(-k_2 t\right)\right) \qquad (6.1)$$

where C_1, C_2, k_1 (min^{-1}) and k_2 (min^{-1}) were fitted parameters which can be determined by fitting the data point (t, C_k^i) using the program Solver in Microsoft Excel and determining the minimum of a sum of squares,

$$\sum_{i=1}^{n}\left(C_{k,observed}^i - C_{k,calculated}^i\right)^2 \qquad (6.2)$$

where n is the total number of data points. Note that this model is not the same as the first order reaction kinetic model used to explain the kinetics of dust particles in solution in Chapter 4, Section 4.3.4.1.

The dissolution of metal from the metal-bearing materials at specific environmental conditions can be thought of as a complex of binding sites such as bonding to exchangeable, carbonate, oxides or organic fractions discussed in earlier chapters (Chapters 3 and 4). Hydrogen ions (H^+) play an important role in displacing Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} from the surface of contaminated solids which can be represented as lumped chemical equilibria of the type:

$$SO\text{-}M^+ \; + \; 2\,H^+ \; \leftrightarrow \; SO\text{-}H_2^+ \; + \; M^{2+} \qquad\qquad (6.3a)$$

or

$$(SO)_2 = M \; + \; 2\,H^+ \leftrightarrow 2\,SOH \; + \; M^{2+} \qquad\qquad (6.3b)$$
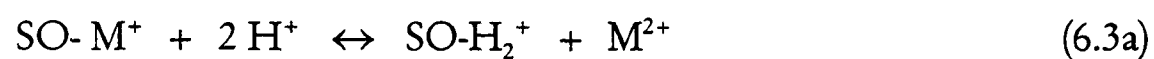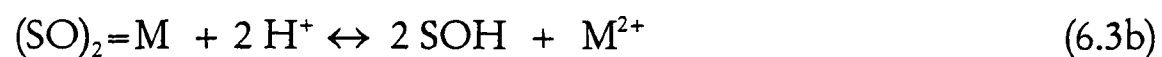
where M^{2+} is the divalent metal ions, SO represents a surface oxygen group and SOH is a surface hydroxyl group. In the presence of chloride ion in the form MCl_x (x = 1, 2), the solubility of M (e.g. Cd, Cu, Pb and Zn) will increase in the GI system (Healy, 1982; Gasser, et al., 1996).

The finest dust (< 125 μm) was chosen for a detailed kinetic study at pH 1, on the assumption that this range of particle is most likely to adhere to children's hands and consequently to be ingested. According to the kinetic model, equation (6.2), (see examples in Appendices Figure 5) the results of the dust dissolution from the simulated gastric solution at pH 1 is shown in Table 6.7. Table 6.7 shows the results of selected parameters and half-life of reactions for four representative finest dust samples using two simultaneous

first order equations at pH 1. The half life is seen to be an effective way of summarising data from the kinetic experiments. The half life of the reaction ($t_{1/2}$) is defined by the time require to consume half of the original amount of compound for a first order reaction, which can be written as:

$$t_{1/2} = \frac{\ln(2)}{k} \qquad (6.4)$$

where k is the rate constant with a unit of time^{-1} (Lasaga, 1981). The half-life of fast reactions (Table 6.7) obtained from kinetic experiments take less than two minutes while in the slow reaction they take a much longer time (68-144 minutes).

Figure 6.4 Time dependent percentages of metal release under simulated gastric condition at pH 1.0, 1.6 and 1.8 saline HCl solution in different dust samples.
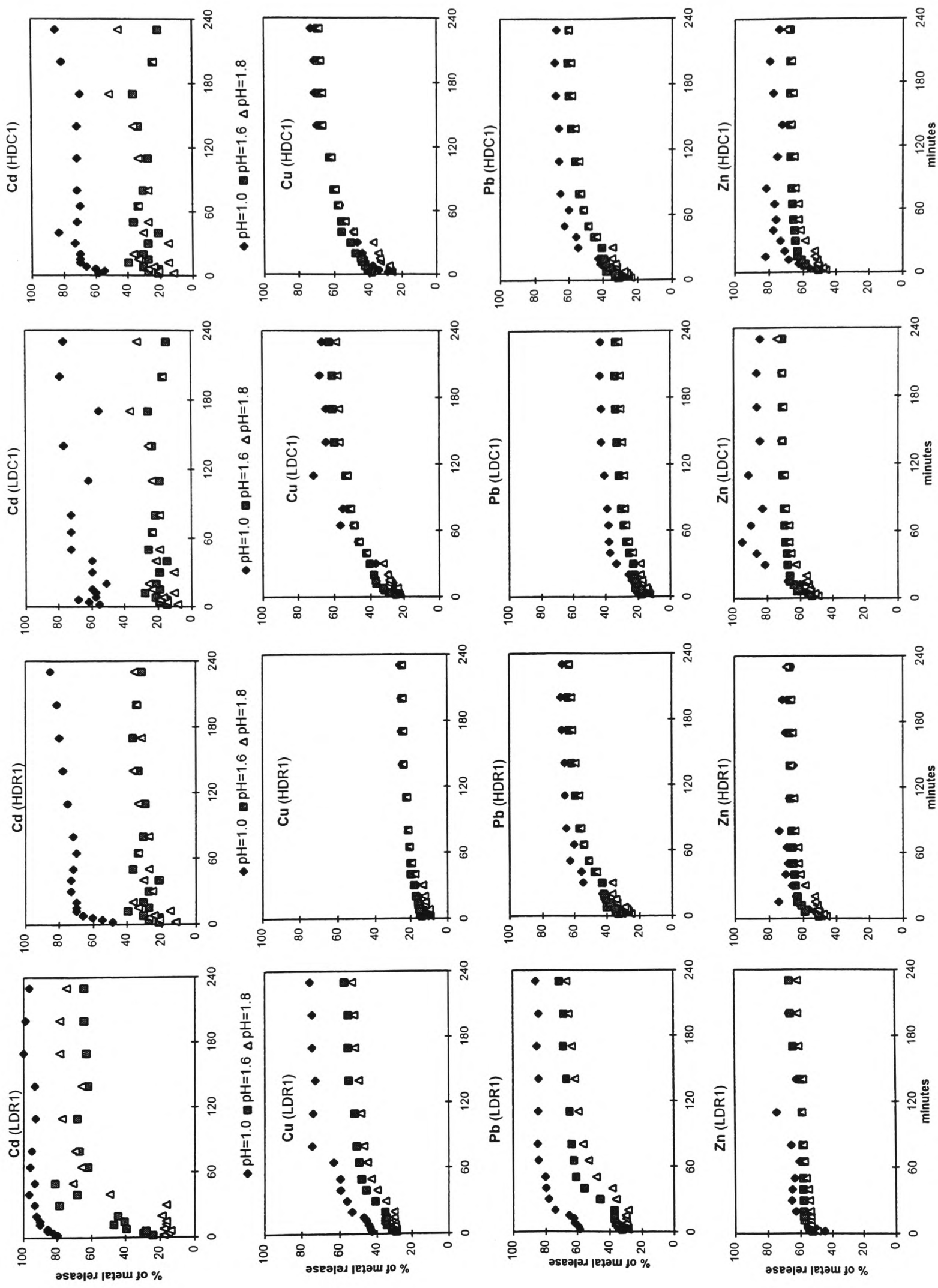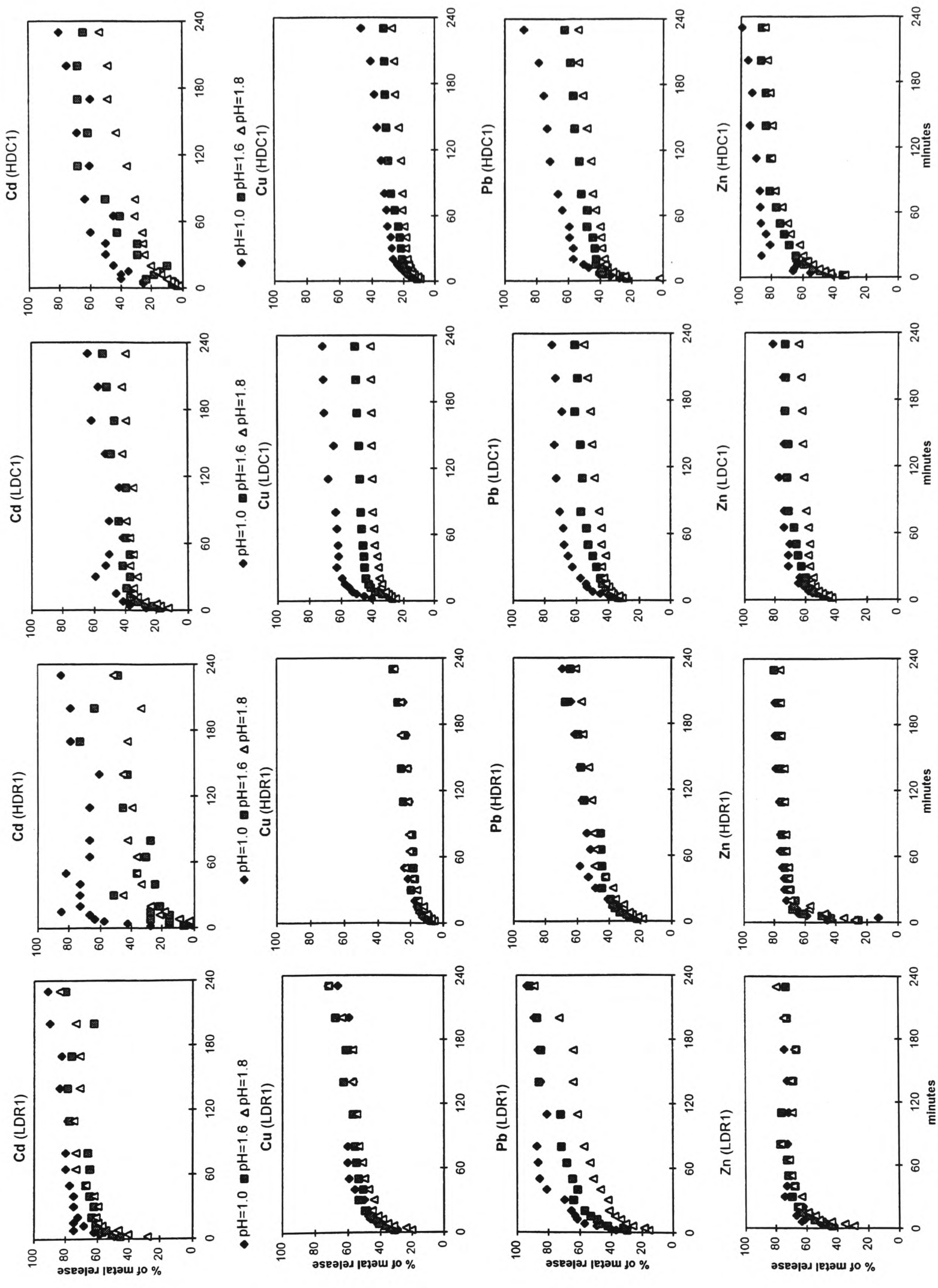
LDR1 : London road dust < 125 mm; HDR1 : Hong Kong road dust < 125 mm; LDC1 : London car park dust < 125 mm; HDC1 : Hong Kong car park dust < 125 mm

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Figure 6.5 Time dependent percentages of metal release under simulated gastric condition at pH 1.0 , 1.6 and 1.8 HCl with 1% pepsin solution in different dust samples.

LDR1 : London road dust < 125 µm; HDR1 : Hong Kong road dust < 125 µm ; LDC1: London car park dust < 125 µm; HDC1: Hong Kong car park dust < 125 µm.

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Table 6.7 Application of two first order reactions kinetic model to Cd, Cu, Pb and Zn for urban street dust samples at pH 1 and temperature 37 °C.

	Cd		Cu		Pb		Zn	
	mean	range	mean	range	mean	range	mean	range
k_1 (min^{-1})	1.59	(0.22-3.19)	0.62	(0.10-0.98)	0.63	(0.19-1.02)	1.83	(0.2-8.5)
k_2 (min^{-1})	0.03	(0.02-0.14)	0.04	(0.001-0.09)	0.02	(0.006-0.036)	0.05	(0.003-0.139)
$t_{1/2}$ (k_1) (min)	1.0	(0.2-3.1)	1.4	(0.7-7.2)	1.3	(0.7-3.6)	1.1	(0.08-3.41)
$t_{1/2}$ (k_2) (min)	144	(5-253)	108	(7-474)	68	(18-177)	76	(5-217)
C_1 (µg g^{-1})	2.8	(0.7-7.0)	72	(60-121)	349	(178-802)	1300	(482-2062)
C_2 (µg g^{-1})	1.6	(0.1-3.3)	89	(4-166)	332	(181-596)	512	(283-881)
% of metal release:								
after 20 min (%)	60	(37-85)	30	(13-45)	41	(18-62)	76	(61-95)
after 240 min (%)	74	(59-98)	44	(23-59)	60	(24-89)	85	(79-97)
r^2	>0.65		>0.75		>0.85		>0.7	

r^2: the square of the Pearson product moment correlation coefficient.

6.4 Discussion

6.4.1 In vitro, dilute acid extraction under simulated gastric condition

The study of Cd, Cu, Pb and Zn release from urban street dust under simulated gastric conditions demonstrates the role of pH in determining the amount of metal from ingested dust in the stomach. The results showed that high acidity together with Cl⁻ ligands will increase the solubility of Pb in the GI system. Healy et al. (1982) demonstrated the solubility of Pb sulphide in gastric fluid and found that Pb sulphide is extensively solubilised by acidic gastric juice (pH 1 to 3.5) to lead chloride. In contrast to the high amount of Cd and Pb release (up to 90%), for some metals only a small amount ($<$ 10%) of the metal is released from the dust such as under pH 1 acidic gastric juice Cu release from LDC1, LDC2 and LDC3. This further reveals that the different metal ligands in street dust are also likely to influence the metal release mechanism, even though at the low pH of the extraction solution some metal ions still remain bound to particles in the dust.

At pH 1.0, 1.6 and 1.8, the fraction of Pb released from the dust samples were $\leq$ 90%, $\leq$40 % and $\leq$ 15 %, respectively, after extraction by acidic solution after 4 hours. However, Sheppard et al., (1995) found that over 90% of Pb was extracted by dilute HCl after 24 h at pH 2.0 when they investigated 11 soils treated with artificial $Pb(NO_3)_2$. Nevertheless few studies have determined "available" metals using hydrochloric acid as the extractant (e.g. Harrison, 1979), so it is difficult to make comparisons.

Previous studies have suggested that the particle size of metal-bearing media is also an important factor in the enteric mobilisation; the smaller the particle, the more easily it will be dissolved in the stomach or elsewhere in the GI tract (Barltrop and Meek, 1979; Healy et al., 1982; Bornschein et al., 1987). However, no significant difference has been found among selected

particle size ranges (< 125, 125-250 and 250-500 μm) under simulated gastric fluid extraction. This may indicate that the dust particles less than 500 μm in diameter are likely to form a homogeneous group in terms of metal release under simulated gastric conditions.

