CHEMICAL ASSOCIATION OF SOME HEAVY METALS IN STREET DUST

Dissertation submitted to the Jawaharlal Nehru University
in partial fulfillment of requirements for the
Award of Degree of

MASTER OF PHILOSOPHY

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July 2000

Certificate

This is to certify that the research work embodied in this dissertation "Chemical Association of some Heavy Metals in Street Dust" has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, in partial fulfillment of the requirements for the award of the degree of Master of Philosophy. This work is original and has not been submitted in part or full for any other degree or diploma in any other university.

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ACKNOWLEDGEMENT

While writing these words, I feel heartily obliged to all of them, who extended their inconceivable co-operation towards the accomplishment of whatever little I have achieved.

Words alone are inadequate to convey my deep sense of gratitude towards my supervisor, Prof. D.K. Banerjee, Dean, School of Environmental Sciences, JNU, for his indispensable guidance and constructive criticism at all stages of this work. It was primarily his constant support, which lead towards successful completion of this work.

I wish to express my special thanks to Prof. j. Subbarao, former Dean, SES, for the facilities provided to carry out this work.

I record my sincere thanks to Prof. V. Subramanian, for allowing me to use the AAS facility.

My warmest thanks are extended to my friends Swarna, Bala, Charles, Vaishali, Vinod, Abhimanu, Preet, Raza, Bharat, Jaggi, Tumter, Kiran, Ashima, Rajni and Parmod for their encouragement and round the clock help. I am also thankful to my labmates Sudesh and Manoranjan for their cooperation.

I can not eschew to mention my parents and my brother Vicky and sister Sonia, who deserve more then a written acknowledgement. Their affection, constant inspiration and untiring support have sustained my confidence throughout my life.

New Delhi

July, 2000

Anju

Dedicated to . . . ...

My Parents

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Introduction

Today, the accelerated pace of development, rapid industrialisation towards economic stability, ever expanding technological advancement, high level of motorisation and continuously increasing urban agglomeration have led to the increased sophistication and complexity of all systems accompanied by continuously growing environmental degradation in terms of pollution of all components of the environment.

The pollutants present in the environment are divided in two main categories i.e. degradable and non-degradable. Among the non-degradable pollutants, a widespread interest in trace element research in the agricultural, environmental and life sciences has emerged especially over the last half century because of their ecological significance due to their toxicity and accumulative behaviour (Purves, 1985).

Trace elements are omnipresent in the environment, occurring in varying concentrations in bedrock, soil, water, dusts and all biological matter (Bowen, 1979). These are released into the environment from a wide spectrum of natural and anthropogenic sources (Adriano, 1986; Nriagu, 1978). Natural sources are weathering of mineral deposits, emissions from active volcanoes, sea salt sprays, forest fires etc. The main anthropogenic sources are mining activities, industries, burning of fossil fuels, vehicular emissions etc.

In the pre-technological times, the cycling of each trace element had basically reached a steady state and a rigorous control was maintained on its distribution in the global ecosystem. Since the turn of last century due to the expanding technological development, anthropogenic inputs have overwhelmed the natural carrying capacity of the global ecosystem. As a consequence of this the potentially hazardous metals have accumulated in the system implying an inevitable build-up of such elements in the human food chain.

The well known incidences of Minamata (methyl mercury poisoning, in 1953-1960) and Itai-Itai disease (Cd poisoning symptomised by renal damage, anaemia, hypertension, liver damage, osteomalacia and other skeletal deformities, in 1960's, Nordberg, 1974) in Japan awakened the public conscience to focus attention on the hazardous role of trace elements in human beings. Several trace elements, specifically, Pb, Cd, Hg, As, Cr and others are well known to exert adverse health effects and no homeostasis mechanism is known for them. At least 18 metals and metalloids and/or their compounds have been shown to be the initiators of carcinogenic activity in animals: the metals are Al, Sb, As, Bi, Be, Mn, Ti, Cd, Cr, V, Co, Cu, Fe, Ni, Se, La and Zn (Jennette, 1981). Nriagu and Pcyna (1988) has estimated that the toxicity of all trace elements being released in the environment, far exceeds the combined total toxicity of all the radioactive and organic wastes. Toxic effects of some metals are listed below in Table 1.1.

Table 1.1. Special toxic effects of some metals

Metal	Toxic Effects
Ni	can produce cancer of lung and sinus
As	can cause vomiting and abdominal pain, bronchitis, dermatitis and possible cancer
Cd	can cause hypertension and heart enlargement resulting in premature death.
Cr	Cr (VI) can cause lung cancer, chromate acts as irritant to eyes, nose and throat, chronic exposure may lead to liver and kidney damage.
Fe	ingestion in excessive quantities inhibits the activity of many enzymes; inhalation of iron dust can cause benign pneumonia-coniosis and can enhance harmful effects of SO_2 and various carcinogens.
Pb	cumulative poison can affect blood, kidneys, nervous system and brain.

(Sittig, 1976; Duffus, 1980)

Most trace elements tend to accumulate in mammalian tissues, even at low exposure doses and any long-term exposure may be

expected to represent a subtle health hazard. Symptoms of trace metal toxicity are usually non-specific and retrospective rather than early warning or prospective, thus alterations in the vital signs become manifested only after the intoxication process has advanced. Possible health effects by trace elements are most likely to be sub-clinical; the patient either does not show any symptoms, or fails to recognise them Although the current environmental levels of toxic trace elements rarely produce illness or death in the general population, but a large segment of "visibly healthy" population can be suffering from trace element poisoning without even realising it (Nriagu, 1988; Senesi et al., 1999).

Urban systems are highly sophisticated and complex. Each element is commonly found in the urban environment since they are used in both production and consumption related processes (Brown et al., 1990). In urban areas heavy metal pollution arises from a multitude of sources and Table 1.2 lists major sources of a few of them.

Table 1.2. Sources of heavy metals in urban environment

Metal	Sources
Cd	Batteries, pigments and paints, plastics, printing and graphics, waste, wear of car tyre, corrosion of metals, e.g. car bodies, fossil fuel combustion, medical uses, and metallurgical industries.
Ni	Batteries, metallurgical industries, gasoline combustion
Zn	Wear of car tyre, corrosion of metals, e.g. car bodies, fossil fuel combustion, electronics, batteries, pigment and paint, plastics, printing and graphics, medical uses, waste, metallurgical industries.
Cu	Electronics, waste, metallurgical industries, brake dust
Pb	Fossil fuel combustion, e.g. petrol, batteries, pigment and paints, printing and graphics, medical uses, metallurgical industries

(Alloway and Ayres, 1997)
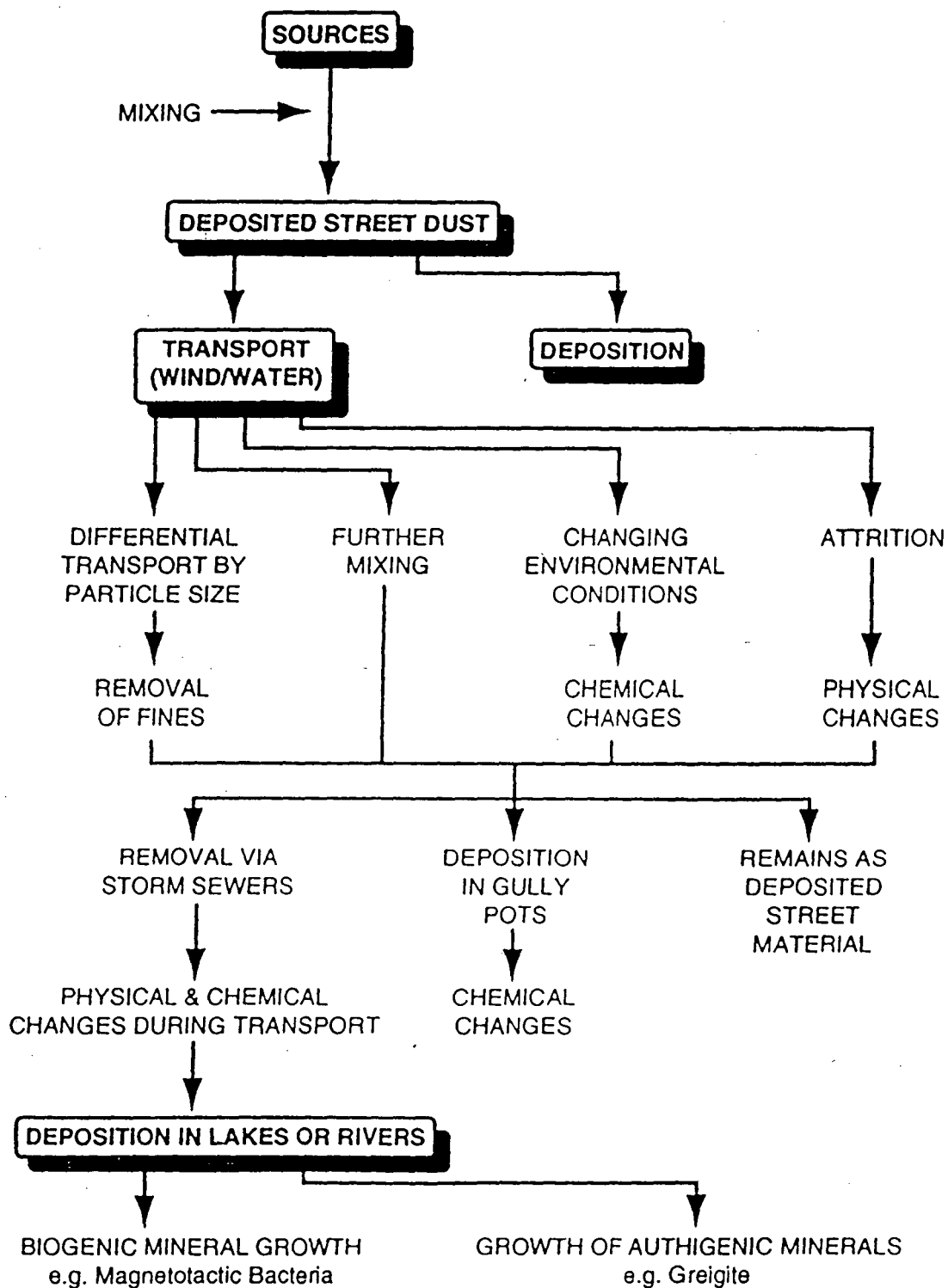
Fig 1.1. Flow chart showing the movement of sediment in the urban environment.

(Charlesworth and Lees, 1999a)

A glance at the Table1.2 shows that major sources of heavy metals are associated with industries, automobiles (exhausts and wear and tear), urban refuses and fossil fuel combustion.

Heavy metals are mostly found associated with the soil and sediments. Fig.1.1 explains the movement of sediments in the urban environment and illustrates the compartmentalisation of urban sediments according to their function in the source -transport (mainly active) -deposit (which are no longer active) cascade. Street dust is the main source from which the further transportation and deposition of heavy metals occurs.

Of the three materials, soil, sediment and dust, which originate primarily from the earth's crust, dust is the most pervasive and important factor affecting human health and well being. It is also the material that has, until the last 20-30 years largely being ignored as a significant source of heavy metal in the environment. It is generally considered as an indicator of the abundance of metals in the local environment (Duggan, 1980). Street dust often contains elevated concentrations of a range of toxic elements and concerns have been expressed about the consequences for both environmental quality and human health especially young children. Young children are identified as the highest risk group for two reasons. Firstly, they are likely to ingest inadvertently significant quantities of dust than adults; and secondly, young children are usually more susceptible to a given intake of toxin than adults. "Pica"(the mouthing of non food objects) and repetitive hand or finger sucking are thought to be the two main dust ingestion routes (more or less) unique to children (Duggan and Williams, 1977; Duggan, 1980)

Street dust has the potential to provide substantial suspended particulate and dissolved loadings of heavy metals to receiving waters and water bodies through storm water runoff (Morrison et al., 1990; Charlesworth and Lees, 1999). On land, vegetables and fruits may be

contaminated with surficial deposits of dusts (Lagerwerff and Specht, 1970).

Numerous sources may contribute to street dust such as soil, cement, vehicular emissions, tyre wear, industrial wastes, and salt sprays (particularly in areas near to ocean) etc., but soil particles are the most predominant (Hopke et al., 1980; Fergusson and Ryan, 1984; Harrison et al., 1981). The elemental composition, patterns of distribution are not common to all urban environments but may vary according to peculiarities of the city such as nature and strength of different contributing sources, deposition and resuspension processes, hydrometereological conditions, municipal street cleaning practices etc. The elemental composition of street dust might vary at different locations within the same city and even in the same locality at small distances (Schwar and Alexander, 1988). The elements present in street dust can be classified into three groups: "natural elements", which originates primarily from soils (Al, Ga, La, Mn, Na, St, Th, Y, K, Ti, Sm and Ce), enriched and therefore "polluting elements" which primarily originate from anthropogenic sources i.e. industrial, tyre wear, salt spray, cement etc., (Pb, Cd, Cr, Zn, Cr, Cl, Br, Co, Ba and Mg) and which have mixed origin (Ca, Ce, Fe, Mo, Ni, Rb, Sr, U), (de Miguel et al., 1997). Sources of polluting elements are of four main types: Road traffic, industrial, weathered materials and specific intermittent episodes.

The principal polluting sources of many trace elements are the gasoline driven automobiles. Elements identified originating from automobiles are Pb, Cd, Cu, Zn, Fe, Cr, Ni and Br. Lead comes from burning of leaded gasoline. Zn and Cd come from tyre wear (Harrison, 1979) and lubricating oils. Zn-diethylcarbonate is used in vulcanisation of tyre rubber and Zinc dithiophosphate is an additive to lubricating oils whereas Cd may be present as an impurity in the original Zn compound used (Legerwerff and Specht, 1970). Br comes from additives in petrol for removal of lead from car engines; therefore

there is a close Pb/Br ratio in dust. Ni is added to gasoline (Shaheen, 1975). Cu is a major component of brake lining and is therefore present in brake dust. Other elements associated with automobiles are As, Ba, Cr and Mn from tyre wears and Cr, Cu and Ni from electroplated metallic parts.

Contribution of industrial sources to trace metal pollution is variable depending upon the type of industry present in the vicinity. Pb, Cd, Cu, Zn, Fe, Ni and Cr are generally identified with specific industries such as lead with battery factory (Fergusson et al., 1980) and news paper print works (Jensen and Laxen, 1985); Zn and Cd from galvanisers; Cr, Cu, Ni and Zn from electroplaters. A number of weathering surfaces and materials can also contribute locally to the trace elements loading to street dust, e.g., Pb might be driven from crumbling old paint works, Fe from corroding Fe products, Ca from concrete material, Zn and Cd from exposed galvanised surfaces. A number of particular circumstances such as redecoration of building painted with metal-based paints can intermittently raise the trace elements levels (Schwar and Alexander, 1988).

Lead is the most frequently investigated element in dust (Solomon and Hartford, 1976; Archer and Barratt, 1976; Duggan and Williams, 1977; Day 1977; Farmer and Lyon, 1977; Ho, 1977 and Fergusson et al., 1980) and has been studied in relation to traffic density, location, mode of driving and vehicle and paint sources as well as industrial sources. Cd is the second element most frequently studied in street dust. Now a considerable body of information is available on Pb and Cd but very little attention has been given to other trace toxic elements such as Cr, Cu, Zn etc., which are frequently encountered in the urban environment. One of the most obvious reasons of more emphasis on Pb might be the expected quantitative greater concentration of the element in comparison to other. Because of the paucity of data on heavy metals (except Pb) in street dust, there is clearly a need for further studies on other heavy metals. There are

strong evidences that dust is an important pathway in the exposure of people, especially the children, to metals. Literature records that the children living in the city have relatively high blood levels of Pb, which have been attributed to the ingestion of dust containing Pb (Waldron, 1975; Duggan and Inskip, 1985).

Toxicity of all trace elements to the biota is well established. Environmental and health effects of trace metal contaminants in dust are dependent at least initially on the mobility and availability of the elements, functions of their chemical speciation and partitioning with or on dust matrixes. However there is little information available upon which to base an assessment of this question. Most studies in trace elements in street dust have concentrated on total levels with little emphasis on chemical forms. According to Bernhard et al. (1986), to assess the environmental impact of polluted environmental component the measurement of total trace metal levels is not enough. So it is necessary to have the knowledge about the speciation of the element.

Speciation of the trace elements can be determined theoretically by thermodynamic calculation or by experimental techniques. Thermodynamic models available till now only suggest the expected trace element species distribution. The results may be different from real solid speciation because of the important role of kinetically controlled processes.

Experimental methods include direct instrumental techniques (X-ray fluorescence and Scanning electron microscopy) and chemical methods. Although instrumental techniques of speciation may yield more precise information regarding the identification of metal forms, but these methods are qualitative and often not sensitive enough to detect forms present in very small concentrations.

The chemical approach to solid state speciation is to treat the material with an extracting agent, which attacks a certain phase in solid releasing the trace element either coprecipitated or adsorbed or

incorporated into organic matter. The most common method is that of selective extraction procedures (SEP).

Selective extraction procedures (SEP) are the techniques, which are widely employed to determine the geochemical partitioning of heavy metals amongst solid minerals and organic phase in earth materials (soil, sediment, dust, sludge etc). The procedures involve a succession of chemical reagents that selectively extract or dissolve various targeted phases composing a sample. As heavy metals in various geochemical forms are thought to differ in their degree of mobility and bioavailability, this approach is theoretically very useful for site assessment and risk analysis. Table 1.3 shows the most common phases and the type of extractant used for metal extraction in dusts, sediments, soils and sludges.

Table 1.3. Classification of phases with which metals are associated in dust, sediments and soils.

Classification	Form of association	Extraction process
Soluble	Metal ppt.; pore water	Release to pure water or river water
Exchangeable	Specifically adsorbed, ion exchangeable	Exchange with excess cations
Carbonate phase	ppt or co-ppt	Release by mild acid
Fe-Mn oxide phase	specifically adsorbed, co-ppt	Reduction
Organic phase	complexed or adsorbed	Oxidation
Residual	mineral lattices	Digestion with strong acid

ppt : precipitate
(Harrison et al., 1981)

Although selective sequential procedures are widely used in geochemical research, there are some questions about the accuracy of selectivity of reagents (i.e. a reagent designed to selectively dissolve/extract one phase might also attack others, destroying the selective role of the reagent) and readsorption i.e. metals liberated by selective dissolution/extraction during earlier steps are readsorbed and redistributed artificially amongst the remaining solid phases (Guy et al., 1978; Rendell et al., 1980 ; Tipping et al., 1985). It is widely

recognised that no reagent is perfectly selective, so the fractions recovered are best defined operationally.

In the light of above discussion the objectives of the present study were:

I). To estimate the levels of Cd, Cu, Cr, Zn, Pb and Ni (the pollutants which have the known pollutant properties and are readily available to environment because of their use in both production and consumption related processes) in street dust samples collected from three different locations in Delhi to investigate the differences arising from characteristics of the location i.e. industrial, heavy traffic and rural sites.

II). To detect the microsite variation in metal levels within the same location.

III). Sequential extraction analysis of some selected dust samples (covering all ranges of metal concentrations) to compare the relative environmental mobility and hence bioavailability of the six selected metals.

Literature Review

Street dust, a product of the life style, originates from interaction of solid, liquid and gaseous materials produced from different sources. The elemental composition and the concentrations in street dust, reflect the characteristics of the activities going in the particular area. Generally highly elevated levels of heavy metals are observed in the street dusts.

The two elements, which have been studied extensively, are lead (particularly) and cadmium. Since lead is the most abundant polluting element in the urban environment, highly elevated concentrations are observed in street dusts. Also a wide range of concentrations have been reported in previous studies. Table 2.1 represents the levels of Pb in different cities and locations reported in literature. Cadmium is the second element upon which emphasis was given and Table 2.2 represents the concentrations of Cd reported in street dusts in previous studies.

Perusal of all the available data in Table 2.1 and 2.2 reveals large variability in levels of Pb and Cd. This variability can be as a consequence of different sampling procedures followed, possible fractionation of dust in the sample in terms of particle size and density, spatial and temporal variations and differences in analytical procedures followed; as also discussed by Fergusson (1987).

The methods used to sample street dust are brushing, sweeping, and wiping by using sticky tapes, as well as vacuum cleaner and dust fall. The methods most commonly used are sweeping (Duggan, 1984; Gulson et al., 1994; Ogunsola et al., 1994; Al-Rajhi et al., 1996) or brushing (Archer and Barratt, 1976; Fergusson and Simmonds, 1983; Davies et al., 1987; Culbard et al., 1988). Vacuum technique has also been used in many studies, but surprisingly Archer and Barratt (1976) observed that pump-sampling technique gave a lower average metal concentration than the brush method,

which might be because of preferential collection of light dust and fluff, which tend to dilute the sample. In contrast to this, Harrison (1979) found that the samples collected with vacuum cleaner showed very high concentration of Zn in comparison to samples collected with hand brushing. It appeared that vacuum cleaner contributed to Zn contamination.

Table 2.1. Some typical concentrations of Lead in street dust (in ppm)

Location	Site	Mean/Median	Range	Ref.
Bahrain	All type of locations	742		Madany et al., 1994
Canada	Halifax		674-1919	Fergusson and Ryan, 1984
Cuena(Ecuador)	Urban	293	77-970	Hewitt and Candy,1990
Egypt	Jeddah	125-925	56-1850	Nasrall, 1984
	Hills around Jeddah	7.5	2.5-15	Nasrall, 1984
	Cairo	45-3535		Ali and Nasralla, 1985
Greece	Playground dust	200	15.6-1276	Anagnostopulos, 1985
Hong Kong	Various sites	132-3876		Lau and Wong, 1982
		2974	271-19073	Ho, 1979
India	around Pb smelter	536±39		Chatterjee and Banerjee, 1999
Jamaica	Kingston		817-909	Fergusson and Ryan, 1984
Malaysia		2466		Ramlan and Badri, 1989
Netherlands	Near smelter	859	77-667	Diemel et al., 1981
	Near smelter	761	25-2667	Keizer et al., 1988
NewZealand	Christ,inner city	2790	200-7840	Fergusson et al., 1980
	Busy intersection	6340	1780-12910	Fergusson and Simmonds, 1988
	Christchurch		887-10700	Fergusson and Ryan, 1984
	Christchurch	1223	175-2794	Fergusson et al., 1986.
Nigeria	Lagos(Residential)	172.2	51.1-297.3	Ogunsola et al., 1994
	Lagos(Industrial)	304.9	192.5-417.3	Ogunsola et al., 1994
	Lagos(Highway)	640.6	24.7-1180.4	Ogunsola et al., 1994
	Lagos(Marine area)	218.4	77.9-413.1	Ogunsola et al., 1994
	Lagos(Bus stop)	189.2	43.6-1024.5	Ogunsola et al., 1994
St.Croix		327		Brown, 1986
U.S.A.		1000		Hopke et al., 1980
	Central NewYork		2213-2952	Fergusson and Ryan, 1984

Location	Site	Mean/Median	Range	Ref.
	Champaign-Urbana	600	170-1440	Solomon and Hartford, 1976
	Particle size	120-5080		Dong et al., 1984
		803		Brown, 1986
U.K.	Nationwide survey	786	45-9660	Culbard et al., 1988
	Playgrounds	289	11-6800	Culbard et al., 1988
	Beside motorways	1604-2296		Ellis and Revitt,1982
	Country lane	111		Ellis and Revitt, 1982
	Various sites	1045-2346		Hamilton et al., 1984
	Central London		2008-4053	Fergusson and Ryan, 1984
	School playground	220-5800	90-45000	Duggan et al., 1985; Rundle et al., 1985
	Exhaust replacement		0.5-3%	Chambers et al., 1984
	Lancaster		480-2600	Sturges and Harrison, 1985
	Birmingham	506	62-5100	Davies et al., 1987; Thomas et al., 1985
	Birmingham roadway	805	80-2100	Davies et al., 1987; Thomas et al., 1985
	Birmingham	1630	160-50000	Archer and Barratt, 1976
	Glasgow	960	150-2300	Farmer and Lyon, 197
	London	1200	430-3500	Duggan and Williams, 1977
	Greater Manchester	970	90-10200	Day et al., 1975
	Lancaster	1880	920-3560	Harrison, 1979
	Across a road		11-482	Beckwith et al., 1985
	Near printing works	7500	3700-13500	Jensen and Laxen, 1985
	Along major road		1360-3600	Jensen and Laxen, 1985
	Major arterial road		3610-4420	Warren and Birch, 1987
	Greater London	345*	30-17900	Schwar et al., 1988
	Inner London	540*	84-15300	Schwar et al., 1988
	School playground, redecorated	630-4720	90-74400	Schwar et al., 1988
	School playground, further away	400-1180	110-10200	Schwar et al., 1988

* Median value

Table 2.2. Some typical concentrations of Cadmium in street dust (in ppm)

Location	Site	Mean/Median	Range	Ref.
Bahrain	All locations	1.5		Madany et al., 1994
Canada	Halifax	0.6-1.4		Fergusson and Ryan, 1984
Ecuador	Cuena,urbam dust	0.36	0.23-0.42	Hewitt and Candy,1990
Egypt		149		Ali and Nasrall, 1985
Hong Kong	Various sites	6-28		Lau and Wong, 1982
Jamaica	Kingston	0.8		Fergusson and Ryan, 1984
Netherlands	Near a smelter	1.43,3.81	0.5-16	Keizer et al., 1982
New Zealand	City wide survey	2.0	0.3-16	Fergusson et al., 1980
	Christchurch	1.46	0.5-4.3	Fergusson and Simmonds, 1983
	Christchurch		0.8-1.1	Fergusson and Ryan, 1984
Nigeria	Lagos(Residential)	0.7	.35-1.14	Ogunsola et al., 1994
	Industrial	0.56		Ogunsola et al., 1994
	Highway	0.72	0.62-0.81	Ogunsola et al., 1994
	Marine areas	0.56	0.52-0.60	Ogunsola et al., 1994
	Bus stops	0.75	0.39-1.21	Ogunsola et al., 1994
Scotland	Glasgow	1.4		Schwar et al., 1988
U.K.	Various urban sites	2.7-4.9		Harrison et al., 1981
England	Urban roads	4.6	1.3-10.1	Harrison, 1979
	Car parks	7.0	1-14.6	Harrison, 1979
	Rural areas	2.1	1.0-2.9	Harrison, 1979
	Various sites		0.7-6.8	Ellis and Revitt, 1982
	Ten town survey	2.7	1-210	Culbard et al., 1983
	Various sites		1.0-4.3	Hamilton et al., 1984
	London	5.2-7.4		Fergusson and Ryan, 1984
	Reconnaissance survey	2.0	<1-280	Culbard et al., 1988
	Major urban highway		3.3-4.3	Warren and Birch, 1987
	Greater London	2.5*	<1.2-20	Schwar et al., 1988
	Inner London	3.6*	<1.2-8.7	Schwar et al.,1988
U.S.A.	Urban street dust	1.6		Hopke et al., 1980
	New York	4.6-11.4		Fergusson and Ryan, 1984
	Function of particle size	1.0-29		Dong et al., 1984
Wales	Mining areas	0.7	0.1-3.6	Davies et al., 1985
	Mining areas	0.5	0.2-1.6	Davies et al., 1985

*Median Value

Recently, Bris et al. (1999) have suggested a wet brushing and suction method, which suits to all categories of urban surfaces e.g. asphalted, cemented and floors etc., but the problem with this method is that a heavy set-up is needed and such

sampling necessitates deviation of vehicular and pedestrian traffic. The sampling of deposited dust is open to criticism. The ignorance of the history of the sample means that it is not known whether the concentration has reached over a period of months or decades (Archer and Barratt, 1976). Also some natural fractionation of dust may have occurred in the street dust, so it is possible that a sample contains more or less of one fraction compared with another. So, the method of sampling obviously has influence on the results obtained. Despite of these limitations, the street dust is preferred, as most of the pollutants released from different sources (vehicular, industrial and others) remain suspended in the atmosphere only for short time intervals and are ultimately deposited on the exposed surfaces. Street dust also contributes to suspended particulate matter by resuspension.

Several methods have been used for total metal extraction in different studies and some of them are listed below:

1) Combination of HNO_3 and HCl (Harrison, 1977; Harrison, 1979; Biggins and Harrison, 1980; Duggan et al., 1988; Schwar and Alexander, 1988)

2) Different ratios of HNO_3 and $HClO_4$ (4:1 ratio by Davies et al., 1987 and 9:1 ratio by Warren and Birch, 1987; Hamilton et al., 1984; Jensen and Laxen, 1985).

3) Different concentrations of HNO_3 (4M by Fergusson and Ryan, 1984; 8N by Solomon and Hartford, 1976 and 2N by Day et al., 1975 and Nasralla, 1984).

4) 1:1 mixture of HNO_3 (65%) and H_2O_2 (35%) (Ogunsola et al., 1994).

5) 1:1:2 ratio of HNO_3: $HClO_4$: HF (de Miguel et al., 1997).

6) 1:5:1 ratio of $HClO_4$: HNO_3: H_2SO_4 (Charlesworth and Lees, 1999).

7) Microwave digestion (Leharne et al., 1992).

The different methods have different metal extraction efficiency, so this might be one of the reasons for variability in results in different studies.