High percentages (ca. 60-90 %) of Pb release were found from dust samples collected from the two road (Figures 6.4 and 6.5). This shows that Pb from the road sites dust has a high potential risk for the urban population once it has been ingested. Cadmium is normally more abundant and mobile in dust from LDC and LDR sites while Zn is more mobile from HDR and HDC sites under simulated gastric conditions (Figure 6.3).

In Table 6.6, the significant correlation between Pb /Zn and Cd /Pb may be caused by related sources in geochemical cycle while the significant correlation of Cu/Zn and Cu/Pb may be associated with common man-made activities. However, no consistent pattern is seen and there is no sufficient data to perform a detailed statistical analysis and to determine the source-receptor relationship in urban environment.

6.4.2 In vitro, time dependent metal release under simulated gastric condition

Time dependent Cd, Cu, Pb and Zn release under different pH conditions was determined on representative dust samples for particle size range less than 125 μm. In general, particles in this size fraction adhere more easily to hands (Bornschein *et al.*, 1987; Duggan *et al.*, 1985) and are also readily mobilised in gastric or other acidic media (Healy et al., 1982; Day et al., 1979). The pH of the gastric fluid in children can reach about 1 (Connell, 1974).

Isotope absorption of heavy metals in adults and Pb balance studies in children have been attempted to understand the heavy metal bioavailability

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in the GI tract. Cadmium, Cu, Pb and Zn often exist in the environment as a mixture of metal salts, soil/dust bound metal or metal incorporated into a food matrix. The oral bioavailability of these metals depends on the solubility of these metal forms in the GI tract. In general, the more soluble forms are the more bioavailable (Sheppard, *et al.*, 1995). In the GI tract, the greatest dissolution will occur in the stomach because of the high acidity of the gastric fluid in the stomach. Once the gastric fluid leaves the stomach it will be neutralised in the duodenum with a pH $\cong 7$ and the metal is unlikely to dissolve from the particle under these circumstances.

Under conditions when the metal is readily dissolved in a solvent, the dissolution rate (Healy, 1984) may be represented by the time dependent equation as follows,

$$\frac{dC_s}{dt} = k_s\left(C_1 - C_s\right) = \frac{DS}{h}\left(C_1 - C_s\right)$$
(6.4)

where C_s is the concentration of the metal dissolution in bulk; C_1 is the solubility of the metal in the solvent; D is the diffusion coefficient of heavy metal in the medium; S is the surface of the undissolved solid; h is the diffusion layer thickness around the particle; k_s is the dissolution rate constant. The dissolution rate may vary according to the solubility, diffusion coefficient, thickness of aqueous film, surface area of the particle. The substance may be fully solubilised in theory when particle size decreases to a sufficiently small diameter and S becomes sufficiently small (Healy, 1984). Then the solubility will act as the key determinant of dissolution. Metal may not be effectively absorbed, regardless of the ease of penetration to the cell membranes because of the low solubility of solid particles in gastric fluid. The solubility can be varied by the dissolution medium in the gastric fluid and the pH range in the GI tract.

Although pepsin is an important enzyme for the digestion of protein in the stomach under *in vitro* time dependent simulated gastric conditions, the percentages of Cd, Cu, Pb and Zn released in saline gastric solution were not significantly different after the addition of 1% of pepsin. This shows that pepsin may not have a great influence on metal release from the urban dust samples.

In the time dependent metal release kinetic experiment, a higher amount (μg ml^{-1}) of Cd was released from the London dust than from the Hong Kong dust. The opposite was true for Zn. This observation coincides with the results from the batch leaching experiment in Section 6.4.1. These results suggest that Cd in urban dust from London and Zn from Hong Kong were enriched and attention should be paid to these metals in addition to Pb.

The results (Table 6.7) of the kinetic model for dust samples indicate that the two simultaneous first order equations provide a good fit ($r > 0.8$) to the metal release data. The model suggests the presence of two metal pools reacting at different rates. The corresponding half-life of each reaction pool have been calculated from the kinetic model. The half-life of reactions provides important information with regard to the residence time of metal-bearing dust in the gastric system. The relatively short half-lives suggest that metal release from these samples will be fast under simulated gastric conditions. The mobility of Zn and Cd was greater than that of Pb and Cu after the first few minutes of extraction, because Zn and Cd had a higher percentage release than Pb and Cu.

According to the model, the fast reacting pool of metals are those which have less affinity to the dust and are ready to dissolve in solution form in a very short time while the slow reacting pool of metals are those which are relatively strongly bound to dust and require relatively more time to dissolve

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in the acid solution. Ingested material steadily passes through the GI system and generally the residence time of food in children's stomachs is less than 4 hours (cited by Gasser *et al.*, 1996). Therefore, the period soon after urban dust ingestion by children may pose the greatest risk to their health because the most dissolved forms of metal will become available at a very short time (such as 5 minutes) after dust ingestion.

6.4.3 Comparison with sequential extraction

The matrix of the metal-containing non-food media of geochemical origin is one of the major factors in the metal solubility in the GI tract, and it affects the bioavailability which is an important factor on the toxicity threshold for risk population. Hence physiochemical metal species (studied in Chapters 3 and 4) of dust are also an important influence on the release of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} from the dust in the gastrointestinal tract. The relationship between chemical speciation presented in Chapter 3 and metal release kinetics under simulated gastric conditions shows that the amounts of Cd and Pb released are well correlated with the sum of the first four fractions (exchangeable + carbonate + hydrous Fe/Mn oxides + organic fractions) of a sequential extraction, while the amount of Cu released only correlated with the sum of the first three fractions (Figure 6.6). Under gastric extraction, although a high amount of Zn was released ($>70\%$) from the study samples, Zn release was found to have no correlation with the results of the sequential extraction. Hence the sequential extraction may provide valuable information on the ease of metal released from dust particles, according to the operational definition of the differences of geochemical fractions and this may possibly be used to describe the metal dissolution kinetic from the well controlled laboratory experiments in the case of Cd, Cu and Pb as in the present study. However, sometimes the operational application of a sequential extraction fails to describe the metal release kinetics, such as in the case of Zn in the present study.
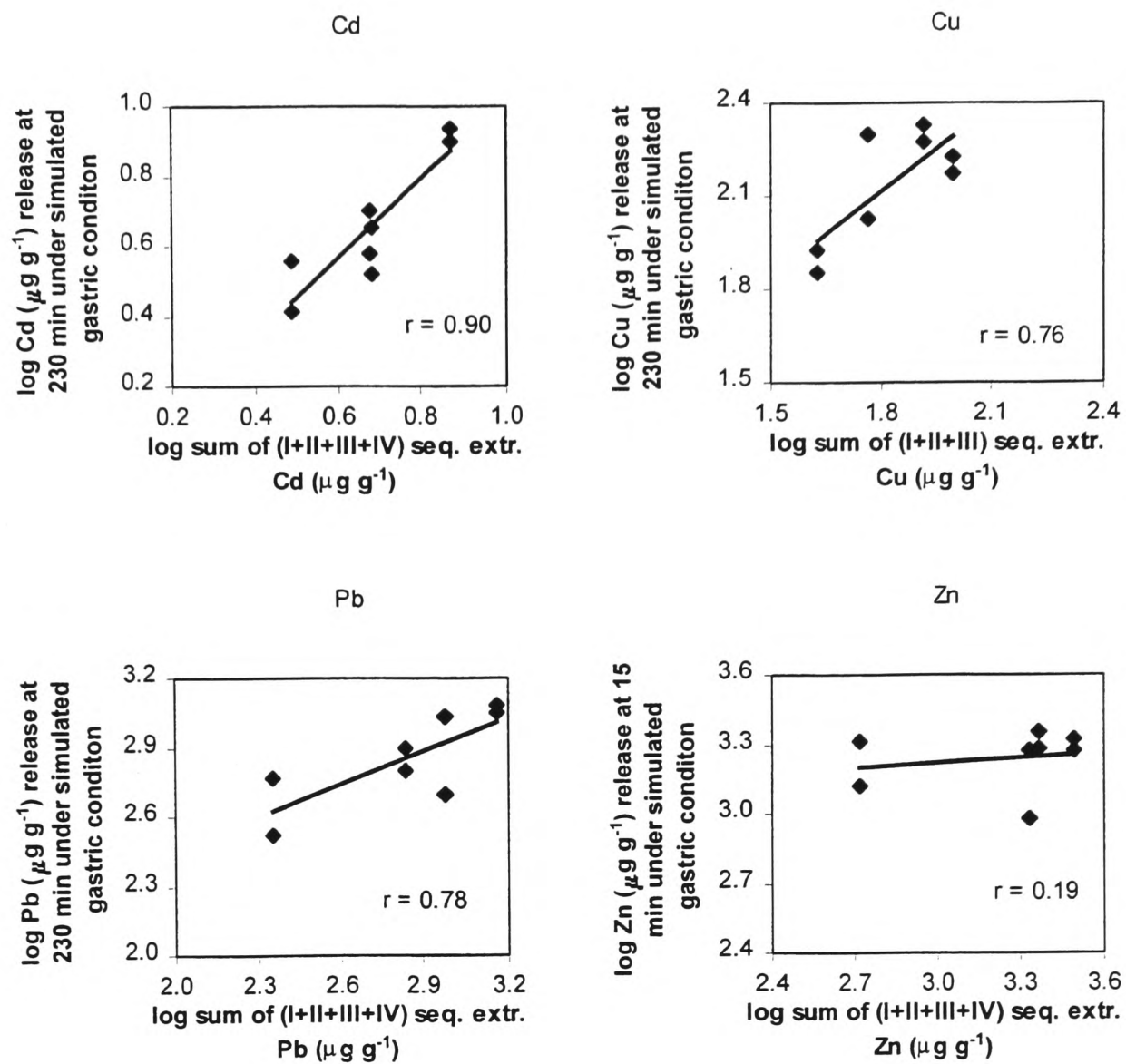
Figure 6.6 Correlation of the sum of the first four fractions (I: exchangeable; II: carbonate; III: hydrous Fe-Mn oxides; IV: organic fraction) of sequential extraction for Cd, Cu, Pb and Zn versus Cd, Cu, Pb and Zn release from the dust sample after 230 min at pH 1.

6.5 Summary

Under batch simulated gastric conditions, the percentages of Cd released from the London dust were significantly higher than those from the Hong Kong dust, while more Pb was released from the road dust than from the car park dust. There are some differences in availability under a simulated gastric conditions which were not apparent in the chemical leaching test presented in Chapter 4.

According to the time dependent simulated gastric conditions, the mobility of the Zn and Cd from the dust samples was higher than that of Pb and Cu. Metal dissolution rates and kinetic modelling using two simultaneous first order reactions suggest that there are at least two major metal pools reacting at different rates (fast and slow) which is similar to the kinetic study at pH 1 in Chapter 4 Section 4.3.4.1. The half-life of the fast reaction ranged between 0.2-3.1, 0.7-7.2, 0.7-3.6 and 0.08-3.41 minutes for Cd, Cu, Pb and Zn respectively, while the slow reaction half-life ranged between 5-253, 7-474, 18-177 and 5-217 minutes. The relatively short half-life suggests that metal release from these dust samples will be fast under simulated gastric conditions and go to completion in the gastric system.

The addition of 1% pepsin does show some effect on the amount of the metal release from the dust samples in batch studies under simulated gastric conditions although no consistent results have been found. Hence, the role of pepsin in the current simulated gastric studies requires further work to clarify its effect on metal release from dust.

The overall dissolution of Cd, Pb and Cu from urban dust under time dependent simulated gastric conditions at pH 1 after 4 hours correlated well with different fractions of metal in the sequential extraction

reported in chemical leaching test. The Cd and Pb release are positively significantly correlated with the sum of the first four fractions (exchangeable + carbonate + hydrous Fe/Mn oxides + organic fraction) of Tessier's sequential extraction, while Cu release depends on the first three fractions of sequential extraction (exchangeable + carbonate + hydrous Fe/Mn oxides fraction).

In general, heavy metals were readily released during the first 20 minutes under simulated gastric conditions. After 4 hours, Cd, Cu, Pb and Zn release from dust samples reached 75%, 45%, 60% and 85% respectively. These fractions are much higher than those fractions found in most natural environments (see Chapter 4 Section 4.3.4).

Given these high percentages of release and the length of the time that material takes to pass through the GI system, it would be appropriate to use the total metal concentration in dust in a risk assessment based on the availability of Cd, Cu, Pb and Zn through the ingestion pathway.

FRACTIONATION AND BIO-TOXICITY OF HEAVY METALS IN URBAN DUSTS COLLECTED FROM HONG KONG AND LONDON

7.1 Introduction

Heavy metals have a long residence time in the environment and can be accumulated in food chains so they can have long-term hazardous effects on biota. With the increasing awareness of the long-term effects of many heavy metals in different media (e.g. dust, soil, sediment, water and air), research has focused on short-term bioassay tests which attempt to quickly alert dischargers as well as monitoring agencies of potentially toxic conditions (Dutka and Kwan, 1981). Traditional chemical tests cannot ensure that all toxic chemicals of consequence will be identified and measured in the sediment of interest; nor can they be used to estimate synergistic effects among compounds in a mixture. Biological toxicity testing has, therefore, become an important tool in supplementing the traditional environmental monitoring programs based on chemical tests to characterise complex chemical mixtures in sediment and water.

7.1.1 Biological toxicity

Biological toxicity testing is based on exposing test organisms to all the bioavailable chemicals in a test sample and then noting the changes in biological activity, such as reproduction and respiration (Ribo *et al.*, 1985). The selection of organisms for a biological toxicity test depends on the chemicals present in the sample, the prediction to be made, the time required and costs involved in performing a test. Toxicity is commonly described as a complex continuum of biochemical, physiological, whole organism,

population and community responses among a broad diversity of living organisms (Luoma, 1995). Simplicity is both a requirement and an advantage of bioassay methodologies. Simple bioassays are less expensive and more amenable to standardisation than field studies. If bioassays were direct indicators of environmental damage, they could be used to predict the level of environmental toxicity required for the management of metal contaminants (Blum and Speece, 1990; Long et al., 1990).

Although bioassays based on contaminants present in the dissolved phase in aquatic environment, sediment bioassays have also been recently developed (Ross et al, 1988; Chapman, 1988; Burton and Scott, 1992).

7.1.1.1 Higher plants

Methods of seed germination and root elongation of higher plant species have been recommended for ecotoxicity tests by many legislative organisations (USFDA, 1987; OECD, 1984). These methods have also been successfully used to screen the metal tolerance of plants and to study metal toxicity to plants (e.g. Wong and Bradshaw, 1982; Wong and Lau, 1985; Baker et al., 1994). Plants are essential in the processes of nutrient cycling and soil and sediment stabilisation (Wang and Freemark, 1995) and also produce oxygen for other organisms; therefore the toxicity effect of toxic substances on plants can directly or indirectly affect the structure and function of ecosystems as well as individuals. All plants respond to an increase in heavy metal concentration in their immediate environment. For essential elements, the response (measured by yield) progresses from deficiency through tolerance and eventually to toxicity when the heavy metal concentrations are increased. In the case of non-essential elements, only the tolerance and toxicity stages are observed. For most metal toxicants, toxicity is first experienced in the root tips of plants; however plants are further influenced by metal toxicity via such mechanisms as

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damage of enzyme systems, genetic damage to DNA via metal binding, as well as toxic effects (Freeman, 1995).

7.1.1.2 Algae

Algae have been widely used as toxicity test organisms because they are essential components of aquatic ecosystems; algae are also at the base of food chains and produce organic substances on which most other forms depend (Benenati, 1990). Furthermore, algal bioassays are relatively simple, rapid and inexpensive when compared with other toxicity tests using fish and invertebrates (Wong and Coulture, 1986). The algal toxicity test has been widely adopted by various environmental regulatory bodies in North America and OECD countries (Wang and Freemark, 1995).

7.1.1.3 Luminescent bacteria

Traditional bioassays for testing sediment and soil samples are normally performed on water or solvent extracts; however this might underestimate or overestimate the exposure routes (Ongley *et al.*, 1988, Kwan and Dutka, 1990). A newly developed Microtox® Solid-phase Test using luminescent bacteria may eliminate these problems (Brouwer *et al.*, 1990; Kwan and Dutka, 1992; Kwan, 1993) and may indicate the true bioavailability of tested samples. The luminescent bacteria bioassays are widely used for acute toxicity tests primarily because they are easy to perform and results can be obtained within a short period of time (Nohava *et al.*, 1995).

7.1.2 Aim

The aim of this study is to compare the chemical forms of Cd, Cu, Pb and Zn contained in different urban dust samples from Hong Kong and London and to assess the toxicity of these urban dust samples using organisms at different trophic level: *Dunaliella tertiolecta* (*D. tertiolecta*, a dino-flagellate

green alga), *Brassica chinensis* (*B. chinensis*, a Chinese white cabbage), *Lolium perenne* (*L. perenne*, rye grass) and *Photobacterium phosphoreum* (*P. phosphoreum*, a luminescent bacterium). Correlations between chemical leaching test data and the results of toxicity tests are also studied.

7.2 Materials and methods

7.2.1 Study sites and sampling

Only the dust samples collected in September 1995 from London and in March 1996 from Hong Kong were used for the study of biotoxicity. Also used were the background soil samples collected from the Hong Kong and London sites. The sampling details and methods of chemical characterisation have been discussed in Chapter 4.

7.2.2 Bioassay methodologies

7.2.2.1 Seed germination and root elongation

To test the effect of urban dust on seed germination and root growth of the two plants, *B. chinensis* and *L. perenne*, elutriates from the urban dusts of 5%, 10%, 20%, and 40% (w/v) were prepared using distilled water and shaken at 150 rpm for 24 h before filtering through an Advantac 5 C filter paper. Twenty seeds were placed on filter papers in petri dishes with 1 ml of elutriate added every two days (see Appendix 1 Figure 1). Distilled water was used as a control. All the treatments were triplicated. The seeds were placed in a growth chamber with a temperature of 22 ± 3 °C and a light/dark cycle of 16 h/8 h and light intensity (lumen m^{-2}) of 4000 ± 500 lux (TES 1332 Digital Lux Meter). The percentage of seed germination and root length were recorded at days 2, 4 and 7 for *B. chinensis* and at days 4 and 7 for *L. perenne*.

7.2.2.2 *Algal bioassay*

The toxic effects of elutriates were assessed by the algal bioassay method modified from the standard ASTM STP 988 (Ross et al., 1988). *D. tertiolecta*, an unicellular green microscopic alga belonging to estuarine and marine plankton was chosen. The algal stock was cultured in 50 ml of MAV enrichment medium (Droop, 1969) at a constant temperature of 25±3 °C. An illumination period were maintained at 16 h /8 h light/dark cycle with a light intensity of 4500 ± 500 lux. The algal cultures were prepared for inoculum while the growth of *D. tertiolecta* was in the log phase.

Elutriates of dust samples were prepared by mixing one part of dust samples and four parts of artificial seawater following the methods described by Ankley (1991). The supernatant or elutriate was separated by using a Corning refrigerated centrifuge at 25000 rpm for 30 minutes before filtration through autoclaved 0.45 μm Millipore membrane filters. Five concentrations of each dust sample elutriate, 5%, 20%, 40%, 60% and 80% were selected with 0% of dust elutriate serving as the control and artificial seawater (prepared from commercially available salt: Marinemix, manufactured by Wiegandt Ltd, Krefeld, Germany) was used as a diluent. Elutriates of dust samples were stored at 4°C in a dark cold room. The preparation of different concentrations of elutriates is detailed in Table 7.1.

Table 7.1 The preparation of different percentages of dust elutriates

The preparation of dust elutriates						
dust elutriate (ml) (one part of dust sample was mixed with four parts of artificial seawater)	0	0.5	2	4	6	8
artificial seawater (ml)	8	7.5	6	4	2	0
algal culture (ml)	1	1	1	1	1	1
x 10 MAV enrichment medium (ml)	1	1	1	1	1	1
final volume (ml)	10	10	10	10	10	10
final percentage of dust elutriate (%)	0%	5%	20%	40%	60%	80%

For elutriate preparation, 25mm x 150mm screw type culture tubes were used. Prior to use, the culture tubes were washed with phosphate free detergent and 10% HNO_3 and then rinsed with distilled water and autoclaved. Each culture tube contained 10 ml of a different concentration of test elutriate with 5×10^4 cells ml^{-1} of the initial inoculum density of algal culture. All samples were treated in triplicate and were kept in suspension by an orbital shaker at 110 rpm (see Appendix 1 Figure 2). The temperature was maintained at 25 ± 3 °C with a 16 h/ 8h light /dark cycle and a light intensity of 4500 ± 500 lux.

At the end of 48 h and 96 h, the numbers of cells in each tube were determined by haemocytometry. The percentage increase or decrease in cell numbers at different elutriate toxicant concentrations during the test period as compared to the control was calculated using Wong and Couture's (1986) approach. The calculation is based upon the comparison of the areas below the growth curves and the inhibition of the cell growth (I_A) and is calculated as follows,

$$I_A = \frac{A_C - A_t}{A_C} \times 100\% \qquad (7.1)$$

where A_C is the area below the growth curve of the control and A_t is the area below the growth curve of toxicant-exposed cells. The EC_{30} values were determined by probit analysis (Wong and Couture, 1986) using the SAS computer software. EC_{30} was used instead of the more common EC_{50} for two higher plants and the green alga because EC_{30} has a more sensitive response than that of EC_{50}. The EC_{30} is the effective concentration to reduce the root length of the control or the algae growth of the control by 30 %.

7.2.2.3 MicroTox

In 1978, the Microtox® test was developed by Beckman Instrument company as a fast (<0.5 h run a test), reproducible, precise (with coefficients of variation of 10-20% compared to 30- 40% for fish), sensitive, accurate, standardised, cost effective and convenient method of conducting bioassays. The Microtox® test is based on the inhibition by a pollutant of the light output of luminescent marine bacterium *P. phosphoreum* after a period time exposure at 15 °C; the degree of inhibition is used as an index of the level of chemical exposure (Dutka and Kwan, 1988). Professor Frank Johnson pioneered the use of the light output of luminescent bacteria as an index of potency of physiologically active compounds in the 1940s (Iseberg, 1993). In 1974, Johnson and co-workers published the study on the factors important to the emission of light by luminescent bacteria and an equation for toxicity in "*The Theory of Rate Processes in Biology and Medicine*" (Iseberg, 1993). Hence, the basis of the Microtox® test was formulated, which uses the ratio of the activity lost to the activity remaining (Γ) to express the toxic effect. The ratio Γ uses a log-log linear equation to relate the toxic effect (Γ) to the concentration of the toxicant (C),

$$\ln(\Gamma) = b \ln(C) - \frac{\Delta G}{RT} - \frac{p\Delta V}{RT} \qquad (7.2)$$

The slope b represents the number of toxicant molecules combining with the target molecule. The intercept is a composite function of free energy (ΔG) and volume (ΔV) changes. R is the universal gas constant, p is the pressure and T is the temperature. Calculation of Γ for a number of serial dilutions of a sample can be shown as follows:

$$\Gamma = \frac{I_{tc}}{I_t} - 1 \qquad (7.3)$$

where I_{tc} is the light level (I) at incubation time (t) of the control (C) and I_t is the light level (I) at incubation time (t), for various sample concentrations. The concentration when Γ equals 1 represents an EC_{50} effect (the effect concentration causing 50% light loss) .

The Microtox® Solid-phase Test based on the Detailed Solid-phase Test Protocol (Microtox® model 500, Microbics Co.) has been developed recently. The method for the solid-phase testing allows the test marine bacteria, *P. phosphoreum*, to come into direct contact with the solid-particle-bound toxicants, in an aqueous suspension of the test sample, enabling the detection of soluble and insoluble toxic materials. Bacteria are sensitive indicators of contaminant stress and they can respond rapidly to changes in their environment. The end-point used in this study was the 20-minute EC_{50}.

7.3 Results

7.3.1 Seed germination and root elongation

There was over 90% seed germination in all the samples, which suggests that metals had no influence on seed germination. The percentage root response

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is given as the average reduction of root length exposed to the toxicant during the test period as compared to the control. The EC_{30} values were calculated based on Figures 7.1 and 7.2 and are shown in Table 7.2. The results show that road dust had a greater toxic effect at 96 h than at 48 h on *B. chinensis*; but, there was no specific trend in the 96h- and 168h- EC_{30} for *L. perenne*.

7.3.2 Algal toxicity test

Figure 7.3 shows the percentage response of *D. tertiolecta* cells to dust elutriates of different dilutions. The percentage response is calculated by comparing the average reduction in the number of algae cells exposed to the toxicant during the test period, relative to the control. The method of calculation followed Wong and Couture (1986). For *D. tertiolecta*, the ranges of 48h-EC_{30} and 96h-EC_{30} were from 1.09% to 32.70% and from 4.12% to 69.93%, respectively. For HK dust, the values of 96h-EC_{30} were higher than those of 48h-EC_{30}.

7.3.3 Microtox® Solid-phase Test

The Microtox® Solid-phase Test (SPT) detects the overall toxic response to all pollutants in the dust samples. Data obtained from the Microtox® Solid-phase Test are reported as that dilution of a sample elutriate which produces a 20 min-EC_{50} effect (50% decrease in the bacterial light output). The results of the Microtox® SPT test 20 min-EC_{50} are listed in Table 7.2 and these show that the toxic effect was associated with the small-sized dust samples.
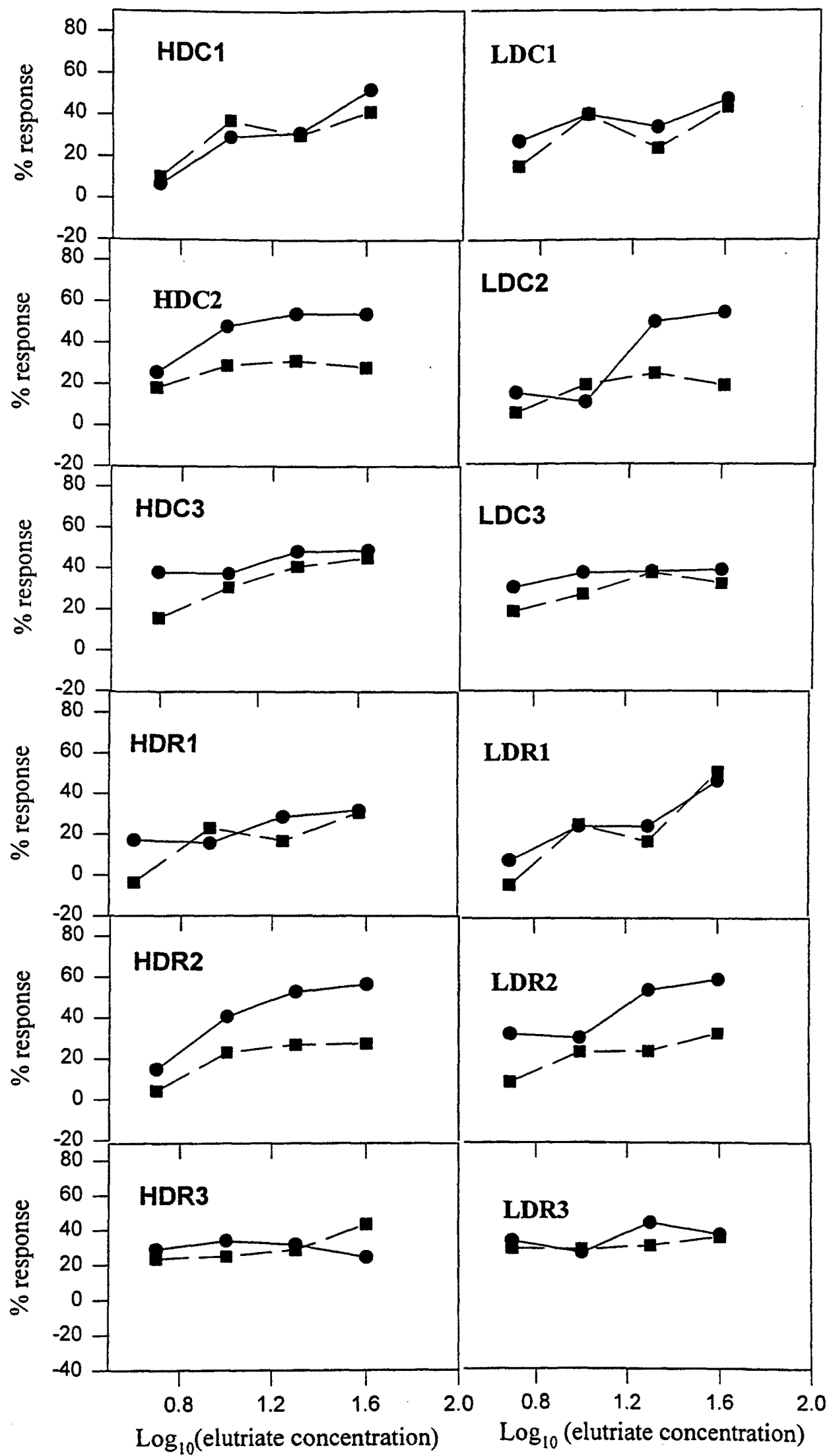
Figure 7.1 Response of Brassica chinensis to dust elutriates of different dilutions(%). A positive value indicates the % inhibition in root growth, while a negative value represents the % increase in root growth, i.e. a stimulating effect.

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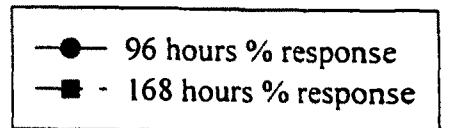
Figure 7.2   Response of *Lolium perenne* to dust elutriates of different dilutions(%). A positive value indicates the % inhibition in root growth, while a negative value represents the % increase in root growth, i.e. a stimulating effect.