Although there are considerable number of studies on concentrations of heavy metals in street dust, the vast majority of them have been carried out in developed countries with long histories of industrialisation and crucially in case of lead extensive use of leaded gasoline. Very few studies have been made in developing and underdeveloped countries and reliable data on pollutant metal concentrations and distributions in such areas is extremely sparse. So there is a need to obtain information on basic environmental parameters in these areas.

Sources of dust and its trace metal content

Investigation of sources of dust and hence it's trace metal content have been approached in two ways. The most common method has been to consider trends in concentrations of the individual elements with respect to some source. A decrease of concentration with distance is the evidence for the proposed source. The second approach is to make use of multi-elemental data from which by using statistical techniques, source receptor models can be proposed.

Street dust: Trends in trace metal concentrations

The study of trends in concentration of individual trace element in street dust in order to establish their sources mostly focuses on pollution elements. Sources are of four main types: road traffic, industrial, weathered material and specific intermittent sources.

The principal polluting source is the petrol driven automobiles. Elements originating from the automobiles are Pb, Cd, Cu, Zn, Fe, Cr and Ni. Lead comes from the petrol, whereas other elements come from wear and tear of the vehicles, such as Zn and Cd come from tyre wear (Shaheen, 1975). Evidence for the source derives from trends in

concentrations with traffic density, distance from road, urban and suburban differences and mode of traffic.

The trends in concentration with traffic density has been studied by Archer and Barratt (1976); Duggan and Williams (1977); Day (1977); Fergusson et al. (1980); Lau and Wong (1982); Fergusson and Simmonds (1983); Hamilton et al. (1984); Nasrall (1984); Leharne et al. (1992) and Ogunsola et al. (1994).

The studies of Archer and Barratt (1976) in Birmingham, Duggan and Williams (1977) in Greater London, Fergusson and Simmonds (1983) in Christchurch, Hamilton et al., (1984) in new London, Nasrall (1984) in Jeddah city (Egypt) and Leharne et al., (1992) in Globetown (U.K.) found a decrease in metal levels from high traffic density main road to low traffic density residential side streets. Lau and Wong (1982) observed a significant correlation (r=0.93; p< .005) between metal concentrations (Pb, Cd, Zn, Cu & Mn) and the annual average daily traffic (AADT). Ogunsola and coworkers (1994) also found similar observations.

Decrease in metal concentrations in street dust with the increasing distance from the road were detected by Warren and Birch (1987) and Brown (1986) in their studies on A13 Newham way (East-London) and central Charlotte Amalie, St. Thomas, U.S. Virgin Islands respectively.

Urban/rural differences were shown by Hewitt and Candy (1990) in and around Cuena (Equador) indicating that the extent of metal contamination was restricted to urban area. Day (1977) has also compared the Pb concentrations in urban and rural street dust samples and the urban samples were found to have significantly higher concentrations in comparison to the rural samples. However Ellis and Revitt (1982) and Terharr and Aronow (1974) have offered the contradictory evidences concerning metal levels in dust with traffic density and urban/rural differences, respectively. Ellis and

Revitt (1982) observed that the urban /residential and rural samples exhibit comparable values for Cd, Cu, Fe, Mn and Pb. Similarly, Terharr and Aronow (1974) found equal Pb levels in rural and urban yards at corresponding distances from painted houses and concluded that nearly all the Pb in dust around the houses is due to paint.

The dependency of metal levels in street dust on mode of driving i.e. stop, start, accelerating the vehicle and installation of new traffic light was observed by Fergusson et al. (1980) and Fergusson and Simmonds (1983). Fergusson et al. (1980) indicated high lead levels at the traffic intersection in comparison to other intermediate sites and attributed this to the traffic density, mode of driving i.e. stop, start, acceleration of the vehicles in Christchurch (New Zealand). The effect of automotive emissions on roadside soils has also been investigated with respect to traffic density (Lau and Wong, 1982; Garcia and Millan, 1994; Ward et al., 1977), distances from road (Lagerwerff and Specht, 1970, Ndiokwere, 1984, Garcia and Millan, 1994; Albasel and Cottenie, 1985; Muskett and Jones, 1980; Burguera and Burguera, 1988) and depth in the soil. (Lagerwerff and Specht, 1970; Ward et al., 1977; Burguera and Burguera, 1988). In common the metal concentrations in soils were well correlated with traffic densities, decrease with distance from the road and with depth in the soil profile.

Pb and Br are the traditional marker elements for motor vehicular pollution but Pb is rapidly disappearing as the marker element as leaded gasoline is being phased out. Huang et al. (1994) suggested that Zn, Br and Sb could be used as the marker elements for vehicular emissions, as these are emitted in considerable amounts.

A reduction in Pb content in gasoline has been announced in many countries. The effect of reduction in lead concentration in gasoline has been assessed on the Pb level in blood (Thomas et al.,

1999); street dust (Ho et al., 1990; de Miguel et al., 1997) and air borne particulate matter (Page et al., 1988). The results of Page et al., (1988) has shown 52-61% fall in air lead with 63% reduction in petrol lead.

Industrial sources are varied and elements such as Pb, Cd, Cu, Zn, Fe, Cr and Ni have been identified with specific industries (Archer and Barratt, 1976; Jensen and Laxen, 1985; Davies et al., 1987; Schwar et al., 1988; Fergusson and Kim, 1991; Gulson et al., 1994; Chatterjee and Banerjee, 1999). The geographical distribution of elements Cd, Cu, Pb, Zn and Fe in street dust in Greater London clearly shows the lower concentration in rural/residential areas and distinct high concentration in areas associated with industrial activity (Schwar et al., 1988). Investigation of some local hotspots in Central London identified newspaper printworks as significant source of street dust lead (Jensen and Laxen, 1985). Fergusson and Kim (1991) detected elevated concentrations of Cd, Zn and Pb in street dust with industrial use of the metal, in particular, electroplaters for Cd and Zn, galvanizers for Zn and battery factory and spray painters for Pb. Chatterjee and Banerjee (1999) and Archer and Barratt (1976) observed very high levels of lead-in-dust in the immediate vicinity of lead smelter (Calcutta) and a factory using Pb (Birmingham) respectively.

Higher mean concentrations of lead in industrial areas in comparison to the residential areas were observed by Leharne et al. (1992) and Davies et al. (1987).

Under particular situations such as vicinity to mining areas, the orebody might contribute significantly to the metal in dust. Gulson et al. (1994) by lead isotopic method (^{206}Pb/^{204}Pb) determined that orebody lead contributed more to small size fraction of street dust in comparison to large size fraction.

In general the development of some spatial/temporal trend in metal-in-dust are observed with respect to a certain source. It has often been assumed that heavy metal loadings on highway surfaces are directly related to traffic density. However, a collation of published metal levels in street dusts does not substantiate this assumption e.g. in the vicinity of a network of roads or when more than one source contribute to metal-in-dust, there might not be a significant spatial/temporal variation. Day et al. (1975) observed a reasonably uniform dispersal of Pb in dust in Manchester. Indeed no general pattern with respect to major roads or industrial sites emerged. They concluded that presumably, more or less complete mixing of lead from various sources must have occurred giving a reasonably uniform Pb levels in dusts. Similarly, Ho (1979) could not detect a significant correlation (r= 0.084,P >0.01) between lead levels and traffic density in his study on Pb contamination in Hongkong.

A number of materials in urban areas might contribute to street dust from weathering processes. The elements Pb, Cu, Zn, Cr and Cd have been identified as coming from weathered materials (Fergusson and Simmonds, 1983; Schwar et al., 1988; Solomon and Hartford, 1976 and Terharr and Aronow, 1974). In the study of Fergusson and Simmonds, (1983), the variation of Pb and Zn in street dust with weather conditions helped to identify sources. After heavy rain, lead levels fell as dust was washed away, whereas Zn levels increased, probably from washing off of the weathered material present on the galvanized iron house roof.

A number of particular circumstances can intermittently raise trace element concentrations in dust, though this may not significantly affect levels in long term. One process that has marked effect on Pb concentration in dusts is the redecoration of houses painted with lead based paints (Schwar et al., 1988). Some localised sources can also significantly attribute to metal-in dust e.g. very high concentration of Pb (0.5-3%) in exhaust replacement centres

(Chambers et al., 1984) and car parks and garages (Leharne et al., 1992, Harrison, 1979). The only plausible explanation for these results was the existence of some localised source of Pb i.e. lead rich particles dislodged from the exhaust systems of the cars subjected to considerable mechanical vibrations.

Some additional factors also might play significant role in metal levels in dusts; one such factor is the nature of road surface e.g. a concrete surface can yield high levels of metals, compared to an asphalt surface (Shaheen, 1975). The concentrations of the elements Pb, Cu and Zn tend to increase from the pavement to gutter to the center of the road (Duggan and Williams, 1977; Ellis and Revitt, 1982; Beckwith and Ellis, 1985; Davies et al., 1987). The variations are probably as a result of size fractionation of dust particles, the smallest occurring in roadway and the dilution of dust farther away from road surface by materials such as soil. Studies by Fergusson and Ryan (1984), Ellis and Revitt (1981) and Al-Rajhi et.al. (1996) revealed that the concentration of a large proportion of elements (Cu, Pb, Th, Zn, Mn, V, Al, Ca, Ti, Sm, Cd, Hg, Cr, Si, la, Ni, As and Co) except a few (K, Na, Cl and Br) increases with decrease in particle size.

Weather is also an important factor influencing metal levels in dust. The levels of metals generally fell after heavy rain, presumably because the materials are carried into storm water runoff either as dissolved or as particulate load (Fergusson et al., 1980; Fergusson and Simmonds, 1983; Hamilton et al., 1984; Fergusson and Kim, 1991)

Street dust: Multi-element trace metal concentrations

Multi-element analytical data on dust provides concentration profiles of the metal-in-dust. This together with information on sources enables deduction to be made as to the sources and their relative contributions. Some of the techniques used are single and multiple regression analysis (Fergusson and Simmonds, 1983;

Fergusson and Hayes, 1980; Keizer et al., 1982; Warren and Birch, 1987), chemical element balances (Fergusson and Ryan, 1984; Hopke et al., 1980), F-test (Fergusson et al., 1986), factor analysis (de Miguel et al., 1997), Principal component analysis (de Miguel et al., 1997), coefficient of variation (Fergusson, 1987), enrichment and abundance factors (Fergusson and Ryan, 1984; Fergusson et al., 1986; Ferguson and Simmonds, 1983; Leharne et al., 1992), cluster analysis (de Miguel et al., 1997; Ogunsola et al., 1994) and element concentration ratios (Fergusson and Ryan, 1984).

The significant findings are that the main component of street dust is soil and that the elements in street dust fall into two groups; those that are primarily soil based and those that are from pollution sources (Fergusson et al., 1986; Fergusson and Ryan, 1984; Fergusson and Simmonds, 1983). The elements Hf, Th, Sc, Sm, Ce, La, V, Al and K are considered to be soil based and a more detailed study of ratios (i.e. with respect to the size of the dust particles) suggests that the soil contribute more to the larger size particles than to the smaller size particles (Fergusson and Ryan, 1984). The enriched and therefore polluting elements include: Pb, Se, au, Zn, As, Cu, Sb, Cr, Cl, Br, Cd, Ca and Na. Whilst the more explicit statistical analysis (Factor analysis, Principal component analysis and Cluster analysis) performed on the multielemental data by de Miguel et al. (1997) suggests that the chemical elements can be classified into three groups according to their source: "urban" elements (Ba, Cd, Co, Cu, Mn, Pb, Sb, Ti, Zn), "natural" elements (Al, Ga, La, Mn, Na, Sr, Th, Y) and elements of mixed origin or which have undergone geochemical changes from their original sources(Ca, Cs, Fe, Mo, Ni, Rb, Sr, U).

Data summarised by Waldron and Stofen (1974) shows a marked increase in oral toxicity of Pb compounds with increasing water solubility. Chamberlain et al. (1978) used radioactive lead to investigate the absorption of Pb through the gut and observed highest uptake with rather soluble $PbCl_2$ taken after fasting and lowest

uptake with highly insoluble PbS. So clearly before full assessment of the likely health hazards associated with dusts can be made, information is required on the speciation of metals in dust.

Most studies on trace metal in dust have concentrated on the metal levels with little emphasis on chemical speciation. But the determination of total metal is insufficient to assess the environmental impact of polluted dusts.

Trace element speciation in dust

The speciation of trace elements can be determined by theoretical thermodynamic calculations or by experimental techniques. Thermodynamic models available till now only suggest the expected trace element species distribution. Results may be different from the real solid state speciation because of the important role of kinetically controlled processes. Experimental procedures include direct instrumental techniques (X-ray fluorescence, Scanning electron microscopy etc.) and selective extraction procedures.

Instrumental techniques

The methods generally used are scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS), X-ray powder diffraction, and Mossbauer spectroscopy. The SEM/EDS method gives elemental concentration at a particular spot in a sample from which the speciation can be deduced. X-ray diffraction gives the diffraction pattern from specific compounds, but does require the compound to be crystalline. Olson and Skogerboe (1975) and Biggins and Harrison (1980) used the XRD for lead speciation in soils and street dust respectively. Biggins and Harrison (1980) concluded that crystalline compounds can account at most for only a few percent of total metal in dust, and that alternate approaches to speciation are required.

Solid state instrumental analysis, with a scanning electron microscope with energy dispersive X-ray analysis and microscopic analysis was used to locate sources of the elements (Sturges and Harrison, 1985; Linton et al., 1980). Material originating from car was detected by its association with iron. The lead near the curb was estimated to be almost all automotive in origin, whereas near buildings, paint was the major contributor, with 10-20% from automotive sources (Linton et al., 1980).

Although the instrumental techniques can yield more precise information regarding the identification of metal forms, but these methods are qualitative and often not sensitive enough to detect forms present in very small amounts.

The chemical approach for trace element speciation

The chemical approach to trace element speciation is to treat the material with an extracting agent, which attacks a certain phase in the solid, releasing the trace elements either co-precipitated or adsorbed or incorporated into the organic matter. The most common method is that of selective sequential extraction.

In a sequential extraction, several selective reagents are used consequently to extract "operationally defined phases" from solid matter in a set sequence. A number of selective sequential extraction schemes are cited in literature i.e. McLaren and Crawford, 1973; Gupta and Chen, 1975; Tessier et al., 1979; Shuman, 1979; Salmons and Forstner, 1980; Shuman, 1985; Gibson and Farmer, 1986; Miller et al., 1986; Kersten and Forstner, 1986; Rauret et al., 1989; Ure et al., 1993(Bureau Communautaire de Refrence, 1992); Leleyter and Probst, 1998. The most commonly isolated phases in different sequential extraction schemes are: Exchangeable, Carbonate bound, Fe-Mn oxide bound (Reducible), Organic (Oxidable) and Residual. The reagents used in different sequential extraction schemes (SES) for selective isolation of soil/sediment phases are listed in Table 2.3.

Table 2.3. Soil/Sediment phase nominally isolated and the extractant used in different sequential extraction procedures

Phase isolated or extracted	Reagent or method of isolation	Ref.
Exchangeable	1 M NH₄OAc, 1M MgCl₂, 1M BaCl₂, 1M Mg(NO₃)₂, 0.43M HOAc, .05M CaCl₂ 0.5MCa(NO₃)₂	Gupta and Chen, 1975; Gibson and Farmer, 1986. Kersten and Forstner, 1986; Gibbs,1973 human, 1979; Tessier et al.,1979 Meguellati, 1982 Leleyter and Probst,1998 Ure et al., 1993 McLaren and Crawford,1973 Miller et al., 1986
Carbonate bound	1M NaOAc	Tessier et al.1979; Kersten and Forstner,1986;Gibson and Farmer,1986; Leleyter and Probst,1998
Fe-Mn Oxide bound	Acidic hydroxylamm -onium Ammonium oxalate Sodium dithionate	Tessier et al., 1979; Kersten and Forstner, 1986; Gibson and Farmer, 1986. Leleyter and Probst, 1998; McLaren and Crawford, 1973; Shuman, 1979 Shuman, 1985; Gibbs, 1973; Gupta and Chen, 1975.
Organic	30% H₂O₂/HNO₃ NaOCl K₄P₂O₇	Tessier et al., 1979; Kersten and Forstner, 1986; Gibson and Farmer, 1986; BCR, 1993; Gupta and Chen, 1975; Shuman, 1979; Leleyter and Probst, 1998; Gibbs,1973; Shuman, 1985 McLaren and Crawford, 1973 Miller et al., 1986
Residual	HF-HClO₄ HNO₃ conc.(hot) HF-aqua regia HF-HClO₄-HNO₃ Fluxing with Lithium metaborate at1000°C	Tessier et al.,1979 Kersten and Forstner,1986 Miller et al., 1986; Gibson and Farmer, 1986 Hall and Pelchat, 1999 Gibbs, 1973

Although SES are widely used for geochemical research but there are some significant limitations associated with the selectivity of

the reagents, the redistribution of trace elements during extraction, the deficiency of a reagent dose if metal content is too high (Ramos et al., 1994) and the inability to distinguish between metal associations with organic matter and sulfides (Adamo et al., 1996). A reagent designed to selectively dissolve/extract one phase may also attack others, destroying the selective role of that reagent. Once an element has been released in solution by a reagent, it may then redistribute itself among the remaining solid phases, before the solid and solution are separated (Guy et al., 1978; Rendell et al., 1980; Tipping et al., 1985; Rapin et al., 1986; Xiao-Quan and Bin, 1993).

Howard and Shu (1996) and Howard and Vandenbrink (1999) have suggested the use of chelating agents such as NTA (nitrilotriacetic acid) to counteract resorption, but the use of NTA might has the possibility of dissolving non-targeted phases especially in the calcareous soils/sediments, which are rich in limestone.

It is well recognized that no reagent is selective perfectly, so the fractions recovered are best defined "operationally' i.e. by the procedures, reagents or extractants used to isolate them, despite the fact that the phase may be ill-defined or the procedure insufficiently specific.

Even though a few sequential extraction schemes have met common acceptance but lack of uniformity in different schemes does not allow the results to be compared. Out of all schemes the most commonly used and the thoroughly researched is that of Tessier et al., (1979). This method also has some problems regarding selectivity and resorption. In spite of these problems there is good agreement between different studies on soils, sediments and street dusts. The reagents and conditions for selective sequential extraction of trace elements by using Tessier's method are listed in Table 2.4.

Table 2.4. Reagents and conditions for the selective sequential extraction of trace elements according to Tessier et al. (1979) scheme

Phase	Form	Reagent	Time (h)	Temp (°C)
Exchang-eable	Ion-exchange and adsorbed	1M MgCl2, pH 7	1	≅20
Carbonate	Coprecipitated and adsorbed	1M NaOAc, pH 5	5	≅20
Fe/Mn oxides and hydroxides	Coprecipitated and adsorbed	0.04M NH2OH.HCl 25%HOAc	6	≅96
Organic	Coordinated and adsorbed	0.02M HNO3, 30%H2O2	3	≅85
Residual	Mineral and Silicate lattice	40% HF, 72%HClO4		Boil

As discussed earlier, there are only a few studies on street dusts, which have used the sequential extraction schemes for speciation of trace elements (Harrison et al., 1981; Gibson and Farmer, 1984; Fergusson and Ryan, 1984; Hamilton et al., 1984; Fergusson and Kim, 1991 and Charlesworth and Lees, 1999a). In all these studies except the one (Gibson and Farmer, 1984), the scheme designed by Tessier et al. (1979) was applied. The observations on trace element portioning in street dusts are listed in Table 2.5.

Perusal of the data in Table 2.5 indicates a quite similar pattern for trace metal fractionation in street dusts, despite the fact that the above mentioned studies were carried out in quite different kind of situations. The results indicate that Pb and Zn are mainly bound with Fe-Mn oxide and carbonate fractions, Cu with organic fraction, whilst Cd is nearly equally distributed between exchangeable, carbonate and Fe-Mn oxide fractions. Out of all the four metals Cd is the only metal, which is appreciably associated with exchangeable fraction. These results can be used as a guide to metal availability and the overall order of metal availability is Cd>Pb=Zn>Cu, which was also suggested by Harrison et al., (1981).

Table 2.5. Typical sequential extraction (%) of Pb, Cd, Cu and Zn from street dust.

Metal	Exchang-eable	CO$_3^{2-}$	Fe-Mn Oxide	Organic	Residual	Ref.
Pb	1.5	43	38	7.5	10	Harrison et al., 1981
	13	28	32*	14	13	Gibson and Farmer, 1984
	1.9	34	44.2	7.1	11.2	Fergusson and Ryan,1984
	1	42	38	20	4	Hamilton et al., 1984
Cd	20	38	28	8	6	Harrison et al., 1981
	27	19	16*	22	16	Gibson and Farmer, 1984
	17.7	31.4	38.3	7.8	4.7	Fergusson and Ryan,1984
	5	42	25	24	4	Hamilton et al., 1984
Cu	7	18	4.5	58	12	Harrison et al., 1981
	11	4	11*	43	31	Gibson and Farmer, 1984
	1.3	8.6	11.3	53.2	25.6	Fergusson and Ryan,1984
	2	8	5	70	18	Hamilton et al., 1984
Zn	2	44	43	7.5	4.5	Harrison et al., 1981
	10	23	25*	16	26	Gibson and Farmer, 1984
	3.4	30.2	50.8	9.1	6.6	Fergusson and Ryan,1984
	3	30	35	13	18	Hamilton et al., 1984

*All values are in percentages
The sum of easily and moderately reducible fractions

Study

Area

Delhi, the administrative capital of India, lies between $28^0 26'$ and $28^0 53'$ north latitude and $76^0 51'$ and $70^0 22'$ east latitudes. It is situated in the north of India, 160Km south of the Himalayas. Delhi has the Thar Desert of Rajasthan to the west, the central hot plains to the south and cooler hilly region to the north and east.

Climate

Delhi has a tropical semi arid climate with extremely hot summer and moderately cold winters. July to September is the typical monsoon season. Monsoons act as " scrubber " for the pollutants. Maximum rainfall occurs during July.

Climate and natural sources play an important role in the pollution level of Delhi, in addition to the anthropogenic sources. The region has regular pre-monsoon feature of *Andhi,* the dust storm. Westerly winds from the Great Indian Desert bring a large amount of particulate matter, as high as 500-800 tons/sq.mile. Ground based temperature inversions are also regular feature in winters, which also restricts the mixing height to low levels, limiting the pollutant dispersal.

Delhi has an area of 1483 Km^2. It's present population is estimated to be 12.77×10^6.

The WHO has classified Delhi as one of the ten most polluted cities of the world. The major sources of pollution in Delhi are vehicles, thermal power plants, industries and domestic refuses.

Vehicles

Most of the vehicles in India are concentrated in urban areas and an astounding 48.8% of the total number of vehicles are registered in just three metros. Delhi has 29% of the total, Mumbai 11.2% and Calcutta 8.3%(Kumar, 1997). Motor vehicle registration rose by 20 times between 1971 and 1997. The total number of vehicles registered in Delhi at the end of 1997 was 28,48,000 (Handbook on transport statistic in India, 1999).
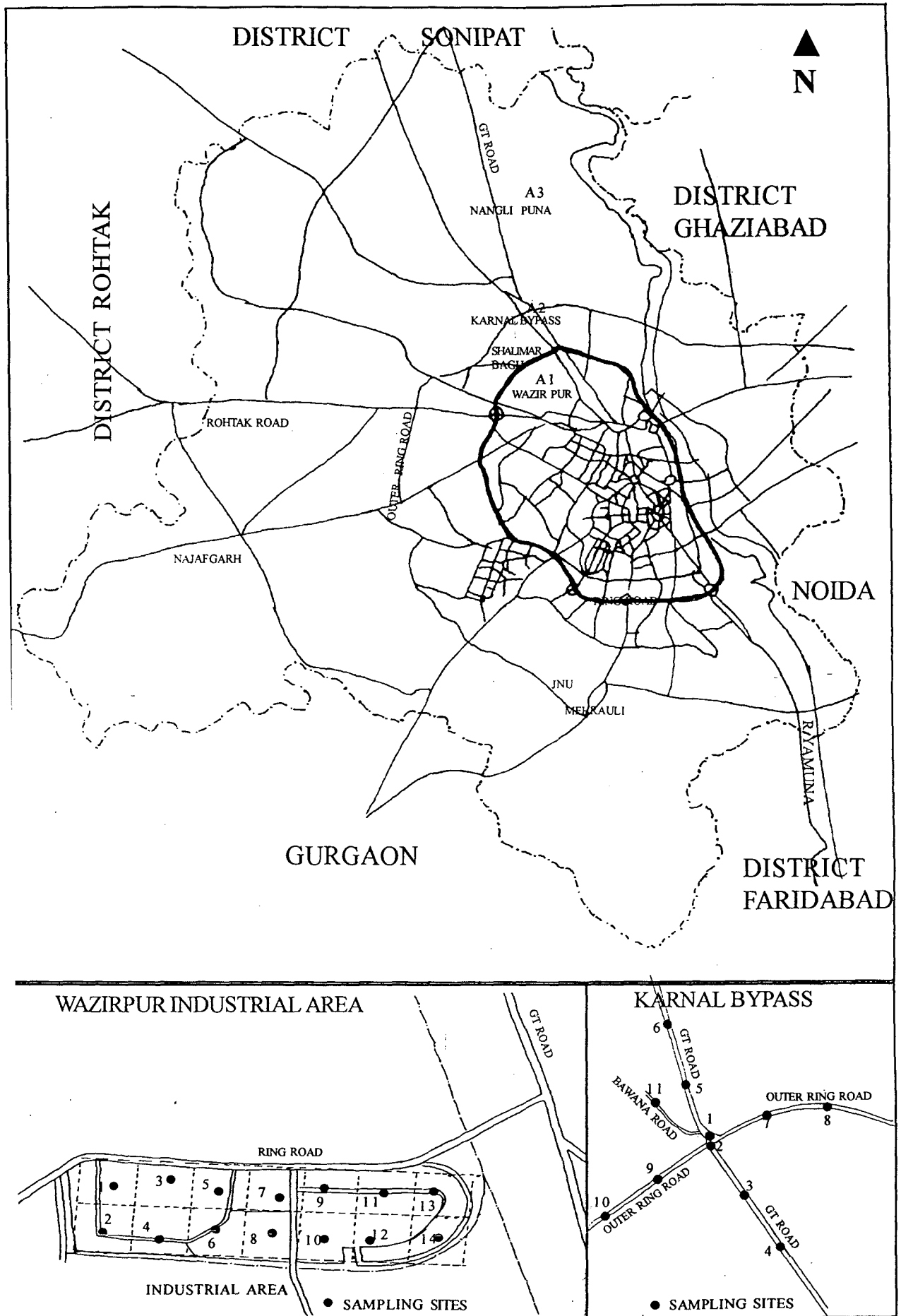
Fig.3.1. Map showing the Study Area.

Considering the impact of vehicular pollution emissions on the environmental quality, Environmental Pollution Control Authority took the initiatives to reduce the vehicular pollution. A gradual phased reduction in the lead levels of gasoline was announced. Prior to 1996, the lead levels were 0.56g/l, which was reduced to 0.15g/l in 1996 and 0.013g/l from 1/1/1999 (CPCB, 1999)

Industries

The National Capital Territory (NCT) of Delhi has one of the largest clusters of small-scale industries in India. There was a more than 500% increase in industrial units from 18,500 in 1961 to 93,000 in 1993 (CPCB, 1995) The comparative growth of industrial sector in Delhi can be summarised as shown in Fig. 3.2. The industrial establishments in Delhi are situated in 28 Industrial sites most of which are located in residential zones. The nature of industrial activities varies from fabrication of garments, electrical appliances, consumer electronics, printing and publishing, electroplating, pickling etc. (Office of the Commissioner of Industries, Delhi, 1996).

Study area

For the present study the selection of three sites was made on the basis of regional anthropogenic activities, The sites selected were Wazirpur Industrial Area, Karnal Bypass and Nangli Puna. These sampling points are schematically shown in Fig.3.1. their description is given in Table 3.1.