● 96 hours % response
■ 168 hours % response

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Figure 7.3 Response of *Dunaliella tertiolecta* cells to dust elutriates of different dilutions(%). A positive value indicates the % inhibition in cell growth, while a negative value represents the % increase in cell number, i.e. a stimulating effect.
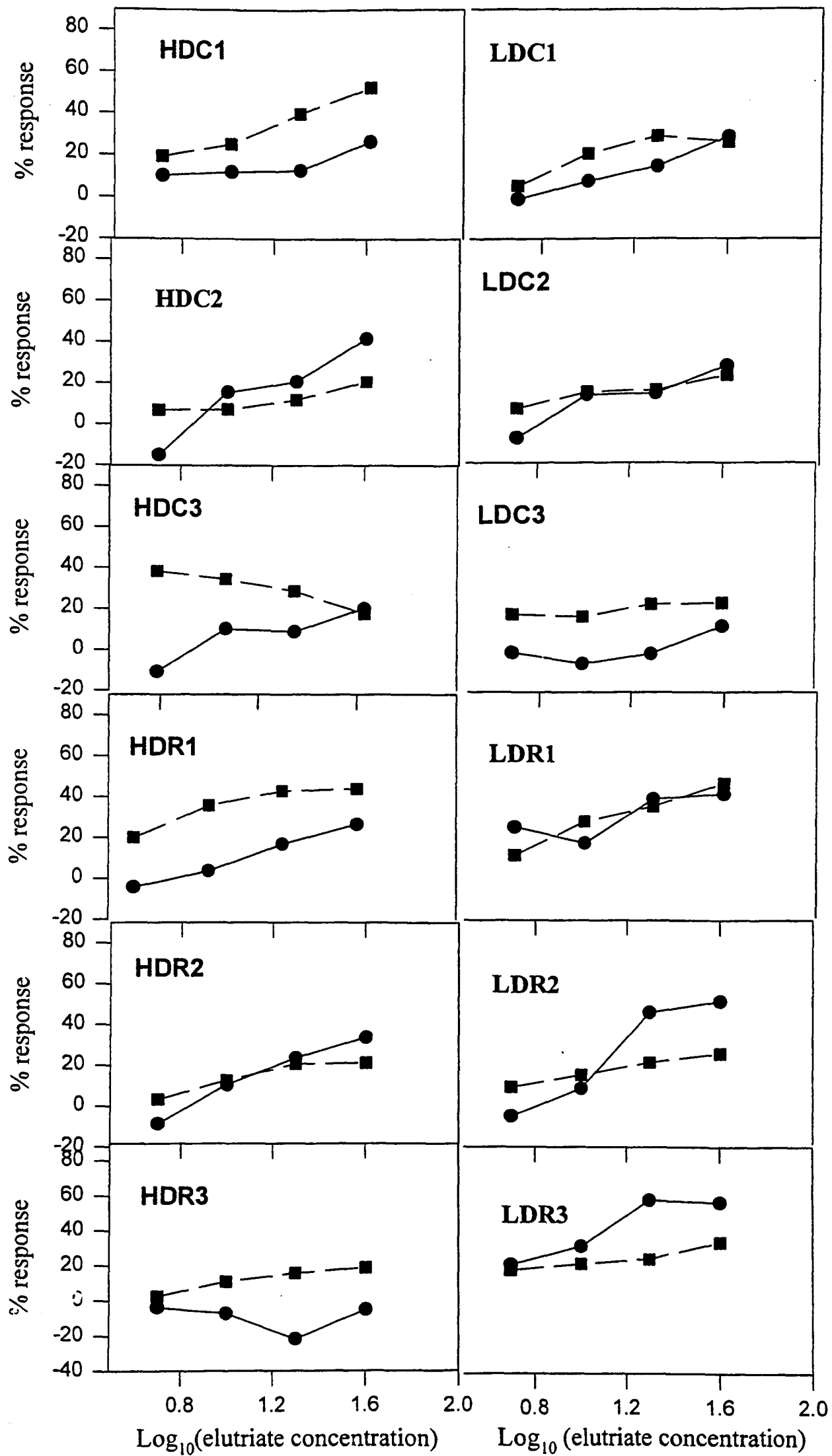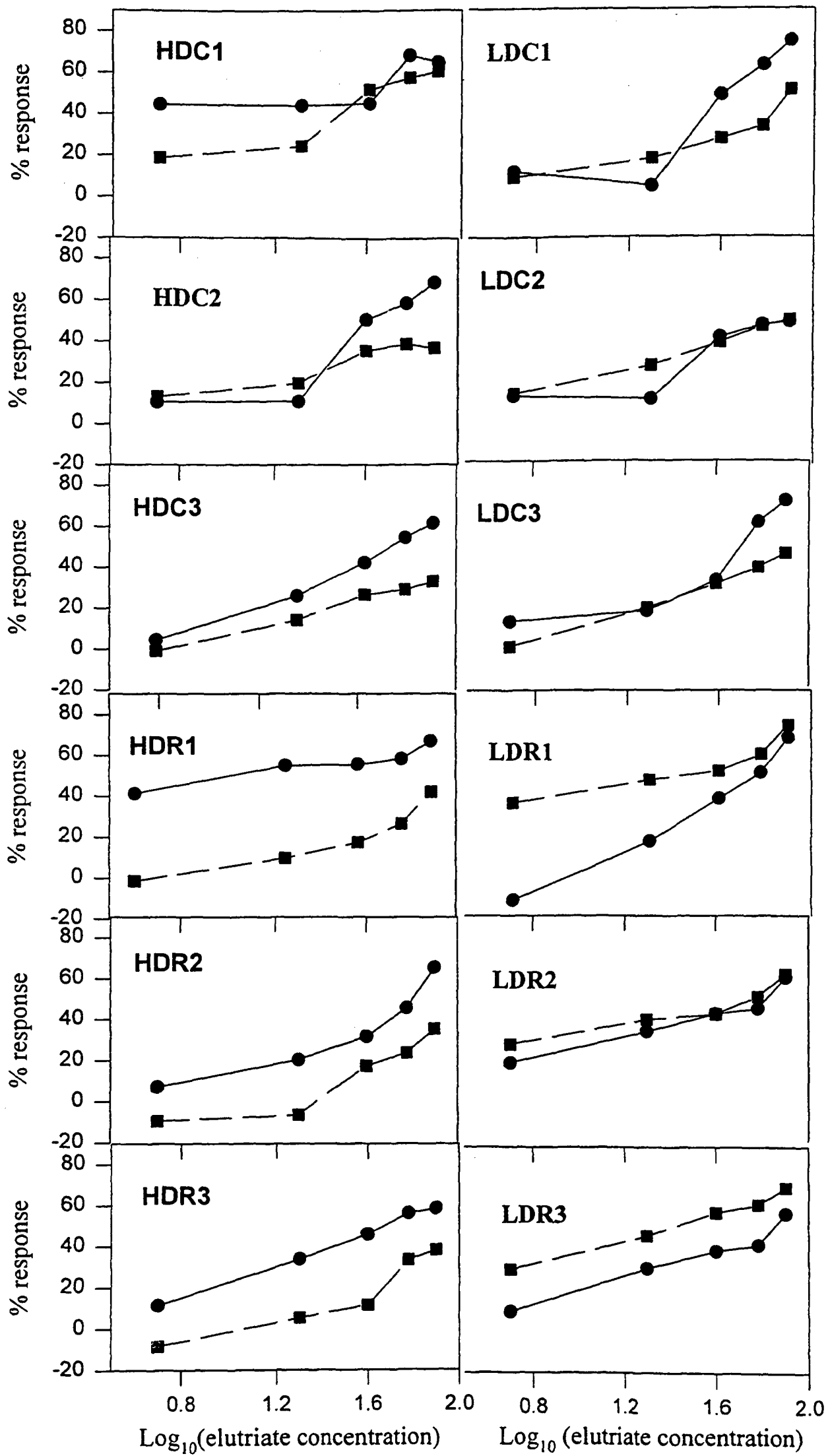
— ● — 48 hours % response
— ■ - 96 hours % response

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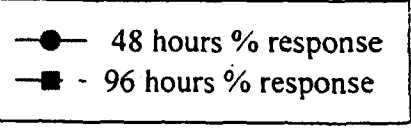
Table 7.2 The results of bioassays: all the numbers are explained as the percentage dilution of the elutriates of dust samples.

	LDR1	LDR2	LDR3	LDC1	LDC2	LDC3	HDR1	HDR2	HDR3	HDC1	HDC2	HDC3
DT 48h-EC$_{30}$ (%)	32.70	15.35	23.25	22.92	27.88	23.21	1.09	28.61	17.62	1.33	22.49	24.69
DT 96h-EC$_{30}$ (%)	4.12	8.16	5.49	38.06	21.30	39.67	60.66	69.93	62.78	14.59	34.92	61.37
BC 48h-EC$_{30}$ (%)	64.81	NT	87.17	26.86	NT	41.77	24.81	14.58	66.88	49.28	48.67	33.19
BC 96h-EC$_{30}$ (%)	31.43	8.45	4.14	15.39	4.25	1.58	20.67	5.11	4.08	5.27	13.45	3.37
BC 168h-EC$_{30}$ (%)	59.78	33.40	14.36	14.73	27.32	12.05	20.43	27.40	10.77	13.27	67.52	18.72
LP 96h-EC$_{30}$ (%)	42.25	31.68	NT	76.10	25.76	NT	15.21	18.95	7.39	43.12	51.06	NT
LP 168h-EC$_{30}$ (%)	8.83	56.83	77.60	11.45	NT	13.27	16.04	57.60	26.25	34.09	72.50	NT
Microtox 20 min-EC$_{50}$ (%)	1.96	2.31	2.20	0.50	1.99	2.43	0.79	2.69	3.41	4.48	6.33	7.00

HDR1, HDR2, HDR3: Hong Kong road dust 0-125 mm, 125-250mm, 250-500 mm, respectively.
HDC1, HDC2, HDC3: Hong Kong car park dust 0-125 mm, 125-250mm, 250-500 mm, respectively.
LDR1, LDR2, LDR3 : London road dust 0-125 mm, 125-250mm, 250-500 mm, respectively.
LDC1, LDC2, LDC3 : London car park dust 0-125 mm, 125-250mm, 250-500 mm, respectively.
DT: *Dunaliella tertiolecta*; BC: *Brassica chinensis*; LP: *Lolium perenne*.
NT: effective concentration > 100%

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7.3.4 Correlation between the chemical analysis and the bioassay

The correlation coefficients between the results of bioassay and the chemical data of sequential extraction are used to evaluate that if there is a strong correlation between an effective concentration shown by a biotoxicity test and the chemical composition of dust shown by the chemical data. Therefore it is possible to determine whether for instance, the most mobile exchangeable fraction is the most closely related to the toxic effect. Table 7.3 shows the correlation coefficients between the exchangeable, carbonate, oxide, organic and residual fractions of dust metal content, total metal content and effective concentration of bioassay. A negative correlation suggests that the lower the effective concentration of a reduction in root growth, algal numbers or a decrease in light output of bacteria is related to the higher metal concentration in dust according the data of sequential extraction. In this study, the bioassays used the higher plants, *B. chinensis* and *L. perenne*, and the unicellular alga, *D. tertiolecta* to measure the toxicological effects of water soluble chemicals leaching from dust samples. For *B. chinensis*, a significant positive correlation ($p < 0.05$) was obtained between the 96 h-EC_{30} value and the (i) exchangeable fraction of Cd, (ii) carbonate fraction of Cu, (iii) oxide fraction of Cd, (iv) residual fraction of Pb and (v) total content of Cd. A significant positive correlation ($r = 0.60$, $p < 0.05$) was found between the *B. chinensis* 168 h-EC_{30} value and the 96 h-EC_{30} value. After 48 h, the EC_{30} value of *B. chinensis* correlated significantly ($r = -0.72$, $p < 0.01$) with only the organic content. No significant correlations were found between the EC_{30} of *L. perenne* and the various chemical parameters measured. As for *D. tertiolecta* a significant negative correlation ($p < 0.01$) was observed between the 48 h-EC_{30} value and the exchangeable fraction of Pb. A significant negative correlation was also found between the 96 h-EC_{30} value and (i) the exchangeable fraction of Zn

and (ii) the carbonate fraction of Pb. However, a significant positive correlation ($r = 0.77$, $p < 0.01$) was found between the *D. tertiolecta* 96 h-EC_{30} value and the carbonate fraction of Zn. The Microtox® EC_{50} values showed significant negative correlations with total Cd, Cu, Pb and Zn content in dust; the oxide fraction of Cd, Pb and Zn; the organic fraction of Cu and Pb, and the residual fraction of Pb in the dust samples.

Table 7.3 Correlation coefficients between chemical data and bioassay data.

	Cd (exe)	Cd (car)	Cd (oxi)	Cd (org)	Cd (res)	Cd (tot)	Cu (exe)	Cu (car)	Cu (oxi)	Cu (org)	Cu (res)	Cu (tot)	BC$_{96h}$ EC30(%)
DT$_{48h}$-EC30(%)													
DT$_{96h}$-EC30(%)													
BC$_{48h}$-EC30(%)													
BC$_{96h}$-EC30(%)	0.69 ·		0.61 ·			0.62 ·		0.80 **					
BC$_{168h}$-EC30(%)													0.60 ·
LP$_{96h}$-EC30(%)													
LP$_{168h}$-EC30(%)													
M$_{icrotox}$ -20 min-EC50(%)			-0.69 ·			-0.60 ·				-0.58 ·		-0.69 **	

	Pb (exe)	Pb (car)	Pb (oxi)	Pb (org)	Pb (res)	Pb (tot)	Zn (exe)	Zn (car)	Zn (oxi)	Zn (org)	Zn (res)	Zn (tot)	Organic content(%)
DT$_{48h}$-EC30(%)	-0.75 **												
DT$_{96h}$-EC30(%)		-0.68 **					-0.82 ***	0.77 **					0.79 **
BC$_{48h}$-EC30(%)													-0.72 **
BC$_{96h}$-EC30(%)			0.61 ·		0.71 **								
BC$_{168h}$-EC30(%)													
LP$_{96h}$-EC30(%)													
LP$_{168h}$-EC30(%)													
M$_{icrotox}$ -20 min-EC50(%)			-0.76 **	-0.61 ·	-0.63 ·	-0.77 **			-0.80 **			-0.82 ***	

DT: *Dunaliella tertiolecta*; BC: *Brassica chinensis*; LP: *Lolium perrene*; (exe) : exchangeable fraction; (car): carbonic fraction; (oxi): Fe- Mn oxidious fraction; (org): organic fraction; (res): residual; (tot) : total metal content. Significant difference at *: $p < 0.05$, **: $p < 0.01$ and ***: $p < 0.001$, according to Student's *t* test.

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7.4 Discussion

7.4.1 Seed germination and root elongation

B. chinensis (Chinese white cabbage) has been used as a bioassay in this study not only because it is an important economic crop and hence there could be environmental health implications, but also because it has a fast germination rate of less than 4 days. *L. perenne* (rye grass) is also used as it is an internationally recognised species for toxicity testing (Wong and Bradshaw, 1982).

Seed germination has been used as a toxicity test for agriculture and composts and for sewage sludge when applied to soils for agriculture/forest (Wong et al., 1981; Wong and Chiu, 1986; Wang and Keturi, 1990). Some studies (e.g. Palazzo and Leggett, 1986) have shown that seed germination toxicity tests as being a less sensitive toxicity test method than root elongation. The results of seed germination of B. chinensis and L. perenne did not show significant differences with the various concentrations of extracts from dust samples, whereas root growth seemed to be a more sensitive parameter in these experiments.

The results in Table 7.3 show that according to EC_{30} value, B. chinensis has the highest root growth inhibition at 96 h($EC_{30} \cong 2\%$), followed by 168 h ($EC_{30} \cong 11\%$), and 48 h ($EC_{30} \cong 15\%$). Therefore, 96 h may be the most sensitive end point for root elongation for testing of B. chinensis. L. perenne has a more sensitive EC_{30} value at 168 h ($EC_{30} \cong 9$ -12%) than at 96 h ($EC_{30} \cong$ 42- 76%) with the finest London dust particles. The direct harmful effects of the water extract of roadside soils on seed germination and root growth of B. chinensis have been shown by Wong and Lau (1983). Heavy metals in soluble forms are highly toxic to plants; for instance, Wong and Bradshaw

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(1982) showed that 1.85, 0.02, 1.7 and 1.6 $\mu g\ ml^{-1}$ of Cd, Cu, Pb and Zn respectively, inhibited the normal root growth of L. perenne by 50%. The root elongation method (Wilkins, 1957) using higher plants has been commonly employed and refined by many researchers as a simple, rapid and easy technique to test toxic concentrations of heavy metals. The main pathway of heavy metal entry into a plant is from the soil through the roots; in soil solution, metal ions can reach plant root surfaces either by diffusion, provided there is a concentration gradient; by mass-flow, which can be induced by water depleting processes in the plant itself such as transpiration and evaporation; or there may be a process of ion exchange between a clay and a root in contact with it.

Significant positive correlations were found between the EC_{30} at 96 h for B. chinensis and the exchangeable fraction of Cd, the carbonate fraction of Cu, the oxide fractions of Cd and Pb, the residual fraction of Pb and the total content of Cd.

7.4.2 Algal toxicity test

Table 7.2 shows that the EC_{30} value of London road dust samples showed a greater effect at 96 h ($EC_{30} \cong 4\text{-} 8\%$) than at 48 h ($EC_{30} \cong 15\text{-} 33\%$) for the inhibition of the growth of D. tertiolecta. However, in Hong Kong dust samples, the higher sensitivity of EC_{30} was found at 48 h ($EC_{30} \cong 1\text{-} 29\%$). Significant negative correlations were found between the EC_{30} at 48 h for the inhibition of the growth of D. tertiolecta and exchangeable fraction of Pb and between the EC_{30} at 48 h for D. tertiolecta and the exchangeable fraction of Zn; as well as the carbonate fraction of Pb and Zn (Table 7.3). The exchangeable fraction and the carbonate fraction of Pb and Zn are the fractions which is immediately available in the natural environment. For instance, the exchangeable fraction of metals readily occurs under the neutral pH conditions, whereas the carbonate fraction is available subject to acid

conditions at a pH of about 5 similar to that of acid rain (Tessier *et al.*, 1979). These results seem to suggest that Pb and Zn may be two toxic pollutants in the urban dust samples causing growth inhibition of *D. tertiolecta*. Such contamination has been implicated as a cause for the decline of aquatic vegetation including algae (Wang and Freemark, 1995). Algae act as primary producers in transferring energy to the higher trophic levels (Christensen and Scherfig, 1979) and form the first link in the food chain, and hence the algal bioassay test is commonly used to evaluate effluent toxicity.

D. tertiolecta may have internal detoxifying mechanisms that may result in a tolerance to heavy metals (Steemann-Neilsen and Kamp-Neilsen, 1970; Davies, 1976; Heuillet et al, 1986). In addition, certain algae protect themselves from toxic metals by extracellular excretions either by their cell walls acting as a barrier or by their cell excreting organic material, which chelates metals both of which prevent metal uptake (Fogg and Westlake, 1955; Butler *et al.*, 1980 and Kaplan *et al.*, 1987). For the algal bioassay, the relationship between metal sorption to algal cells and toxicity is still unclear.

Microtox® Solid-phase Test

Kwan and Dutka (1995) interpreted the EC_{50} values for Microtox® as follows: (1) the Values for k_{sw} available from the literature and which are used in environmental risk assessment for the EPA's river model are 6.5 ml g^{-1} for Cd, 35 ml g^{-1} for Cu and 900 ml g^{-1} for Pb. value equal to or less than 0.5% are classified as very toxic, (2) the EC_{50} value greater than 0.5% and equal to or less than 1.0% as moderately toxic; (3) the EC_{50} value greater than 1.0% as not toxic. The 20min-EC_{50} of the finest car park dusts from London (0.5%) and the finest road dust from Hong Kong (0.79%) can therefore be classified as very toxic and moderately toxic, respectively.

The Microtox® EC_{50} values show significant negative correlations with total and different fractions of individual metals. It has been demonstrated that Microtox® is the most sensitive assay in the detection of Cu, Zn and mercury (Dutka and Kwan, 1981, 1984; Dutka et al., 1983; Dutton et al., 1986; Codina et al., 1993). Three different fractions (oxide, organic, and residual) of Pb have significant negative correlations with the Microtox® 20 min- EC_{50} values. In addition, the Microtox® EC_{50} values show consistently significant negative correlations with the total metal content of Cd, Cu, Pb and Zn. This further reveals that total metal content serves as the most relevant parameter in the Microtox® toxicity test for street dust. In this case, the Microtox® 20 min- EC_{50} value did not have any significant correlation with exchangeable and carbonate fractions of metals.

7.4.3 The relationships between different bioassays and chemical analysis

There is no significant correlation between the different bioassays except the significant positive correlation of the EC_{30} of root elongation of *B. chinensis* at 96h and 168 h. Williams *et al.* (1986) suggested that the comparability of bioassays is limited by the different test sample sensitivities of test organisms. *B. chinensis* and *L. perenne* are both higher plants but they respond differently to toxic effects of urban dust. Taxonomic differences between higher plants have been reported to have a much greater influence on plant response to chemical toxicity than did the testing methods (Fletcher *et al.*, 1990).

7.5 Summary

Measures of three different biological responses (root growth, population growth and light output) of biota (plants, algae and bacteria) were employed to evaluate the toxicity of Cd, Cu, Pb and Zn in urban road dust in laboratory experiments. The results of bioassays were further studied to find

any possible links between the different forms of Cd, Cu, Pb and Zn binding in dust obtained using the chemical speciation.

D. tertiolecta showed adverse effects to road dust extraction solution and the results of algae toxicity test also showed significant negative correlation with the exchangeable and carbonate fractions of Pb and Zn in dust. The results of the Microtox® Solid-phase Test showed a significant negative correlation with the total Cd, Cu, Pb and Zn contents and also the oxide, organic and residual fraction of different metal content in dusts. *B. chinensis* showed significant positive correlations with different fractions of Cd, Cu and Pb. This suggested that Cd, Cu and Pb may not be the major toxicants causing the adverse effects on the root growth of *B. chinensis*. There were no specific trends found in the results of the higher plant, *L. perenne* between different dust samples.

The bioassay experiments on higher plant and algae showed that the time a species is exposed to a toxic metal is a crucial factor in measuring the toxicity of the medium. In other word, different time scales show different toxicity effects on species.

The results of the present study show that none consistent trends or corrections have been found between results of bioassays and results of chemical analysis. In addition, there is not enough evidence to support the hypothesis that these metals were the only contaminants causing the suppression effect of algae and bacteria in dust.

Chapter Eight

GENERAL DISCUSSION AND CONCLUSION

8.1 Introduction

In recent years as a consequence of integrated pollution control and environmental assessment legislation, there has been a trend toward setting environmental standards and formalising procedures for environmental risk assessment. The focus of this thesis has been on the area of heavy metal in urban road dust. One characteristic of urban road dust is that formal and systemic procedures for risk assessment are hard to apply. This is because the sources of the contamination are diffuse and widespread and therefore difficult to control and the behaviour of the constituents of the dust in the atmosphere, soil and water is not well known and is hard to predict.

The main objectives of this thesis were to examine the application of practical operationally defined approaches to the risk assessment of heavy metal in urban street dust.

The principal aims were to assess whether heavy metals in road dust pose a risk. The focus is how could one set an environmental standard for heavy metal concentrations in road dust or whether setting an environmental standard is even appropriate in this case. Road dust was chosen as the topic as it is a common, available and a possible source of contamination to which the benefits of the application of techniques, such as process controls and best available technology are not easy to assess. An extensive series of experimental tests were applied to typical road dust samples. All the chemical tests, biological tests and the theoretical model developed were applied to the same set of samples and this enabled one to compare results in

a consistent way in order to develop the most appropriate risk assessment. This thesis provides a contribution to research in risk assessment to the field of non-regulated contaminated media.

Roadside dust has been subject to numerous measurements of composition at sites around the world. The amount of roadside dust is much more difficult to define as it is expected to be rather variable in space, because of differences in the distribution of sources. It is also variable in time, because of changes in weather conditions, particularly variations in the rainfall rate and intensity.

In order to assess the possible risk of heavy metals in dust for which no commonly accepted environmental guideline or standard exists, a conceptual model based on randomly occurring dry and wet weather conditions was developed. This model was used to assess contamination in soil next to a road influenced by the road surface runoff and dust re-suspended from the road.

One expects many diverse forms of particles to be part of roadside dust and for various kinds of metal compounds to be associated with these particles. This study reveals, as far as possible in general analytical practice, the detailed chemical profile of the heavy metal in urban dust. It identifies the pH as the major component which governs the metal release mechanism from dust.

8.2 Problem of risk assessment of metal mobility

It is important in studies of heavy metals in the environment to understand the relationship between the anthropogenic release and future consequences for man and the environment (Salbu and Steinnes, 1994). In most risk assessment of heavy metal contamination, a worst case is generally assumed to assess the highest possible impact of pollutants released in the

environment, such as total concentration of heavy metals. However, using the total concentration of metals in contaminated media alone to assess the potential risks to human health and the natural environment may not lead to an accurate understanding of the transformations of pollutants, or to the most relevant routes of exposure. Using the total concentration of heavy metals may overestimate the potential risks of the contaminant along particular routes of environmental exposure and may increase the costs of remedial decisions, especially when remedial and clean up actions are considered. At the same time, it may underestimate the potential risks of pollutants through other pathways, (such as the metal distribution between water and sediment compartment) of environmental exposure and lead to insufficient protection of the natural environment. Risk assessments often look at one part of the problem either the source or the effect, rather than considering the system as a whole. For protection, better environment and human health, the risk distributes between different environmental pathways should be fully understood and evaluated at an acceptable level.

Assessing the potential mobility of the heavy metal in different environmental pathway is still unsatisfactory and imprecise, because of the complexity of the processes and mechanisms of heavy metal movement at the interface of environmental media, such as soil and water. The mobility, reactivity and availability of environmental chemicals or pollutants, such as heavy metals, in the natural ecosystem are highly dependent on the particular form of the heavy metal binding (Forster and Wittman, 1979). It is clearly desirable to have methods available which take these complexities into account and one that can be performed in a practical and operational manner.

8.3 Harmonization of Chemical Approaches

The main idea of this research is to use the same set of samples to test a number of different operational approaches, in order to find out whether there is a way to derive a general methodology to assess the heavy metal contamination of this kind. Two road side locations in two cities were used in the study, with samples collected at different times. They were chosen to see if there was any consistency between the chemical leaching methods for different samples. The different chemical leaching methods lead to different results, showing complex release patterns which are not easy to interpret. The results indicate that the pH of the extraction solution is the main variable influencing metal leaching which in turn brings consistency to the large data set produced. The chemical approaches considered are as follows:

8.3.1 Sequential extraction

The sequential extraction approach provides profound information on the partitioning of metals in road dust and soil, and enables a better understanding of the mobility and bio-availability of metal to be estimated. The chemical speciation results suggest that the metal distribution in street dust regardless of locations is relatively consistent. Cadmium is mainly associated with the exchangeable, carbonate and Fe-Mn oxide fractions. Copper is predominately associated with the organic fraction while lead and zinc are associated with the carbonate and Fe-Mn oxide fractions (see Chapter 3).

Application of a sequential extraction technique revealed relatively low Cu, Pb and Zn levels in the exchangeable fractions, which indicates a correspondingly low degree of bio-availability of these metal in urban road dust under neutral condition. Cadmium is therefore more likely to become mobile because of high exchangeable fraction. Among all five fractions, the residual fraction (ca. 10% in this study) may be considered as of no

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immediate environmental concern as it is unlikely to be released under natural environmental conditions. However, the sequential extraction method provides no direct method of assessing the potential risk of Cd, Cu, Pb and Zn in road dust.

Concentrations of Cd, Cu, Pb and Zn in urban dust using the sequential extraction scheme are very similar to those obtained in similar studies carried out in the UK and elsewhere in the world (Harrison *et al.*, 1981; Fergusson and Ryan, 1984; Gibson and Farmer; 1984, Stone and Marsalek, 1996). This consistency indicates the similarity of urban street dust with respect to chemical speciation, despite the complex mixture of sources and processes in the urban environment.

8.3.2 Chemical leaching and acid titration

Chemical leaching approaches using different levels of extraction solutions such as distilled water (DIN-S4), acetic acid (USEPA SW-1310 and SW-1311), and concentrated nitric acid and per-chloric acid (pseudo total digestion) are shown to have very consistent results with the results of pH dependent leaching methods using nitric acid as the extraction solution (see Chapter 4). Different levels of extraction solutions were used to assess different leaching behaviour and potential leachability of heavy metals in urban road dust. Milder chemical extraction solution, such as acetic acid, were employed to give an operational measure of the available fraction of metals which related to release in the short term assuming natural exposure conditions, while more aggressive extraction solutions were considered to reflect the potential release over a longer time scale. In this study, pH has been found to be the main parameter governing the metal release mechanism when compared to the extraction solution and the solid: liquid ratio in the extraction solution.

8.3.3 Time dependent metal release mechanism

Time dependent metal release effects have rarely been taken into account in risk assessment. The neglect of time dependent effects have to be justified if an equilibrium approach to risk assessment is to be applied.

The time-dependent rate of Cd, Cu, Pb and Zn release from road dust is dependent on transport phenomena and chemical reactions, the effects of which are often experimentally inseparable (Sparks, 1989). The rate laws which are either first order or based on other simple operationally defined kinetics, have usually been employed to treat chemical desorption.