Table 3.1. Description of study areas

S.N.	Site	Description
A1	Wazirpur Industrial Area	Industrial-cum-Residential area(400vehicles/h) moderate traffic density
A2	Karnal Bypass	Heavy Traffic area (>5000vehicles/h)
A3	Nangli Puna	Rural area (60 vehicles/h) low traffic density

Growth Trends in the Industrial Units and Employment in Delhi, 1951-1996
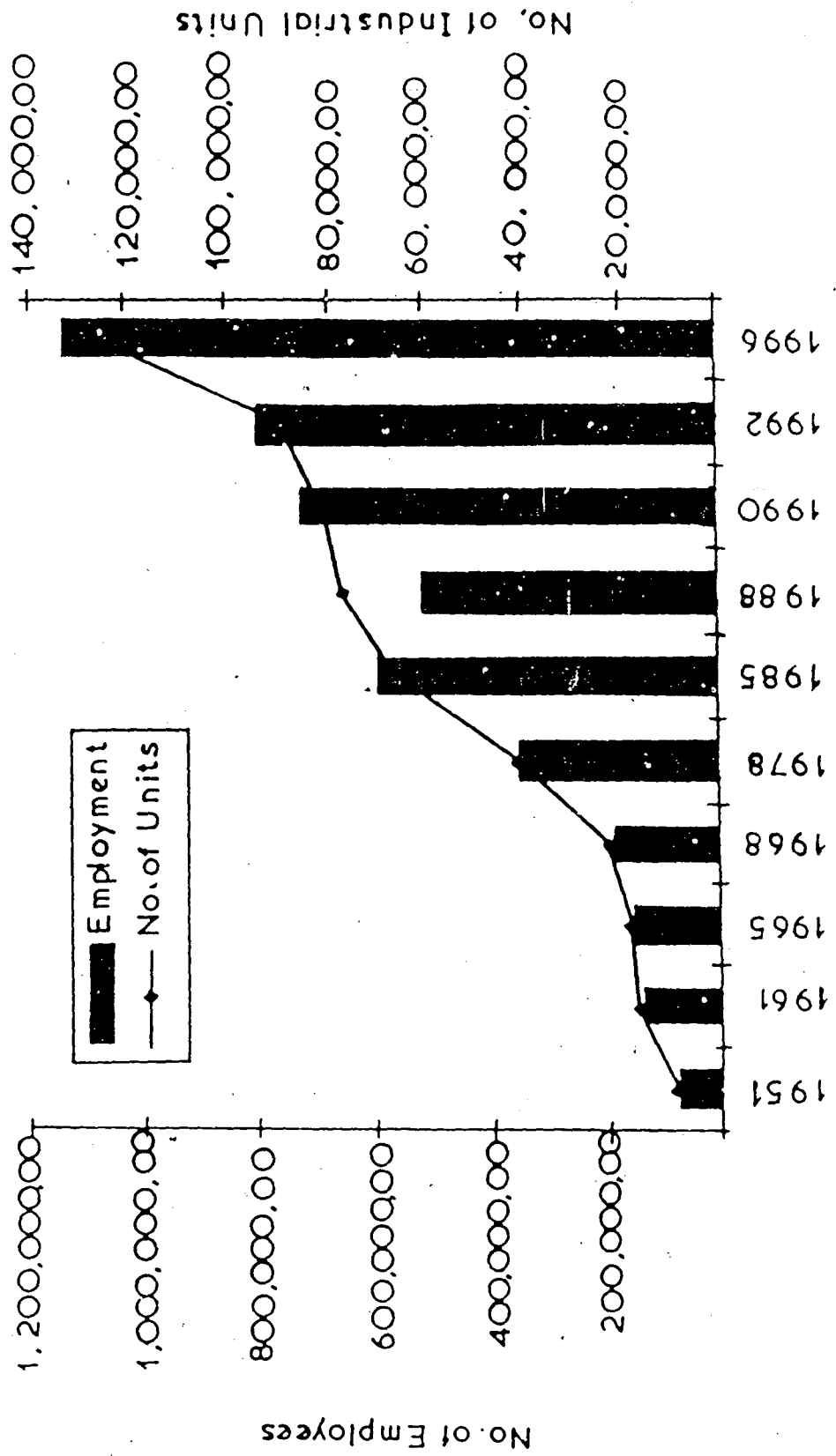
Fig. 3·2

Wazirpur Industrial Area

Wazirpur Industrial Area is located in north-west part of Delhi, covering an area of 210 acres. The two ring transport systems, one, the northwestern ring road and another, the northwestern ring railway system, surround the area. There are approximately 1000 industries in this area, out of which 424 are registered. The main polluting industries are electroplating, rolling,

pickling and textiles. The other industries include rubber, plastic, soap, electronic goods etc.

Table 3.2. List of registered industries in Wazirpur

Block	No. of Industries
A	253
A G-group	089
B	036
C	046
Total	424

(Small Scale Industries Association, Wazirpur 1995)

Due to its large number of small-scale industries and their unmonitored level of pollution, Wazirpur area has emerged as one of the major polluted industrial sites in Delhi.

The entire area is divided into three blocks namely A, B and C. During the last decade there has been a three-fold increase of industries in this area. Everyday huge amounts of toxic wastes are spewing out of these units.

Since the main polluting industries are rolling, pickling, electroplating and textiles, therefore the major raw materials which are used in processing are strong acids such as HNO_3, H_2SO_4, coating materials like Cr and Zn, bleaching powder, dyes, iron sheets etc. These input materials mainly govern the output wastes.

Chromium plating is one of the most widely used forms of electroplating in this area. Usually three steps are used; first,

pretreatment step involves cleaning, derusting by acid or alkali (pickling), defatting and other processes which prepare the basic material for plating; second, plating in which pickled articles are rinsed and placed in wooden or mild steel vats containing bath of electroplating salts. The material being plated is made cathode in an electrolytic cell. Plating baths are acidic in nature and generally contain H_2SO_4, HCl or HNO_3 and the third, the post-treatment process includes washing and drying of the electroplated objects. The electroplating industrial discharge constitutes an important source of toxic metals such as Cd, Ni, Cu, Cr and Zn etc.

At present, the industrial wastes generated from this area do not have a sound and satisfactory disposal system. The wastes are usually dumped out side of the industrial premises. The drained wastewater carrying the toxic materials with it ultimately empties into the river Yamuna, a main source of drinking water for the people of Delhi.

Karnal Bypass

Karnal bypass is a major traffic crossing situated at the intersection of National Highway No.1 (G.T. Road) with the outer ring road. This bypass is the major link between National Capital Territory (NCT) and all the north Indian states i.e. Haryana, Punjab, Himachal Pradesh and Jammu and Kashmir. There is heavy traffic throughout the day at this site.

Nangli Puna

Nangli Puna is a rural site covering an area of about 0.5 X 0.5 km². It is far off from any regional activity, with no industrial area set up nearby and having low vehicular traffic, in the vicinity.

Materials

and

Methods

Sampling Plan

Wazirpur Industrial Area: The whole area was divided into 14 small grids of equal size-0.25 km x 0.25 km each. The sample was collected from the central location of each grid.

Karnal Bypass: The two samples were collected from the intersection and the other eight were collected at distances of 500m and 1km distances in all the four directions of the intersection. One sample was collected from a side road at a distance of 500m from the main road. At each location the samples were collected from both sides of the road and a composite was obtained out of the two.

Nangli Puna: The village was divided into four grids of equal size- 0.25 km x 0.25 km each. Two composite samples were obtained out of the four.

Sample collection

The sampling was carried out according to the well established technique, described by Schwar (1983). The sampling was carried out in first week of Dec.1999 and sampling points are shown in Fig.3.1. Briefly, the dust samples were collected on a dry day using a plastic dustpan and brush. An area generally ranging from 0.5 to 1.0 m² was swept in order to obtain a sufficiently large sample for analysis and to help overcome the problem of localised spatial variation. The collected dust was transferred to selfsealing polyethene bags for transport to laboratory. Care was taken to reduce the disturbance of the fine particles, which are readily lost by resuspension. Recently soiled surfaces and areas where car or vehicles were parked or appeared from the presence of oil stains to have been previously parked were avoided. Any obvious extraneous matter such as cigarette ends and stones etc. were not collected with the sample. Each brush was used once only before giving a thorough cleaning.

Sample storage and processing

After carrying to the laboratory the samples were kept at the room temperature. The samples were screened through a stainless steel sieve of size 500 μm to exclude the materials of extraneous origin such as stones, glass, twigs and other similar large debris. Brass sieve was avoided because Cu and Zn were to be estimated. Gentle crushing between sheets of polyethene before sieving was done. For the present study the grinding was avoided, as it might effect the original nature and surface area of the sample and hence the measured metal levels in total and different fractions. It was considered preferable to analyse a larger sample mass instead of grinding and homogenising, to decrease the effect of heterogeneity of the sample. All further analysis was carried out on sample <500μm.

Analytical techniques

All laboratory ware were of borosilicate glass, polyethene, polypropylene or PTFE. The laboratory ware in contact with sample or reagents were dipped in 4.0 M HNO_3 overnight and rinsed with distilled water. All the chemicals used were procured from Merck, Qualigens and Glaxo (AR grade).

pH

pH of all the samples was determined by following the method described by Okalebo et al., (1993). pH was taken in 1:2.5 (sample : distilled water). In 5.0g of the sample 12.5 ml of distilled water was added, the mixture was stirred for 10 minutes, allowed to stand for 30 min., then stirred again for 2 minutes. The pH was measured on Water and Soil Analysis kit, Model 161E, Electronics India, after calibrating the instrument with buffer solutions of pH 4.0, 7.0, 9.2 and 10.01.

Organic matter

The organic matter of selective samples was determined by Walkley Black method. This method involves the oxidation of organic matter by a oxidising agent added to the sample in excess, and the

subsequent titration of the excess oxidising agent. The method is based on chromic acid oxidation.

Reagents

I.   Standard 1N potassium dichromate ($K_2Cr_2O_7$) solution: Exactly 49.04g $K_2Cr_2O_7$ was dissolved in distilled water and the solution was diluted to 1litre.

II.   Diphenylamine indicator: 0.5g of diphenylamine was dissolved in 20ml distilled water and 50ml of H_2SO_4 was added gradually.

III.   Phosphoric acid (H_3PO_4 85%).

IV.   Sulphuric acid (H_2SO_4 96%).

V.   NaF.

VI.   Ferrous ammonium sulphate solution (0.5N): 196.1g of ferrous ammonium sulphate was dissolved in 800ml of distilled water containing 20ml Of concentrated H_2SO_4 and was finally diluted to 1 litre.

Procedure

Oxidation of organic matter: 0.5g of sample was taken in a 500ml Erlenmeyer flask, 10ml 1N $K_2Cr_2O_7$ and 20ml of H_2SO_4 (conc.) were added and mixed by swirling the flask. The mixture was allowed to stand for 30 minutes. A standardization blank was run in the same way.

Back titration

The solution was diluted with 200ml distilled water. 10ml H_3PO_4, 0.2g of NaF and 30 drops of diphenylamine indicator were added. The solution was back titrated with 0.5N ferrous ammonium sulphate solution. The colour was dull green with chromous ion at the beginning, then shifted to turbid blue as the titration proceeded. At the end point the colour sharply shifted to brilliant green, giving a one drop end point. The blank was run in similar manner.

Calculation

     % organic matter = 10(1-T/S) 1.34

     S - standardisation blank titration, ml ferrous solution

     T - sample titration, ml ferrous solution

1.34 - multiplication factor, when 77% recovery was considered.

Total metal concentrations

For analysing the total metal concentrations the digestion method using HF and aqua regia as described by Loring and Rental (1992) was tried, but a black residue was remaining, even after heating for a long time. So the method described by Agemian and Chau (1975) was followed for digesting the samples.

0.5 g of the sample was transferred to a Teflon cup and 4.0 ml of concentrated nitric acid (16N), 1.0 ml of perchloric acid (60%) and 6.0 ml of hydrofluoric acid (48%) were added. The digestion bomb was sealed and heated at 140°C for 3.5 hours. After cooling the bomb, the contents of teflon cup were quantitatively transferred to a 50 ml volumetric flask containing a solution of 4.8 g of boric acid crystals in about 30ml double distilled water to dissolve the precipitated metal fluorides. The final volume was made upto 50 ml and then stored in a polyethene bottle. After one week the supernatant was decanted and filtered through acid rinsed Whatman 42 filter paper. The filtrate was used for further metal estimation. Digestion for each sample was carried out in duplicates and the mean was taken.

Sequential extraction

For the present study the sequential extraction scheme designed by Tessier et al., (1979) was used. The extractant used and the conditions maintained for extraction of different phases for one gram of the sample are described below. The terminology used is the same as that used by Tessier et al., (1979).

I) *Exchangeable*: 1g sample extracted with 8 ml of unbuffered, 1.0M $MgCl_2$ (pH 7.0) with continuous agitation for one hour at 20±2°C.

II) *Carbonate*: Residue from exchangeable fraction, extracted with 8 ml of 1.0M NaOAc(adjusted to pH 5 with HOAc) with continuous agitation for 5 hours at 20±2°C.

III)   *Fe-Mn Oxide bound*: Residue from carbonate fraction, extracted with 20 ml of 0.04M $NH_2OH.HCl$ in 25%(v/v) HOAc at 96^0C with occasional agitation for 6 hours.

IV)   *Organic bound*: Residue from Fe-Mn oxide bound fraction extracted with 3 ml of 0.02M HNO_3 and 5.0 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was heated to 85^0C for 2 hours, with occasional agitation. A second 3 ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was added and the mixture heated again for 3h with intermittent agitation and then 5 ml of 3.2M NH_4OAc in 20% HNO_3 (v/v) was added with continuous agitation for 0.5 h at 25^0C. The final volume was made to 20 ml.

V)   *Residual*: Residue from organic fraction was digested using the $HF - HNO_3 - HClO_4$ dissolution procedure as used for the total metal extraction.

All the extractions were carried out in duplicates. The extractions except the residual fraction were carried out in 100ml polypropylene centrifugation tubes with tight lids. When continuous agitation was required, samples were shaken lengthwise on an end-to-end mechanical shaker. Heating of samples except the residual fraction was accomplished by using a water bath.

After each successive extraction, separation was done by centrifugation at 5000 rpm for 30 minutes at 25^0C. Supernatant was removed with a pippet, care was taken not to remove any of the solid residues. The supernatant was filtered through Whatman 42 filter paper, acidified with a drop of nitric acid and stored in polyethene bottles at 4^0C. Prior to the start of next extraction step, samples were washed with 8 ml of double distilled water with vigorous hand shaking followed by centrifugation for 30 minutes. The wash solutions were removed and discarded.

Metal detection

Metal detection for both the total metal digests and the sequentially extracted fractions was performed by flame atomic absorption spectrometry, using a GBC model AAS.

Standard solutions for all the metals were prepared as described in the APHA (1995). 100ppm concentration stock solutions for all metals were prepared by either using the metal salt or pure metals. A series of standard metal solutions were made by further diluting the 100ppm stock solution.

Preparation of standard stock solutions

I)   *Cadmium*: 0.100g of cadmium metal was dissolved in 4 ml concentrated HNO_3 acid, then 8.0 ml of HNO_3 was added and finally diluted to 1000 ml with distilled water.

II)   *Chromium*: 0.1923g of CrO_3 was dissolved completely in distilled water, acidified with 10 ml conc. HNO_3 acid and then diluted to 1000 ml with distilled water.

III)   *Copper*: 0.100g of Cu metal was dissolved in 2 ml conc. HNO_3, 10 ml conc. HNO_3 was added and then diluted to 1000ml with distilled water.

IV)   *Lead*: 0.1598g of lead nitrate ($Pb(NO)_3$) was dissolved in a minimum amount of 1+1 $HNO_3$and diluted to 1000 ml with distilled water.