According to time dependent metal release mechanism in this study (see Section 4.4.2 and 4.4.3, Chapter 4), the fraction of dissolved Cd, Cu, Pb and Zn is strongly dependent on the pH of the extraction solution and time elapsed during the extraction. In solid-liquid solutions, the hydrogen ions are strongly attracted to the negative charges on the surface of particles and they can replace most other cations which are not so strongly bound to the solid particle (Alloway, 1990). Hence in more acidic conditions heavy metals are generally more mobile. In this study the time dependent release of metals from road dust could be described by two reactions, with two characteristic time scales. Metal release rates were fast during the first 30 minutes, followed by a much slower release pattern. This implies that the loosely bound metals from urban dust were released more or less instantly when the acidic solution came to contact with the dust. The more strongly bound, or inner fraction of heavy metals within the dust particles, takes a relatively longer time to be released with rate constants dependent on the acidity of the extraction solution.

A fast-slow reaction model (see Section 4.4.3) was applied to study the metal release using a fast irreversible reaction to describe desorption of metal

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bound to outer surface sites and the dissolution of soluble metal carbonates, and a slow reaction to describe metal desorption from more strongly bond sites on dust particles. The results of application of the two reaction model to the data showed good agreement between the model and experimental data.

According to the two reaction model, the characteristic rate constants of Cd, Cu, Pb and Zn release are pH dependent, and a lower pH results in faster metal release.

Although the release kinetics of Cd, Cu, Pb and Zn are best described by one fast irreversible and one slow reversible first order reaction, the results indicate that the individual metals behave differently in different dust samples. This may be due to the different physico-chemical forms of metal binding in the dust particles. Results of sequential extraction provide evidence of the different binding forms of Cd, Cu, Pb and Zn in dust.

The slow irreversible reaction lead to an equilibrium between metal in solution and metal in dust, which can be interpreted as a partition coefficient. The time to reach equilibrium is fast enough to suggest that a partition coefficient can be used to describe the mobility of metal in practical situations. Given the complex nature of the road dust particles the pH dependence of the partition coefficient appears to be the only practical way of including these effects in a risk assessment.

8.3.4 Pathway to exposure

Under normal urban conditions one would expect the fraction of Cd, Cu, Pb and Zn dissolved from urban road dust to coincide with the exchangeable and carbonate fraction released during the sequential extraction. The first flush is the most important period for storm water management, because of the higher acidity of the rainfall and higher concentration of the pollutants

released. For example, Sansalone and Buchberger (1997) in the study of urban roadway storm water runoff in Cincinnati, USA, found that low rainfall pH and average pavement residence time significantly influenced metal dissolution in lateral pavement sheet flow. The concentration of metal in the street dust is just one important factor when assessing the potential risk of metal released from the urban street in surface runoff. The pH of urban rainfall (acid rain effects), the time elapsed and the duration of the rain are also important factors.

The chemical leaching test of urban road dust mobility suggest that there may be a hazard associated with the heavy metal concentration. However, the chemical leaching tests do not themselves provide a way of assessing the risk. The only way of assessing the risk of exposure is to consider the pathway(s) between the dust and possible exposure mechanisms on the target organism or a specific environment media, such as soil or water. This suggests that only by modelling the pathway, or pathways, can the risk be assessed. A single chemical leaching test will only provide information on leaching under specified conditions, so that sequential leaching tests or pH dependent acid titration methods are preferred.

8.3.5 Simulated gastric condition

If one were interested in the pathway of exposure by ingestion of dust, one would need to consider mobility under the highly acidic condition of the human gastric tract. This kind of extraction has been performed (see Chapter 6) and reveals mobility, as expected toward the highest fractions of release.

8.4 Biological toxicity test

The alternative method of risk assessment to chemical leaching tests and modelling the pathway of exposure is to apply a biological toxicity tests as an

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alternative surrogate. The correlation between the chemical speciation tests and the biological tests is not satisfactory (see Chapter 7). Some studies showed that when aquatic organisms were exposed to mixtures of metals, including Cu, Cd, Pb and Zn, the interaction between the metals might vary from antagonism to synergism. The toxicity of the mixtures depends, among other things, on the combination of metals, both qualitative and quantitative, and on biotic factors which may affect the speciation of metals in water. In addition, the effects of those mixtures of metals differed with species of organism. Hence a standard assessment approach using bio-toxicity cannot be simply used as an alternative to performing sequential extraction and chemical extraction tests on urban road dust.

Although biological toxicity tests provide very useful data and are necessary for evaluating contamination materials, the bio-toxicity alone does not provide a completely logical basis for decision making associated with the risks arising from urban road dust. The contaminant(s) responsible for the toxicity should be identified, in order to gain more insight into the usefulness of the two approaches.

8.5 Using partition coefficient in modelling

The mobility of heavy metals in the terrestrial and aquatic environments is reflected by the partitioning between dissolved and solid forms (Kersten and Forstner, 1989). The partition coefficient (k_{sw}), (the ratio between the metal concentration in particles and the metal concentration dissolved in the solution), serves as a good operational method to describe the tendency of a metal to convert between solid and solution. This provides a good measure to estimate the bioavailability of metals in the solid-liquid phase of contaminated media for most environmental risks. The partition coefficient could also be used as a key parameter to assess different environmental conditions under different physicochemical conditions of interest.

Environmental risk assessments often use a partition coefficient to assess the risk of contaminants in different environmental media. The results of this study show that the values of the partition coefficient are affected by the pH and vary among different dust samples (see Chapter 4). Hence in environmental risk assessments the partition coefficient should be considered in conjunction with the pH of the extraction solution. In this study an empirically derived, linear relationship was found between the logarithm of the partition coefficient and between pH 2 and 6 (see Chapter 4) which varies according to metal under consideration.

8.6 Theoretical Runoff Model

In this thesis a theoretical runoff model was derived to describe the pathway of exposure between roadside dust and possible contamination of soil adjacent to a road. This made use of an empirically derived pH dependent partition coefficient, but showed that the risk was also equally dependent on a number of other physical and chemical parameters, such as rainfall rate, emission factor, traffic flow, road geometry etc. The results of assessing the risk of Cd, Cu, Pb and Zn in the road dust on the soil adjacent to a road using the theoretical runoff model (see Chapter 5), in an idealised worst case concluded that Pb in street dust may pose a potential risk to soil next to the road while Cd, Cu and Zn have no risk concern in this study according to the ICRCL Guideline. Although the parameters used in this study cannot be accurately quantified, the model did provide a first estimate of the potential risk from the various variables and pinpoint the dominating parameters. Clearly the risk from Pb will decrease in cities where the use of Pb in petrol is to be phased out.

The theoretical model illustrates that in risk assessment studies the pathways between source and receptor must be described and predicted. It is

recognised when applying the modelling approach that data is often scarce and there is considerable uncertainty in various parameters.

8.1 Conclusions and recommendation for future research

The results of the application of operational (chemical and biological) approaches and a theoretical runoff model in risk assessment presented in this thesis suggest that in situation, such as heavy metal in urban road dust involving ill defined diffuse sources, there is no simple, quick test or procedure for evaluating risk. Instead it is recommended that chemical leaching methods such as titration under various acid conditions or sequential extraction, despite the burden of chemical analysis involved, are used in combination with theoretical models to evaluate the environmental risk.

The results of this study also shows the importance of chemical speciation upon heavy metal transport and mobility applied to one environmental pathway. Further studies should be considered as follows:

1) Systematic automated studies of dust particles using a SEM after each stage of an extraction procedure.

2) Development of a model for a more realistic exposure pathways e.g. for the eventual discharge of heavy metal to a river taking into account the combined influence of an urban catchment.

3) Knowledge of the relationship between metal speciation and the biological toxicity tests also need further study.

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APPENDICES

Method: WANG 1995

Report name: Cd 228,8

Standard	absorbance	conc.(ppm)
blank	0.000	0.000
standard1	0.012	0.100
standard2	0.028	0.250
standard3	0.051	0.500
standard4	0.095	1.000
standard5	0.166	2.000

Cd calibration curve

$R^2 = 0.9936$

2.00
1.50
1.00
0.50
0.00

0.000   0.083   0.166
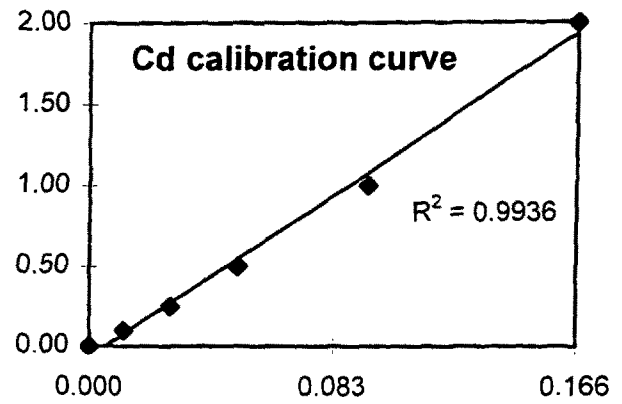
Report name: Cu 324.8

Standard	absorbance	conc.(ppm)
blank	0.000	0.000
standard1	0.014	0.100
standard2	0.070	0.500
standard3	0.140	1.000
standard4	0.263	2.000
standard5	0.535	3.000

Cu calibration curve

$R^2 = 0.9708$

3.000
2.000
1.000
0.000

0.000   0.268   0.535
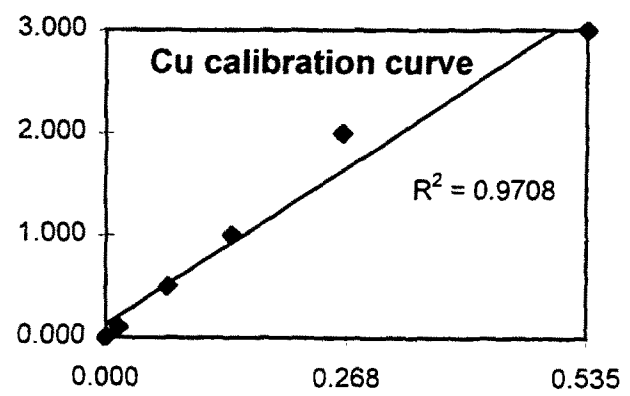
Report name: Pb 217.0

Standard	absorbance	conc.(ppm)
blank	0.000	0.000
standard1	0.011	0.100
standard2	0.027	0.500
standard3	0.048	1.000
standard4	0.243	5.000
standard5	0.383	10.000

Pb Calibration curve

$R^2 = 0.9858$

10.00
7.50
5.00
2.50
0.00

0.000   0.192   0.383
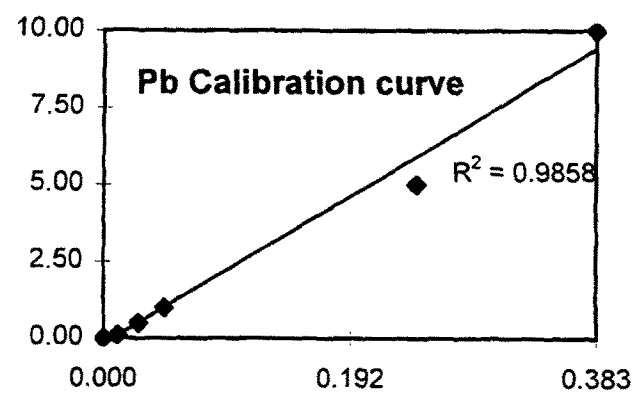
Report name: Zn 213.9

Standard	absorbance	conc.(ppm)
blank	0.000	0.000
standard1	0.008	0.100
standard2	0.024	0.300
standard3	0.028	0.400
standard4	0.031	0.500
standard5	0.051	1.000

Zn calibration curve

$R^2 = 0.9573$

1.00
0.75
0.50
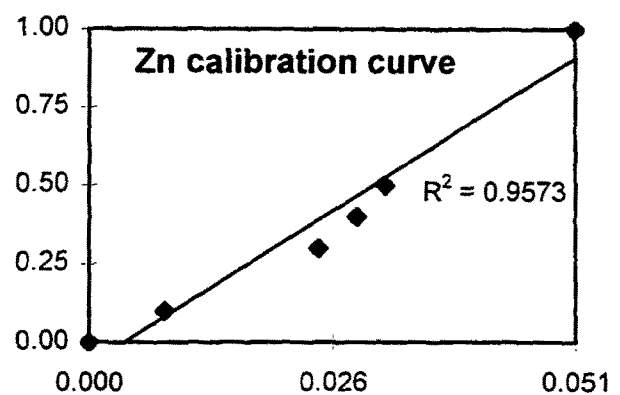0.25
0.00

0.000   0.026   0.051

Figure 1. Calibration Curves of Cd, Cu, Pb and Zn for Flame AAS

Method: WANG1   August 16 1998

Report name: Cd 226.502

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	-0.160	
Low limit:	-0.160	standard1	0.100	0.101	6.227	1.387
High limit:	31.399	standard2	0.200	0.208	12.946	4.018
Correction coefficient:	9.98E-01	standard3	0.300	0.300	18.770	0.159
Standard error:	5.61E-04	standard4	0.400	0.379	23.668	-5.366
		standard5	0.500	0.501	31.399	0.186

Report name: Cu 324.754

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	4.057	
Low limit:	4.057	standard1	0.100	0.058	7.619	-41.742(excluded)
High limit:	35.786	standard2	0.200	0.174	14.735	-12.870(excluded)
Correction coefficient:	9.98E-01	standard3	0.300	0.288	21.715	-3.975
Standard error:	3.68E-04	standard4	0.400	0.400	28.609	0.115
		standard5	0.500	0.517	35.786	3.493

Cd calibration curve

Cu calibration curve
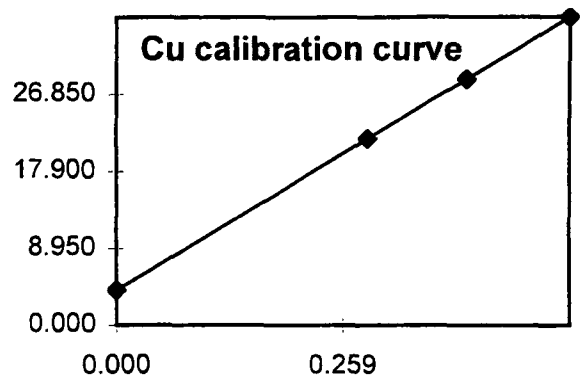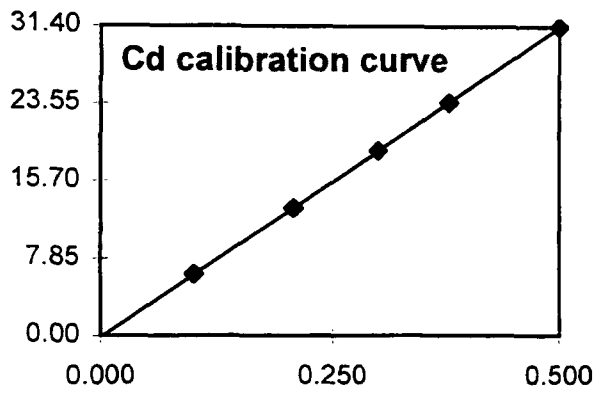
Report name: Pb 220.353

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	0.018	
Low limit:	0.018	standard1	0.100	0.096	0.634	-3.913
High limit:	3.293	standard2	0.200	0.225	1.655	27.733 (excluded)
Correction coefficient:	9.99E-01	standard3	0.300	0.305	1.974	1.750
Standard error:	3.76E-03	standard4	0.400	0.476	3.066	18.954 (excluded)
		standard5	0.500	0.511	3.293	2.223

Report name: Zn 213.856

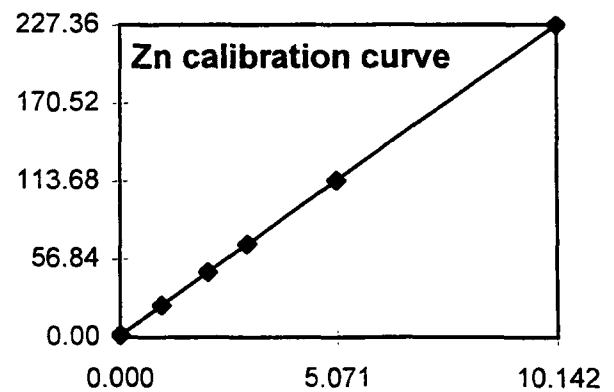| Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	1.694	
Low limit:	1.694	standard1	1.000	0.965	23.115	-3.545
High limit:	227.377	standard2	2.000	2.045	47.207	2.271
Correction coefficient:	9.99E-01	standard3	3.000	2.961	67.584	-1.296
Standard error:	1.02E-03	standard4	5.000	5.050	114.068	1.001
		standard5	10.000	10.142	227.377	1.420

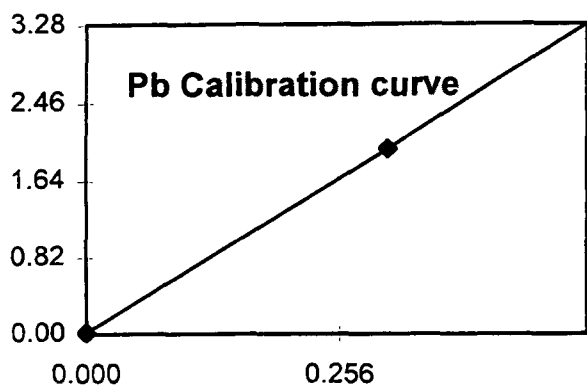Pb Calibration curve

Zn calibration curve

Figure 2(a) Calibration Curves of Cd, Cu, Pb and Zn for ICP-AES

Method: WANG1   August 16 1998

Report name: Al 308.215

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	-0.005	
Low limit:	-0.005	standard1	1.000	1.041	1.030	4.078
High limit:	9.854	standard2	2.000	2.023	2.006	1.143
Correction coefficient:	9.99E-01	standard3	3.000	2.949	2.927	-1.700
Standard error:	2.61E-02	standard4	5.000	4.877	4.844	-2.455
		standard5	10.000	9.917	9.854	-0.826

Report name: Ca 317.933

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	0.043	
Low limit:	0.043	standard1	5.000	4.913	8.050	-1.747
High limit:	122.031	standard2	10.000	10.520	17.188	5.199
Correction coefficient:	9.99E-01	standard3	25.000	25.120	40.982	0.479
Standard error:	1.93E-02	standard4	50.000	48.337	78.819	-3.326
		standard5	75.000	74.852	122.031	-0.198
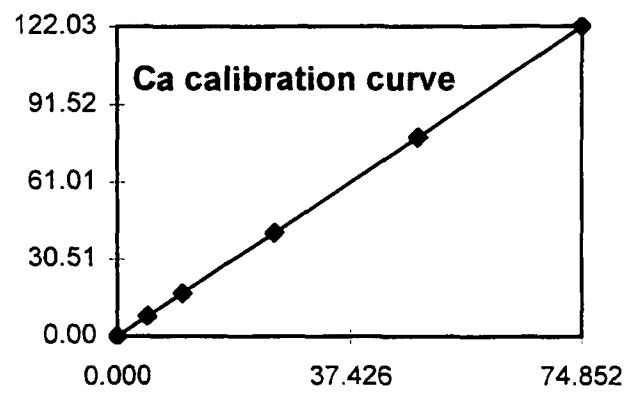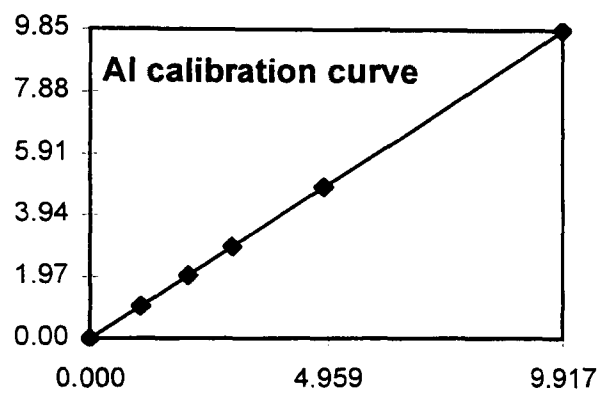
Report name: Cr 267.716

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	-0.236	
Low limit:	-0.236	standard1	0.100	0.114	7.888	13.660 (excluded)
High limit:	35.401	standard2	0.200	0.205	14.402	2.402
Correction coefficient:	9.99E-01	standard3	0.300	0.305	21.536	1.537
Standard error:	3.24E-04	standard4	0.400	0.386	27.355	-3.495
		standard5	0.500	0.499	35.401	-0.282

Report name: Fe 259.940

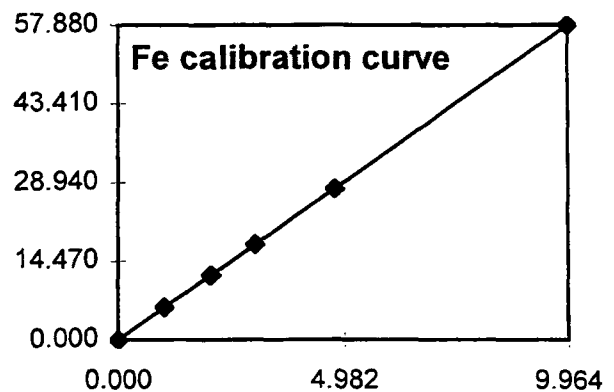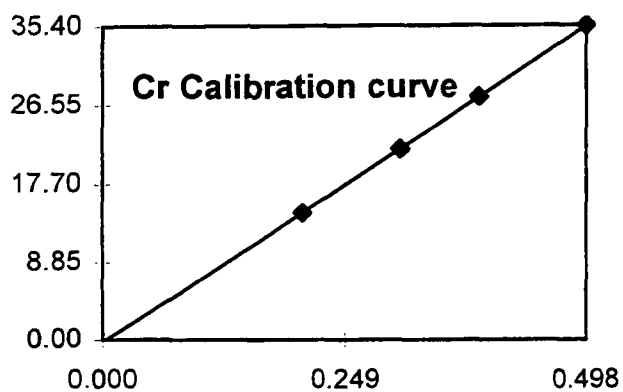| Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	0.036	
Low limit:	0.036	standard1	1.000	1.032	6.029	3.217
High limit:	57.888	standard2	2.000	2.040	11.882	2.018
Correction coefficient:	9.99E-01	standard3	3.000	3.002	17.466	0.071
Standard error:	5.19E-03	standard4	5.000	4.772	27.742	-4.556
		standard5	10.000	9.965	57.888	-0.354

Figure 2(b). Calibration Curves of Al, Ca, Cr and Fe for ICP-AES

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Method: WANG1   August 16 1998

Report name: K 766.490

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	-0.028	
Low limit:	-0.028	standard1	1.000	0.965	0.222	-3.533
High limit:	5.184	standard2	5.000	5.169	1.317	3.385
Correction coefficient:	9.99E-01	standard3	10.000	10.066	2.591	0.656
Standard error:	1.04E-01	standard4	15.000	15.065	3.892	0.432
		standard5	20.000	20.028	5.184	0.141

Report name: Mn 257.610

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	0.027	
Low limit:	0.027	standard1	1.000	1.044	30.301	4.354
High limit:	284.584	standard2	2.000	2.057	59.694	2.838
Correction coefficient:	9.99E-01	standard3	3.000	3.016	87.524	0.535
Standard error:	1.33E-03	standard4	5.000	4.739	137.508	-5.220
		standard5	10.000	9.809	284.584	-1.912
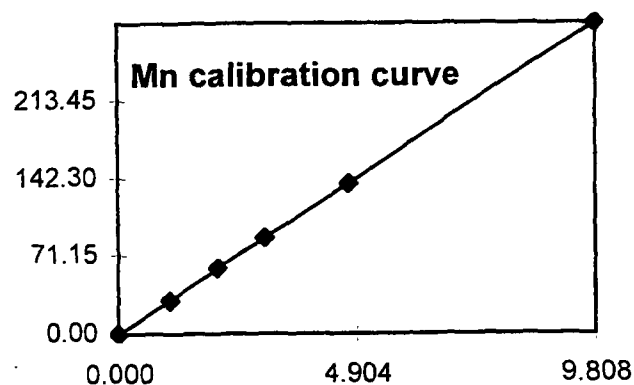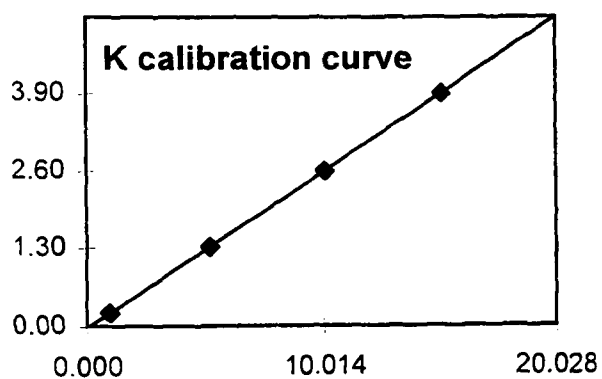
Report name: Ni 231.604

Curve statistics		Standard	conc.(ppm)	calculated conc.	intensity	% difference
Order:	first	blank	0.000	0.000	0.102	
Low limit:	0.102	standard1	0.100	0.095	2.186	-5.436
High limit:	11.284	standard2	0.200	0.205	4.615	2.380
Correction coefficient:	9.99E-01	standard3	0.300	0.310	6.931	3.281
Standard error:	1.59E-03	standard4	0.400	0.394	8.785	-1.511
		standard5	0.500	0.507	11.284	1.463
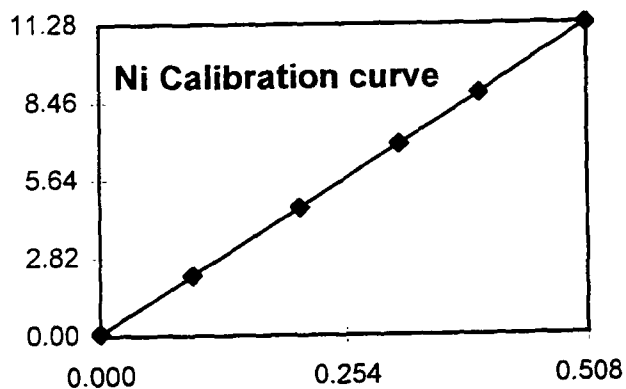
Figure 2(c) Calibration Curves of K, Mn and Ni for ICP-AES

Cd: pH 1 (LDR1)

Cu: pH 1 (LDR1)

Pb: pH 1 (LDR1)
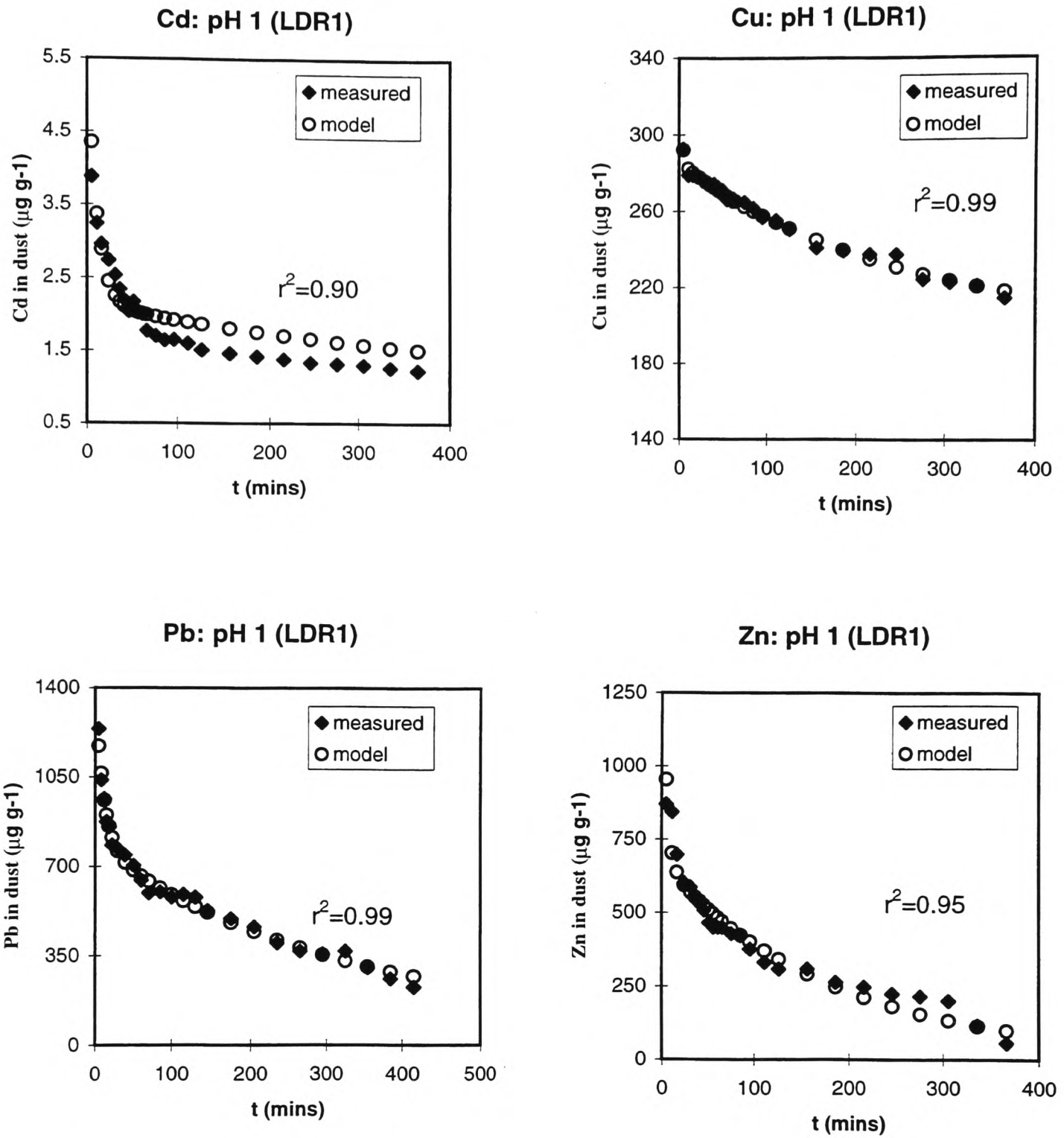

Zn: pH 1 (LDR1)