V)   *Nickel*: 0.100g of Ni metal dissolved in 10 ml hot conc. HNO_3, cooled and then diluted to 1000 ml with distilled water.

VI)   *Zinc*: 0.100g Zn metal dissolved in 20 ml 1+1 HCl and diluted to 1000 ml with distilled water.

Instrument operation

Operating conditions of AAS used for estimating various metals are given in the Table 4.1.

Table 4.1. Working conditions for the AAS

Element	Lamp current(mA)	Flame Type	Wave-length(nm)	Slit Width (nm)	Working Range(ppm)	Sensitivity (ppm)
Cd	3.0	Air-acetylene (oxidising)	228.8	0.5	0.2-1.8	.009
Cr	6.0	Air-acetylene (highly reducing)	357.9	0.2	2-15	.05
Cu	3.0	Air-acetylene (oxidising)	327.4	0.5	2.5-10	.05
Ni	4.0	Air-acetylene (oxidising)	232.0	0.2	1.8-8	.04
Pb	5.0	Air-acetylene (oxidising)	217.0	1.0	2.5-20	.06
Zn	5.0	Air-acetylene (oxidising)	213.0	0.5	0.4-1.5	.008

Results

and

Discussion

Total metal concentrations in the study area

The detected concentrations of the six metals (Cd, Cu, Cr, Ni, Pb and Zn) in the street dusts at the three sites, Wazirpur Industrial Area (A1, W1-W14), Karnal Bypass (A2, KB1-KB11) and Nangli Puna (A3, NG1-NG2) are shown in Table 5.1.

The results are discussed in relation to the mean concentration levels in the three areas and their possible sources. The t-test was used to compare the mean concentrations of all the metals observed in the three areas.

Lead (Pb)

The mean concentrations of Pb in the three areas A1, A2 and A3 were 145.75±36.97, 195.79±69.38and 123.18±3.21ppm respectively. The differences in the mean Pb levels in the three areas were not significant at 99% confidence level, so there was no discernible variation in the Pb levels in the three areas. Only one sample W7, from the Wazirpur Industrial Area, had a very high concentration of 3670ppm(this sample was replaced by the mean lead levels of the site A1 for statistical analysis). The possible explanation for this is the vicinity to the battery recharge centres and spray painters. Fergusson and Kim (1991) had also reported very high Pb levels in the vicinity of the spray painters. The evidence for this point source of Pb comes from the fact that the three samples collected around this site from the adjacent grids were having low Pb levels (W5, W8 and W9).

As a matter of fact, the Pb levels in the three areas are similar; this supports the assumption that the soil particles or some aerial source are the major contributors towards Pb in the street dust. Although direct emissions from the vehicular exhausts (a major source of Pb) have ceased for two years now because of the phasing out of leaded gasoline, lead is still persistent in dust from earlier vehicular exhaust emissions because of it's long residence time in the environment.

The levels of Pb noticed in the present study are comparable with the levels observed for street dust in other developing countries
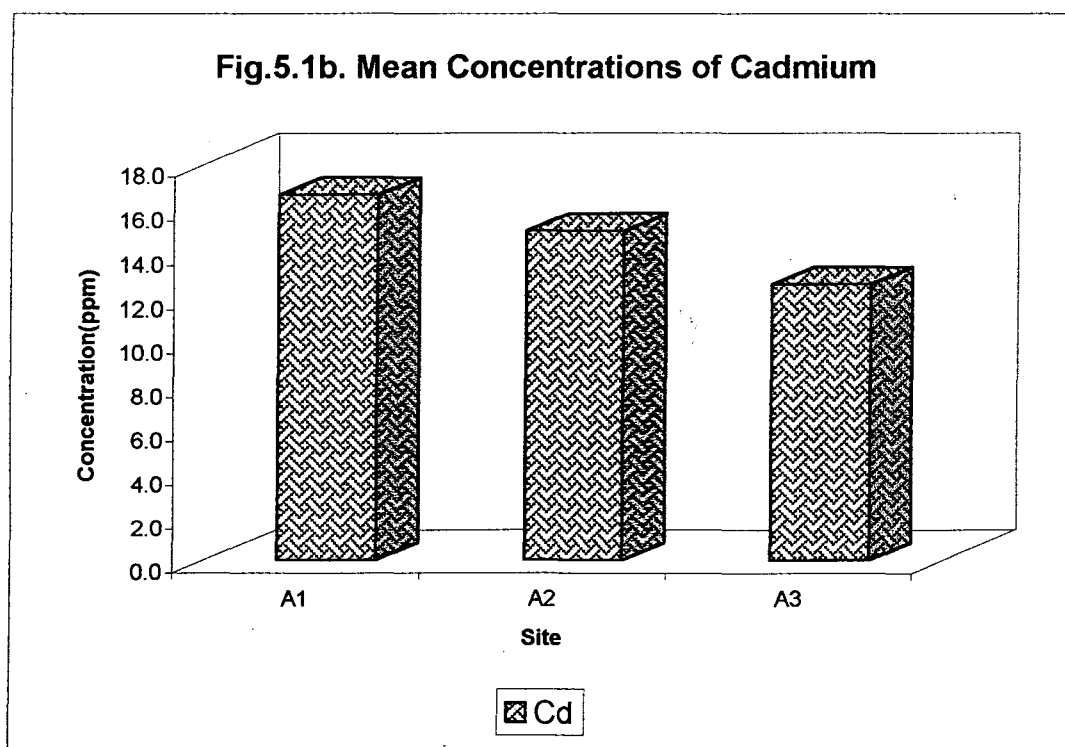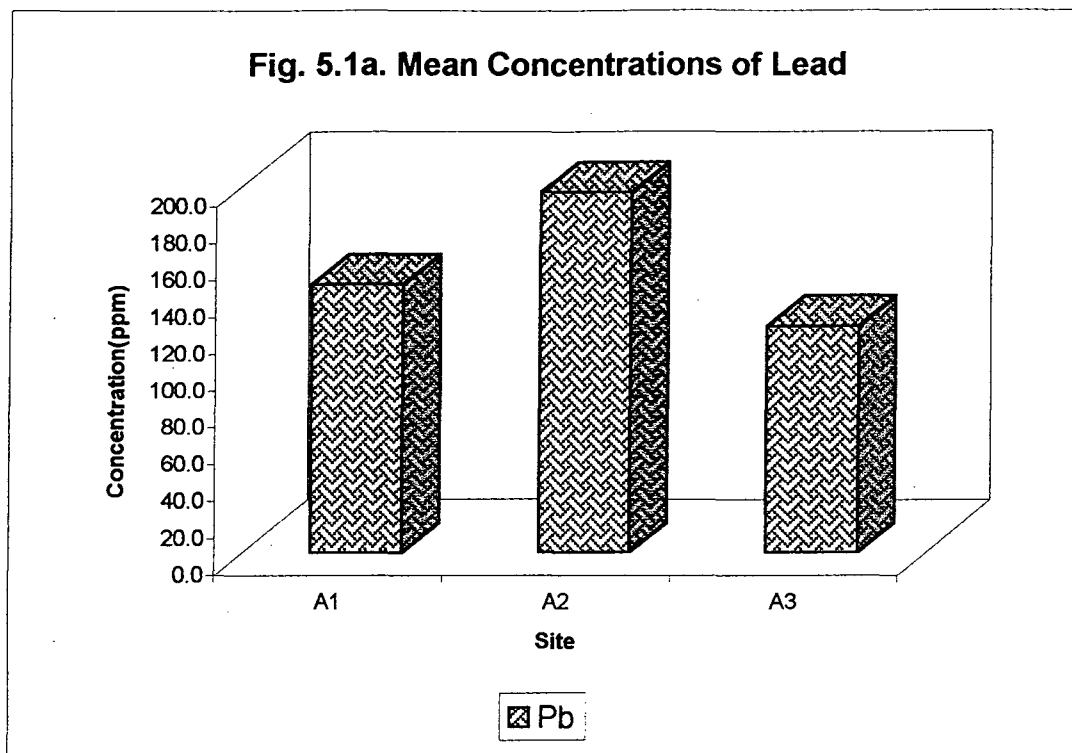
(Nasralla, 1984; Ali and Nasralla, 1985; Lau and Wong, 1982 and Ho, (1979), but are much lower than the levels observed in developed countries.
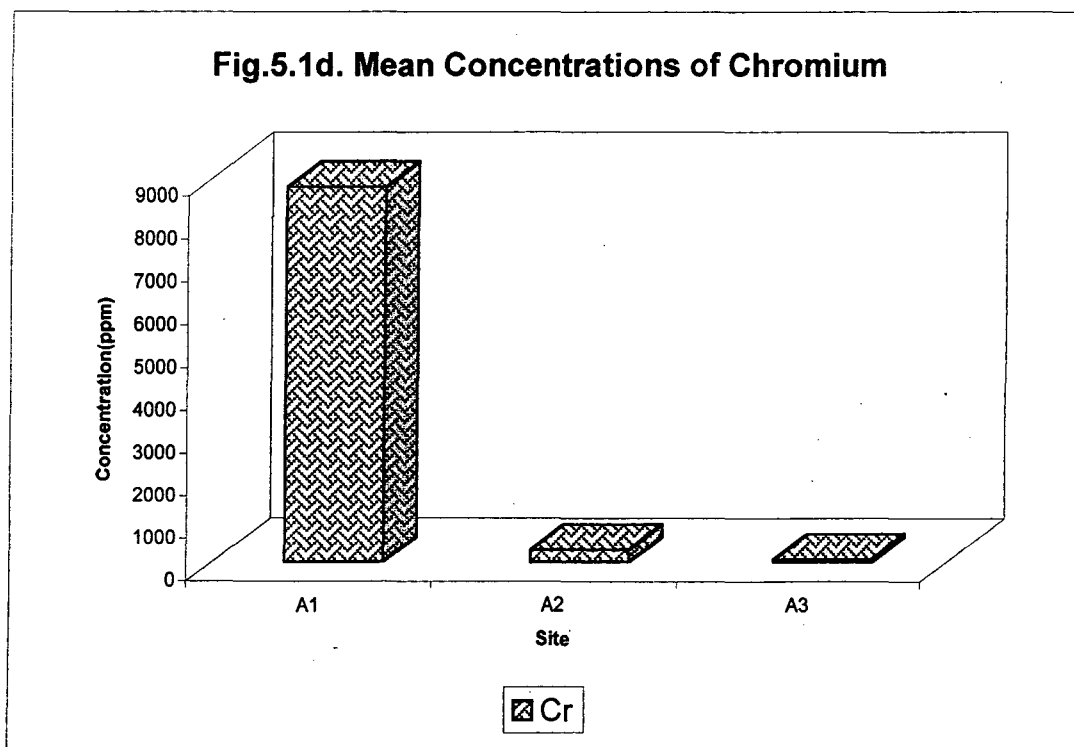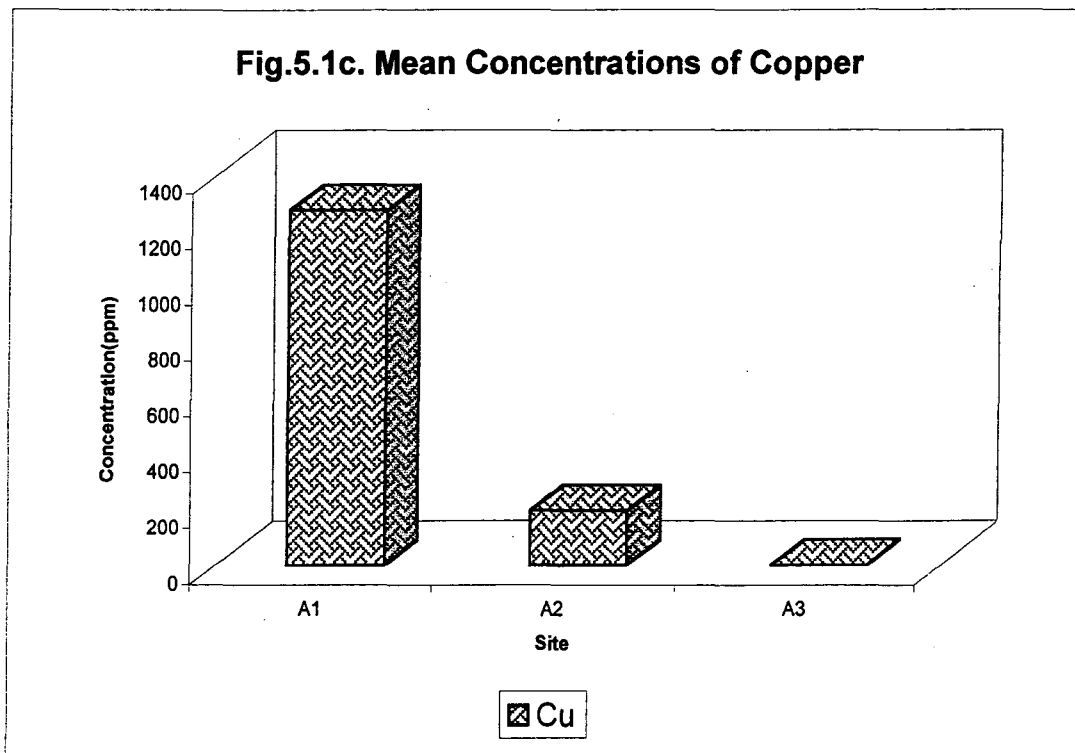
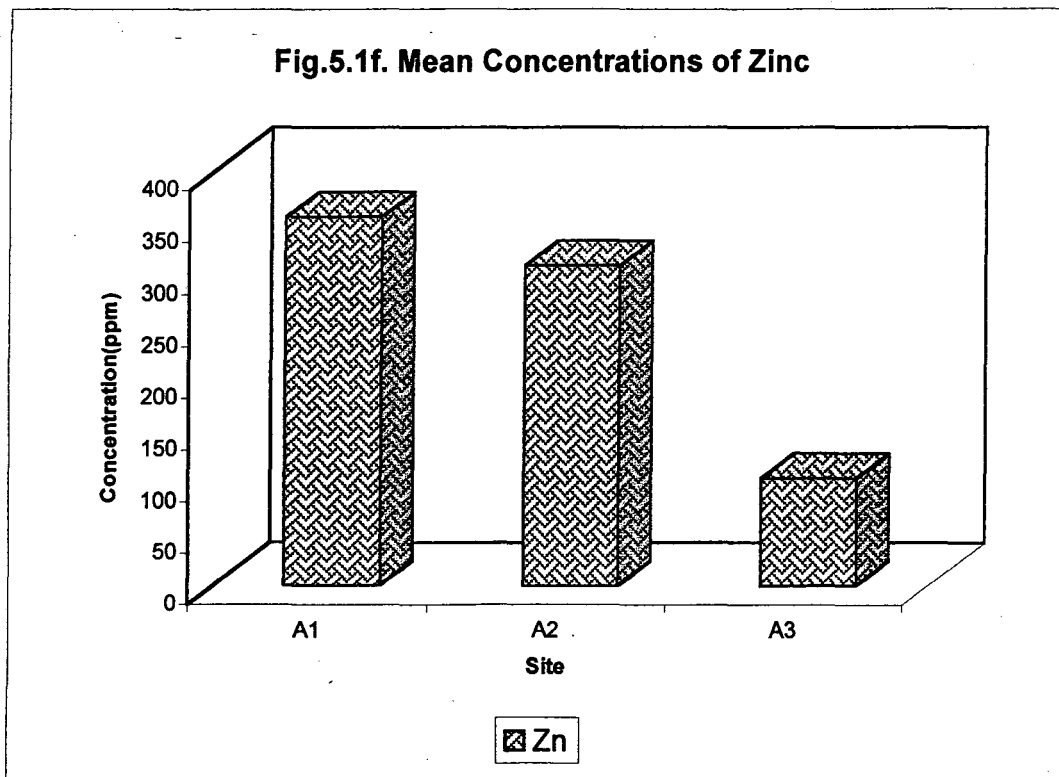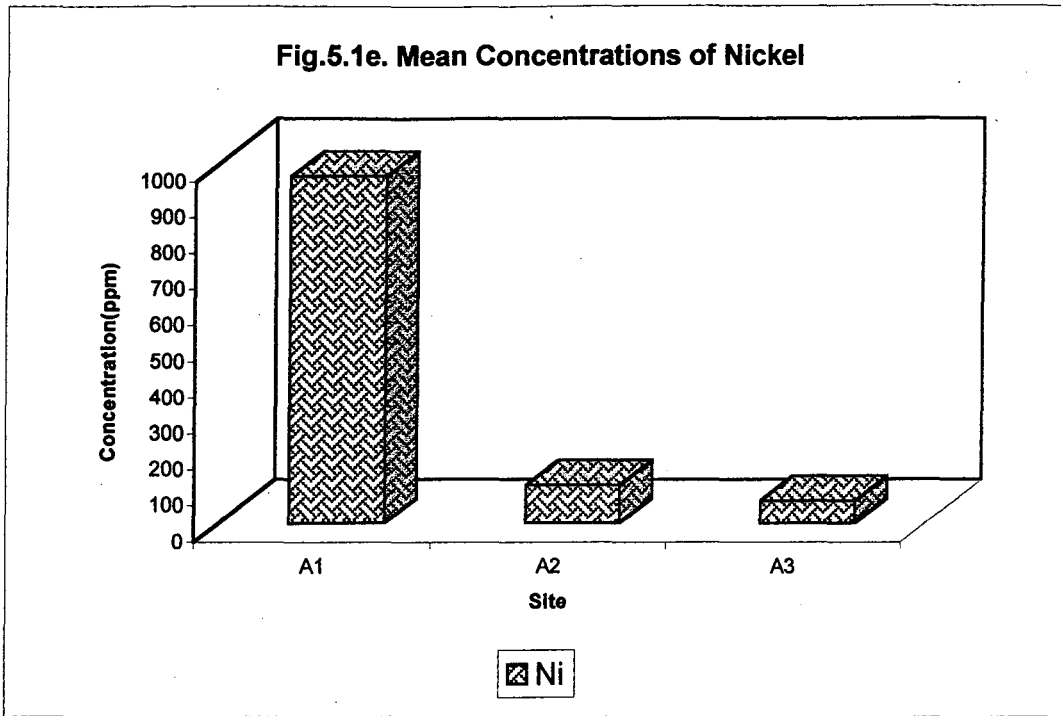## Table 5.1. Total metal concentrations and pH in street dust

Sample	Pb	Cd	Cu	Cr	Ni	Zn	pH
W 1	123.18	18.61	1361.75	10500.00	1086.59	237.45	8.39
W 2	128.41	14.83	2274.32	13250.00	1335.97	283.51	8.00
W 3	86.82	14.06	1246.99	7250.00	921.95	303.14	8.72
W 4	127.73	18.61	1405.46	14250.00	1306.10	339.41	7.77
W 5	107.27	13.31	1443.72	7500.00	867.07	708.64	8.58
W 6	134.55	13.69	1820.77	10000.00	1223.48	214.90	8.10
W 7	3670.0	20.81	434.97	2319.30	347.37	378.63	8.07
W 8	180.00	15.58	853.55	7250.00	775.62	222.48	8.08
W 9	191.36	20.81	902.73	6250.00	684.11	437.45	8.49
W 10	127.73	13.69	1115.85	9250.00	766.46	319.80	8.59
W 11	210.59	19.74	951.91	6250.00	894.51	319.80	9.60
W 12	184.55	20.49	1902.73	12500.00	1388.41	499.20	7.49
W 13	180.00	14.83	809.84	8000.00	757.31	363.92	8.41
W 14	112.64	13.31	1301.64	8250.00	1104.88	359.02	8.52
KB 1	91.36	14.06	103.40	171.80	71.34	378.63	8.79
KB 2	230.00	16.47	128.98	171.80	98.78	420.78	8.79
KB 3	166.36	17.98	310.80	487.50	226.83	338.43	9.63
KB 4	187.06	17.92	307.10	657.37	189.47	353.14	9.05
KB 5	222.35	13.58	148.09	296.90	114.91	186.21	9.27
KB 6	127.73	12.18	73.58	229.98	80.49	209.90	9.30
KB 7	257.27	12.18	128.97	193.29	34.76	241.73	9.39
KB 8	191.36	11.04	244.03	141.40	8.23	547.49	9.45
KB 9	292.94	17.92	285.23	764.34	154.39	303.14	10.13
KB 10	102.73	13.31	234.09	248.30	59.76	180.36	10.20
KB 11	284.55	17.92	174.43	189.62	107.93	241.73	9.00
NG 1	125.45	12.55	N.D.	65.41	62.19	105.69	9.37
NG 2	120.91	12.55	N.D.	65.41	62.19	102.99	9.37

*All values are in ppm except pH.

** pH measured in 1:2.5(street dust : distilled water)

Fig. 5.1a. Mean Concentrations of Lead

Fig.5.1b. Mean Concentrations of Cadmium

Fig.5.1c. Mean Concentrations of Copper

Fig.5.1d. Mean Concentrations of Chromium

Fig.5.1e. Mean Concentrations of Nickel

Fig.5.1f. Mean Concentrations of Zinc

Cadmium (Cd)

The mean levels of Cd in the three areas were 16.60±3.05, 14.96±2.72 and 12.55ppm respectively. The mean Cd concentrations were not differing significantly at 95% confidence level, indicating that the Cd origin is not mainly from any localized activity viz., industrial or vehicular.

The Cd levels detected in present study are comparable with that observed by Fergusson et al. (1980), Culbard et al. (1983) and Schwar et al. (1988) but are higher than the levels observed in most of the other studies.

It seems reasonable to assume that the bulk of Pb and Cd from different sources (vehicular, refuse burning and emissions from industrial processes) are airborne and presumably, more or less complete mixing from various sources would have occurred, giving a reasonably uniform distribution of the two metals.

Copper (Cu)

Mean concentrations of Cu were found to be highest in A1 (1273.3±489.37) and varied from 434.97 to 2274.32ppm. The mean concentration in A2 was194.43±85.16ppm, while Cu was not detected in area A3. The t -test (at 95%confidence level) also showed significant variation in the copper levels in the three areas. The possible reason for very high concentration in area A1 is the presence of metal processing industries (electroplating, pickling and galvanising) in that area. The discharges of these industries are expected to contribute significantly towards the high levels of Cu, Zn, Ni and Cr.

Chromium (Cr)

The samples collected from area A1 exhibited very high levels of Cr with the mean 8772.81±3164.21ppm and the range 2319-14250ppm, which are significantly higher (p<0.05) than those occurring in area A2 (322.94±214.91ppm) and A3 (65.41ppm). Additionally, Cr concentrations were found to vary between samples within the same area. The excessively high levels noticed in A1 are evident from the

presence of metal processing industries in the area, as mentioned earlier.

Nickel (Ni)

The distribution pattern of Ni was almost similar to that of Cr. The mean concentration of Ni in the three areas A1, A2 and A3 were 961.42 ± 294.75, 104.26 ± 65.3 and 62.19ppm respectively. A1, which is an industrial area, was found to have significantly higher concentration (at $p< 0.05$) as compared to sites A2 and A3, while no such difference was noticed between A2 and A3.

Elevated concentrations of Cu, Cr and Ni in the area A1 indicate the possibility of a common source. This can only be the metal related industries in the study site.

Zinc (Zn)

Area A1 and A2 do not have differences between their mean Zn levels ($p<0.05$), but A3 levels were significantly different from both A2 and A3. The high concentrations in the A1 are attributed to discharges of metal processing industries, while in A2, Zn might have it's origin from automotive sources i.e. wear and tear of vulcanized rubber tyres, lubricating oils and corrosion of galvanized vehicular parts. The absence of any significant difference in Zn levels of A1 and A2, but not A3, indicates that Zn has its mixed origin from industrial and automotive sources.

Additionally, both A2 (high traffic density site, >5000 vehicles/h) and A3 (rural site, 60 vehicles/h), have similar levels of Ni and Cr. From this it is indicated that traffic is not the main contributor of these metals in these two sites.

In order to establish inter-element relationships in street dust samples, correlation coefficients for the 6 metals were calculated and are shown in the Table 5.2. A very significant correlation was found between Cr-Cu (0.948), Cr-Ni (0.979) and Cu-Ni (0.967). No other metals were significantly correlated with each other. The significant correlation between the three metals viz. Cu, Cr and Ni indicates a common source for these metals.

Table 5.2. Correlation Matrix

Metal	Cd	Cr	Cu	Ni	Pb	Zn
Cd	1.000					
Cr	0.272	1.000				
Cu	0.223	0.948*	1.000			
Ni	0.307	0.979*	0.967*	1.000		
Pb	0.373	-0.126	-0.120	-0.109	1.000	
Zn	0.220	0.230	0.301	0.242	0.092	1.000

* Significant values

Factor analysis is a statistical technique, which can be applied to a set of variables in order to reduce their dimensionality, i.e. to replace a large set of intercorrelated variables with a smaller set of independent variables. It is commonly applied in environmental studies to deduce sources from the observation data. Factor analysis generates a few underlying "factors" that describe group of variables. Each factor is generally treated as a source. Environmental insight and basic understanding of the data can help to determine the possible sources.

For the present study a factor analysis (using the Principal Component Analysis) was carried out on the correlation matrix to find out the possible contributing factor towards the metal concentrations and thereby determine which metals have a common origin. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors, the percent of variance explained by each of them was calculated and are shown in Table 5.3.

The results in Table 5.3 show that only two eigenvalues are >1 and are explaining only ≈ 76% of variance, the third eigen value which is ≈1 i.e. 0.846 is explaining about 14% of the variance, which is a significant contribution towards explanation of cumulative variance.

So the first three eigenvalues were selected for further analysis, other small but nonzero eigenvalues were discarded in order to establish a probable number of contributing source factor. The initial eigenvalues extracted were "cleaned up" by means of Varimax rotation and are also listed in Table 5.4. The comparison of initial and rotated eigenvalues and their corresponding contribution towards explanation of %variance shows that both the eigenvalues and their corresponding contribution towards the explanation of cumulative % variance has not changed substantially.

Table 5.3. Factor analysis

Total variance explained

	Initial Eigenvalues Extraction			Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	eigenvalue	% of variance	Cumulative % variance	eigenvalue	% Of variance	Cumulative % variance	eigenvalue	% of variance	Cumulative % variance
1	3.148	52.460	52.460	3.148	52.460	52.460	3.010	50.159	50.159
2	1.409	23.490	75.949	1.409	23.490	75.949	1.376	22.931	73.090
3	0.846	14.099	90.049	0.846	14.099	90.049	1.018	16.958	90.049
4	0.534	8.908	98.956						
5	.04730	0.788	99.745						
6	.01532	0.255	100.000						

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization

Table 5.4. Rotated component matrix

Metal	Component		
	1	2	3
Cd	0.282	0.795	0.105
Cr	0.982	0.03053	0.07803
Cu	0.965	-0.00106	0.159
Ni	0.988	0.05994	0.0816
Pb	-0.191	0.854	2.897
Zn	0.151	0.101	0.983

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Rotation converged in 4 iterations.
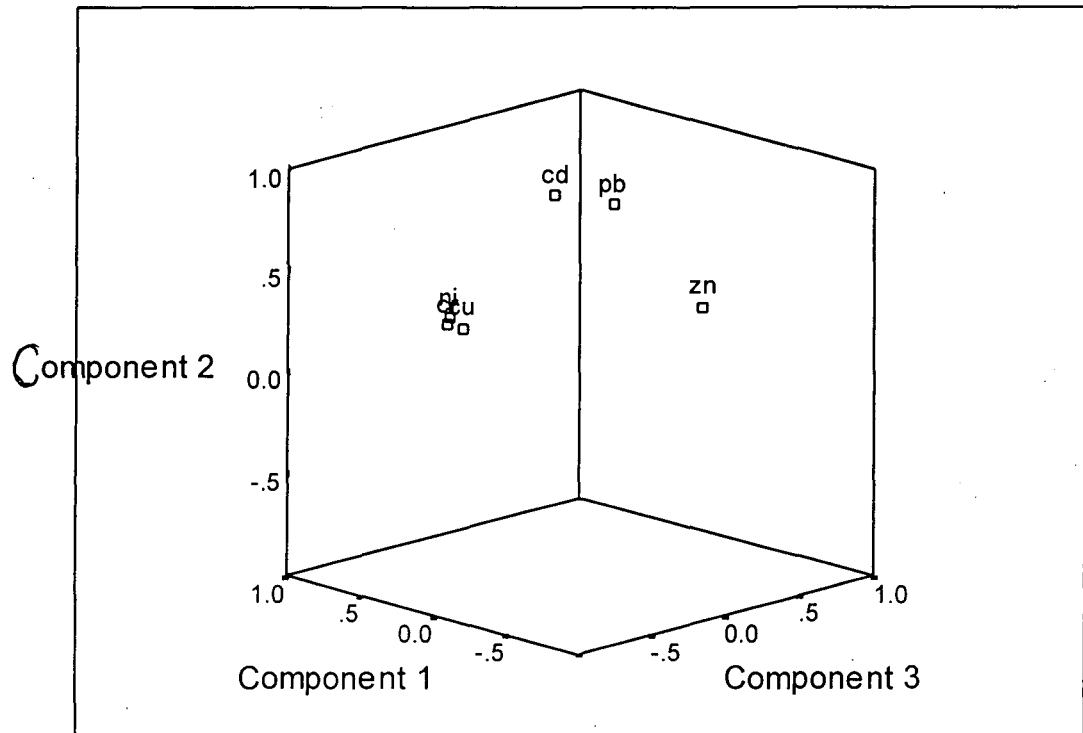
Component Plot in Rotated Space

Fig.5.2.