Figure 3. Correction coefficients between measured data of Cd, Cu, Pb and Zn and calculated data of Cd, Cu, Pb and Zn in dust from the equation (4.17).
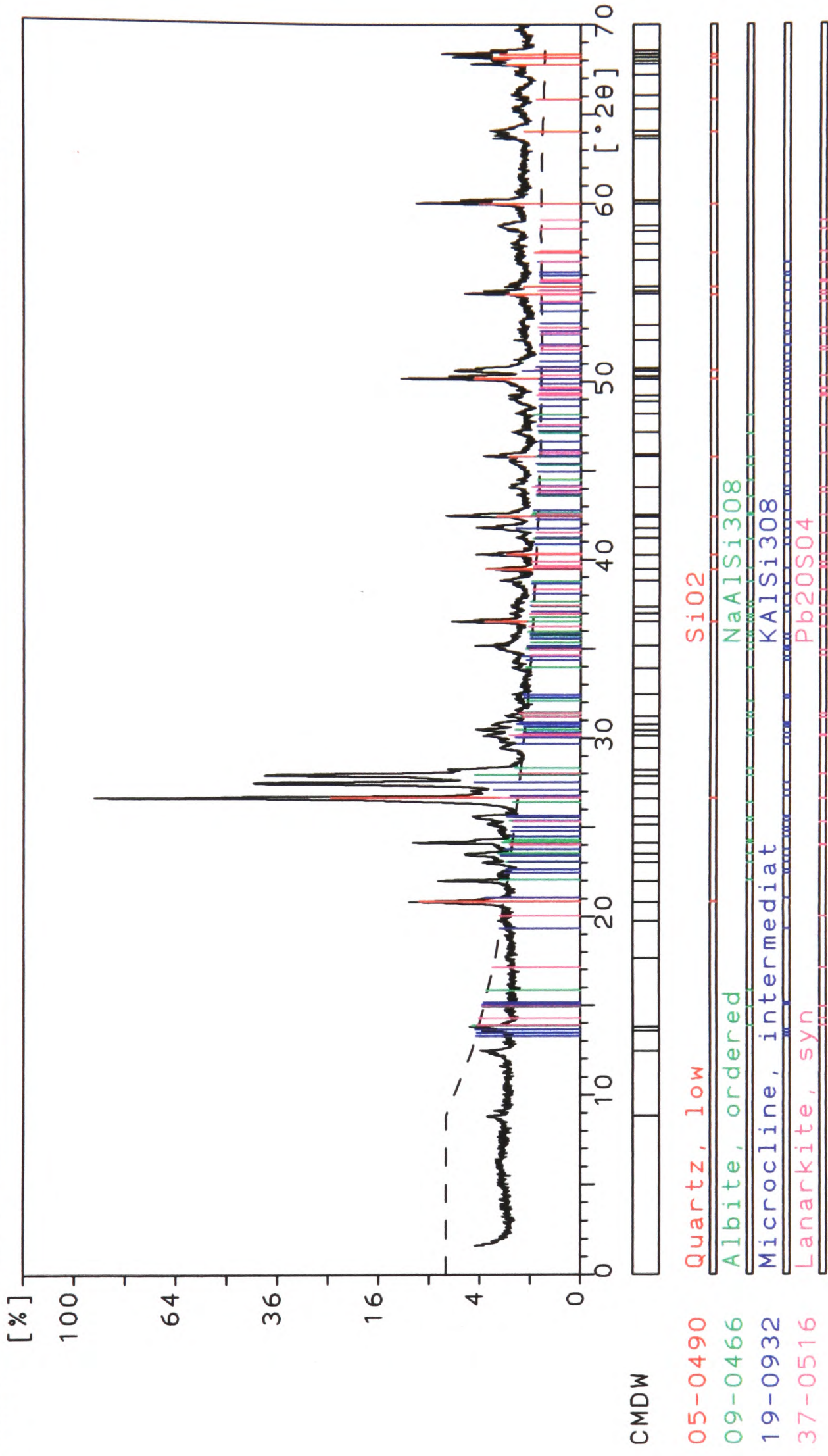
Figure 4 Results of X-ray diffraction analysis of Hong Kong car park dust (HDC1).
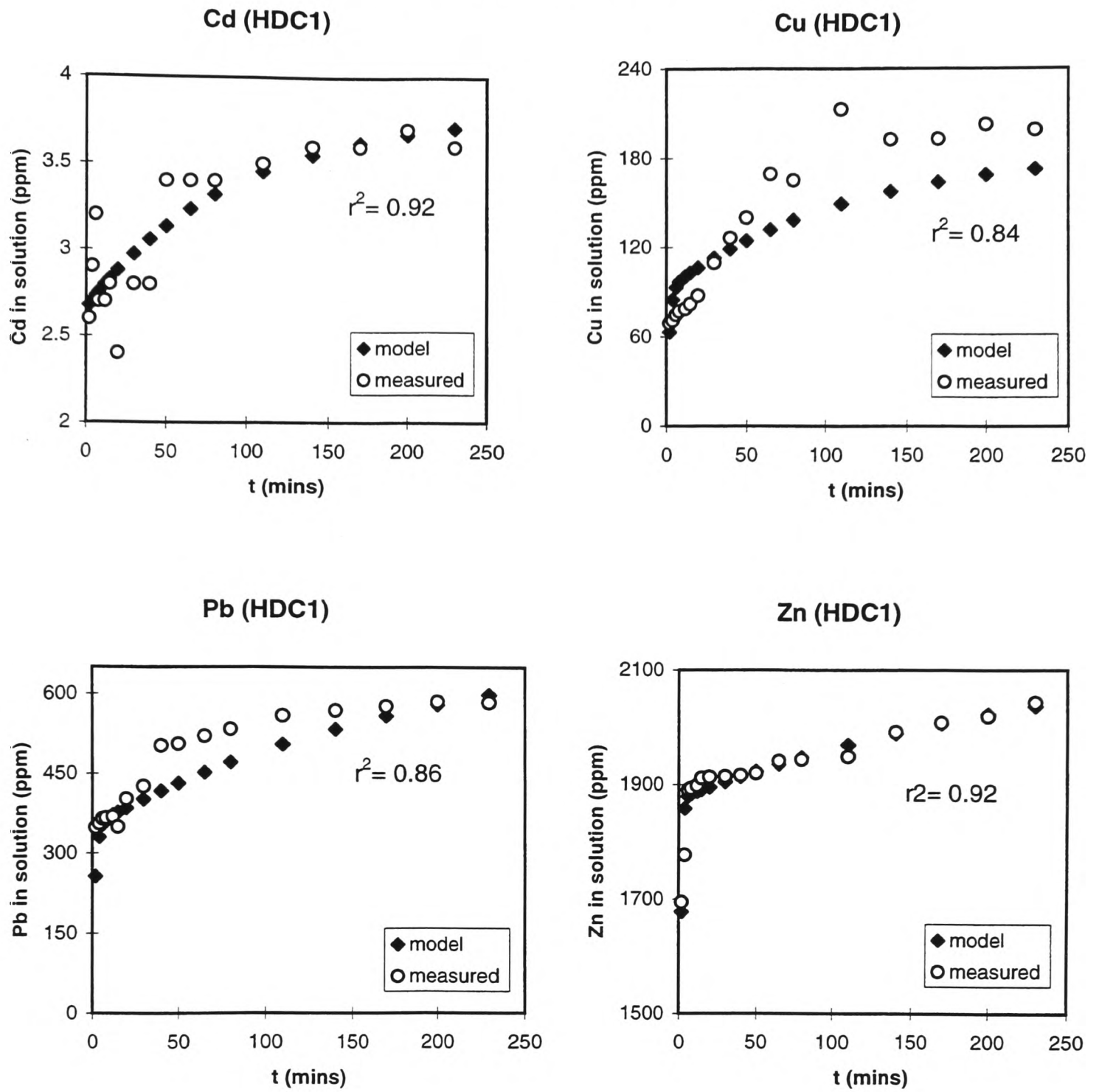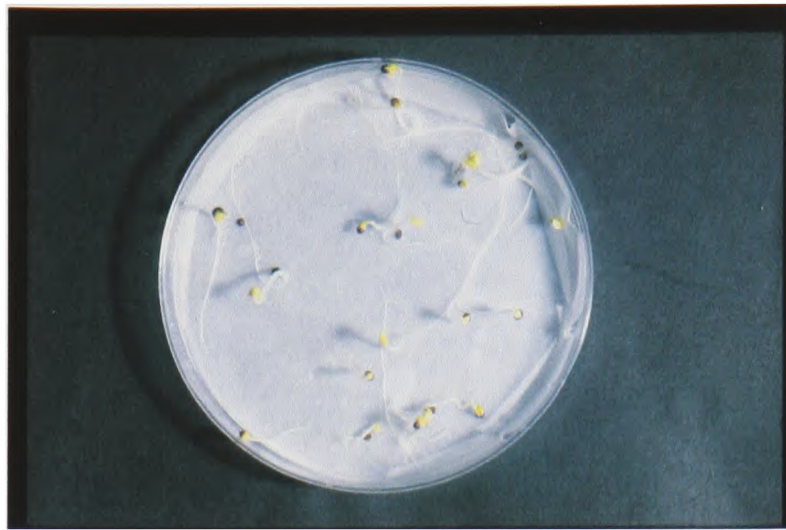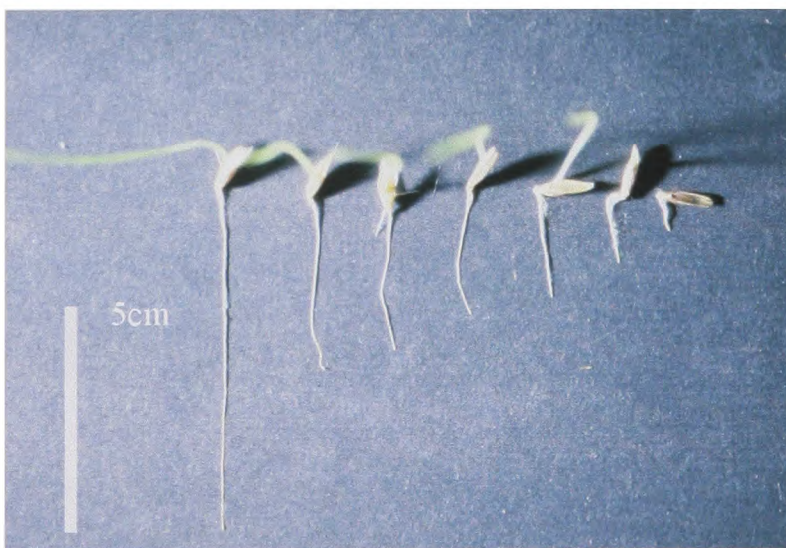
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Simulated gastric conditions

Figure 5. Correction coefficients between measured data of Cd, Cu, Pb and Zn and calculated data of Cd, Cu, Pb and Zn in solutions from the equation (6.1).

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Root elongation: *Brassica chinensis.*

Root elongation: *Lolium perenne.*
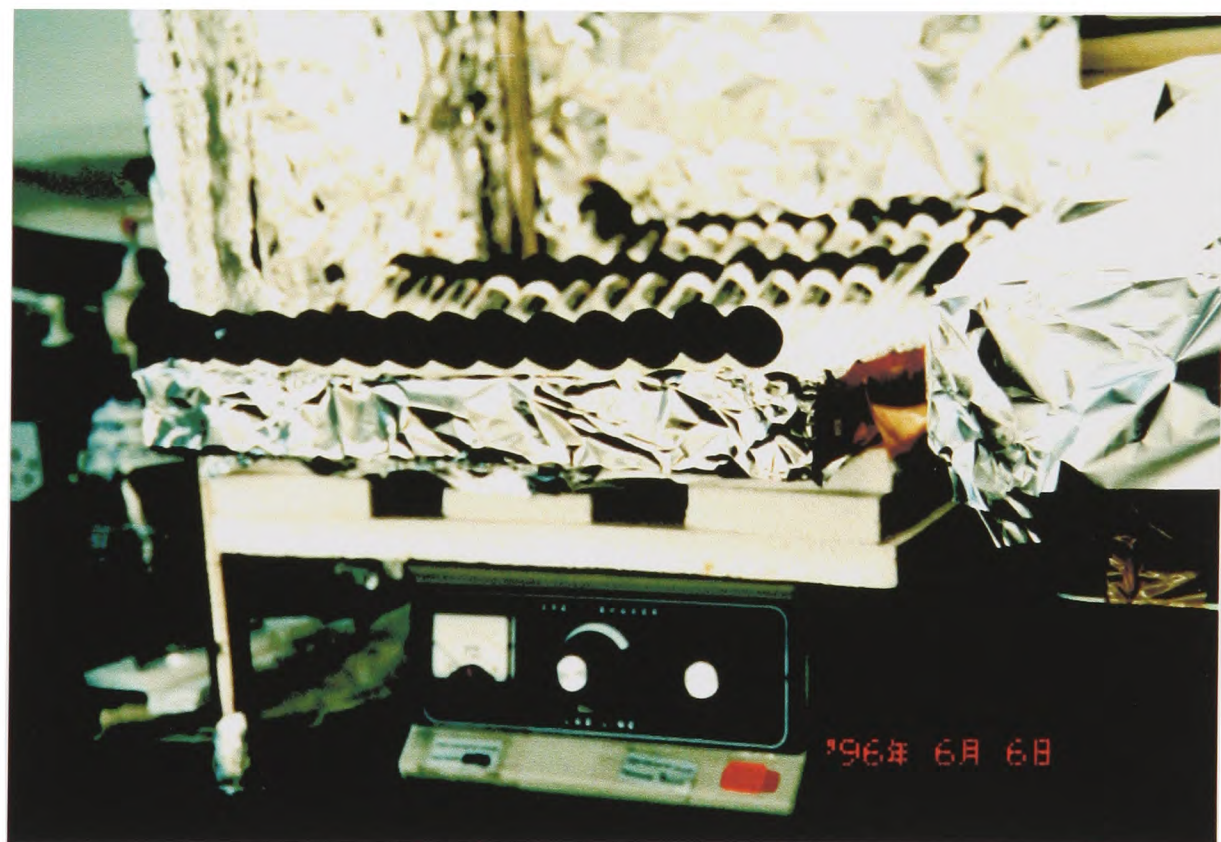
Figure 6   Root elongation: *Brassica chinensis and Lolium perenne.*

Figure 7 Algal (*Dunaliella tertiolecta*) bioassay.

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