It is evident from the rotated component matrix that all the six metals analysed are explained by three factors. The first factor spanning the greater amount of variance (50.159%) includes Cr, Cu and Ni. This factor (source) should be industrial, which is also evident from the presence of various metal processing industries in the area. Pb and Cd are appearing in the second factor, which should be air-borne emissions from various sources, and zinc alone is explained by the third factor, which may have the mixed origin including industrial and vehicular.

Metal speciation in street dusts

Some selected samples (W4, W7, W9, W11, W12, KB2, KB4, KB9 and KB11) covering all ranges of six metals were chosen for sequential extraction experiments. The metal concentrations within the individual fractions of the sequential extraction analysis are shown in Table 5.6a to 5.6f based upon the mean of the duplicate

sub-samples. The recovery of the metals during the sequential extraction was judged by the summed total of each extraction with the independent total metal analysis performed on the separate sub-samples (in duplicates). Total metal recoveries from the sequential extraction analysis are listed in Table 5.5. The recoveries are essentially quantitative within the precision of the method.

Table 5.5. Total metal recovery from the sequential extraction analysis

Metal	% Mean recovery ± S.D.
Cd	97.07 ±5.20
Cu	99.77 ±6.21
Cr	97.02 ±8.86
Ni	97.72 ±9.18
Pb	100 ±14.40
Zn	97.71 ±5.87

Table 5.6a. Percentage distribution of Zinc in different fractions in street dust.

S.N.	Exchangeable fraction	CO_3^{2-} Bound	Fe-Mn Oxide bound	Organic fraction	Residual fraction
W4	1.26 (4.04)	4.30 (13.78)	57.69 (184.77)	11.11 (35.57)	25.64 (82.12)
W7	2.18 (8.17)	18.42 (68.91)	49.09 (183.64)	12.09 (45.23)	18.21 (68.11)
W9	1.24 (5.08)	11.33 (46.23)	60.03 (245.00)	11.22 (45.80)	16.17 (66.00)
W11	1.23 (3.82)	19.50 (60.73)	48.39 (150.68)	9.23 (28.75)	21.65 (67.40)
W12	1.24 (6.02)	17.33 (84.36)	36.79 (179.09)	9.06 (44.09)	35.58 (173.21)
KB2	11.22 (42.18)	42.50 (159.82)	34.93 (131.36)	4.30 (16.17)	7.05 (26.51)
KB4	1.52 (5.93)	15.22 (59.36)	51.76 (201.82)	18.88 (73.64)	12.61 (49.19)
KB9	1.40 (4.13)	31.58 (93.00)	34.58 (101.82)	11.69 (34.43)	20.75 (61.10)
KB11	2.68 (6.56)	27.63 (67.55)	37.46 (91.59)	12.69 (31.02)	19.54 (47.79)

* Values in parenthesis are concentrations in ppm

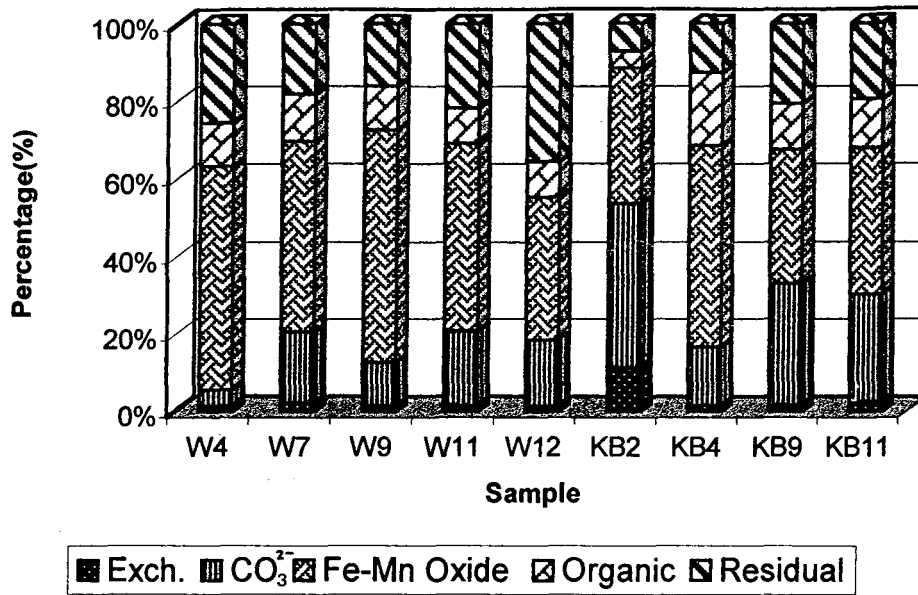Fig. 5.3a.Percentage Distribution of Zinc in Different Fractions
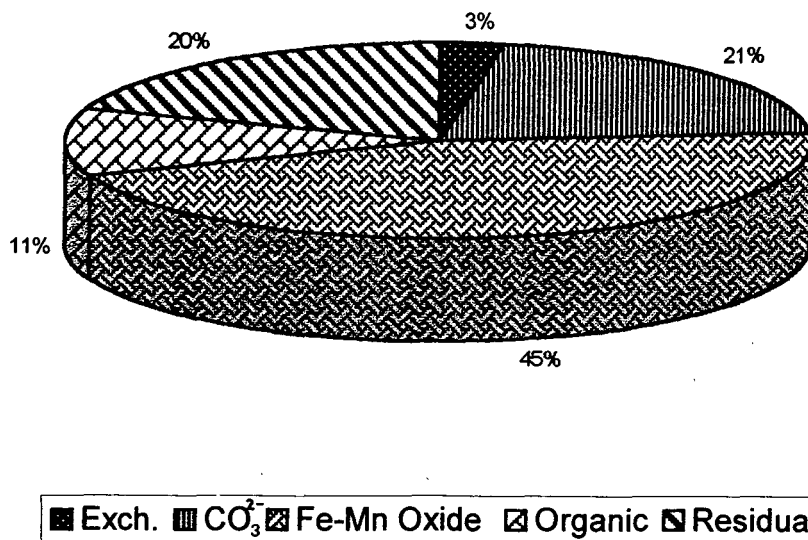

Fig.5.3b. Average Partitioning Pattern of Zinc

Table 5.6b. Percentage distribution of Cadmium in different fractions in street dust.

S.N.	Exchangeable fraction	CO₃²⁻ bound	Fe-Mn Oxide bound	Organic fraction	Residual fraction
W4	25.27 (5.02)	19.45 (3.86)	8.59 (1.71)	4.95 (0.98)	41.73 (8.28)
W7	26.98 (5.08)	20.83 (3.92)	8.30 (1.56)	3.69 (0.69)	40.20 (7.56)
W9	27.03 (5.08)	20.88 (3.92)	7.54 (1.42)	5.23 (0.98)	39.31 (7.38)
W11	25.57 (4.96)	21.40 (4.15)	8.79 (1.71)	0.60 (0.12	43.65 (8.47)
W12	25.53 (5.02)	21.41 (4.21)	9.41 (1.85)	0.59 (0.12)	43.07 (8.47)
KB2	29.82 (4.84)	23.77 (3.86)	9.61 (1.56)	2.49 (0.40)	34.31 (5.57)
KB4	29.19 (4.90)	25.06 (4.21)	9.29 (1.56)	3.27 (0.55)	33.18 (5.57)
KB9	27.28 (4.90)	22.13 (3.98)	9.49 (1.71)	3.06 (0.55)	38.05 (6.84)
KB11	27.81 (4.96)	25.87 (4.61)	8.75 (1.56)	2.27 (0.40)	35.30 (6.30)

Values in parenthesis are concentrations in ppm

Table 5.6c. Percentage distribution of Copper in different fractions in street dust.

S.N.	Exchangeable fraction	CO₃²⁻ bound	Fe-Mn Oxide bound	Organic fraction	Residual fraction
W4	0.44 (5.95)	1.23 (16.66)	1.26 (17.05)	34.92 (472.00)	62.15 (840.00)
W7	2.07 (9.44)	3.27 (14.91)	13.69 (62.40)	42.12 (192.00)	38.84 (177.05)
W9	0.94 (9.22)	1.57 (15.34)	8.22 (80.44)	28.32 (277.00)	60.95 (596.25)
W11	0.75 (6.82)	1.25 (11.41)	12.64 (115.41)	33.07 (302.00)	52.29 (477.50)
W12	0.68 (12.28)	0.82 (14.91)	8.02 (144.92)	29.15 (527.00)	61.32 (1108.5)
KB2	4.11 (5.73)	3.64 (5.07)	11.46 (15.96)	62.06 (86.45)	18.73 (26.09)
KB4	1.48 (4.63)	2.81 (8.79)	11.94 (37.27)	64.69 (202.00)	19.08 (59.56)
KB9	1.54 (3.98)	3.67 (9.44)	18.50 (47.65)	53.18 1(37.00)	23.12 (59.56)
KB11	3.09 (5.29)	8.20 (14.03)	23.05 (39.45)	50.82 (86.99)	14.84 (25.41)

* Values in parenthesis are concentrations in ppm

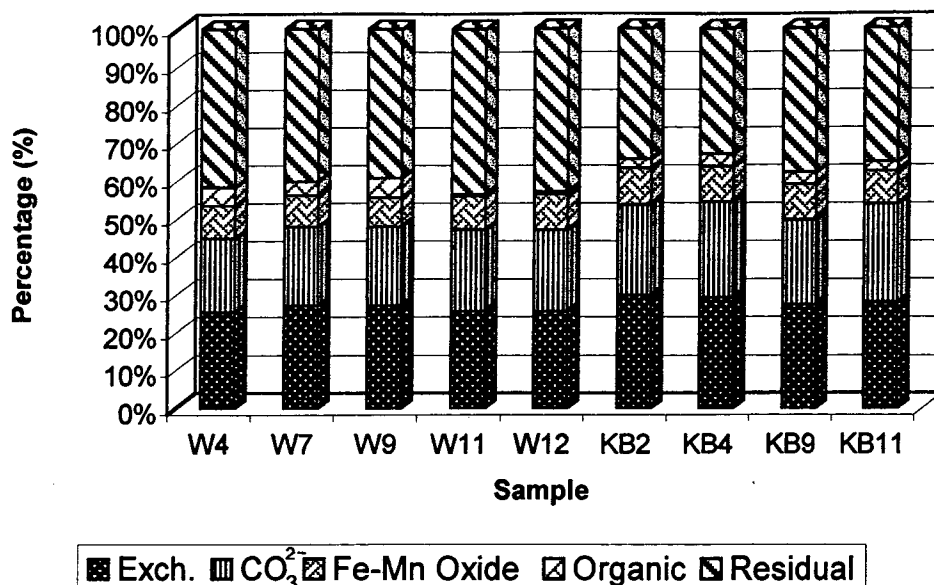Fig. 5.4a. Percentage Distribution of Cadmium in Different Fractions
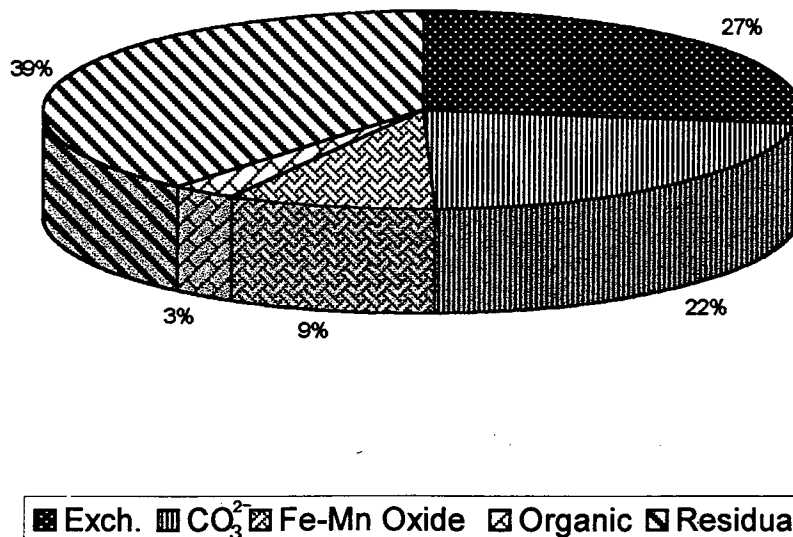

Fig.5.4b. Average Partioning Pattern of Cadmium

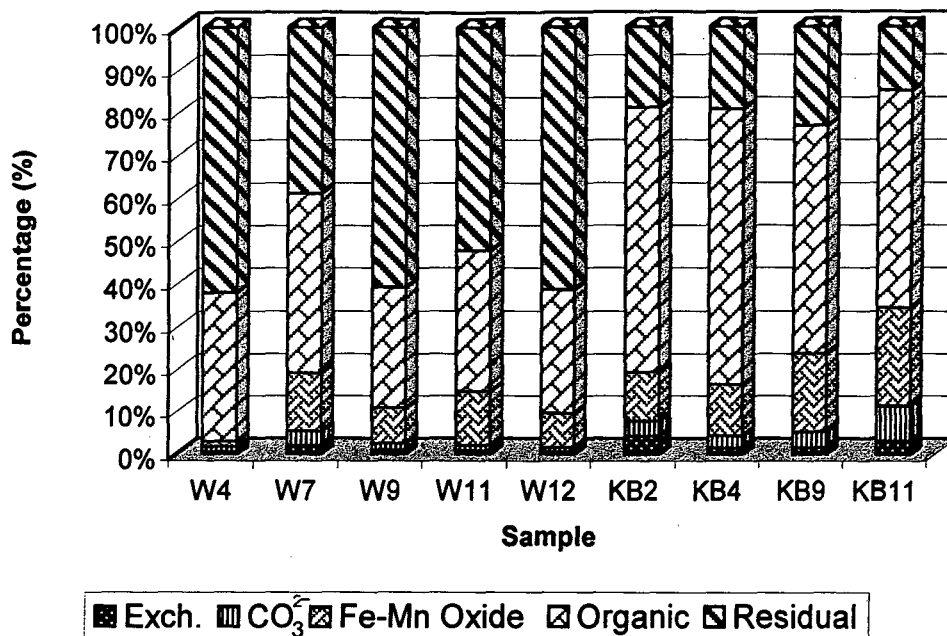Fig. 5.5a. Percentage Distribution of Copper in Different Fractions

Legend: ■ Exch. ▥ CO$_3^{2-}$ ▨ Fe-Mn Oxide ▨ Organic ◨ Residual

Fig.5.5b. Average Partioning Pattern of Copper

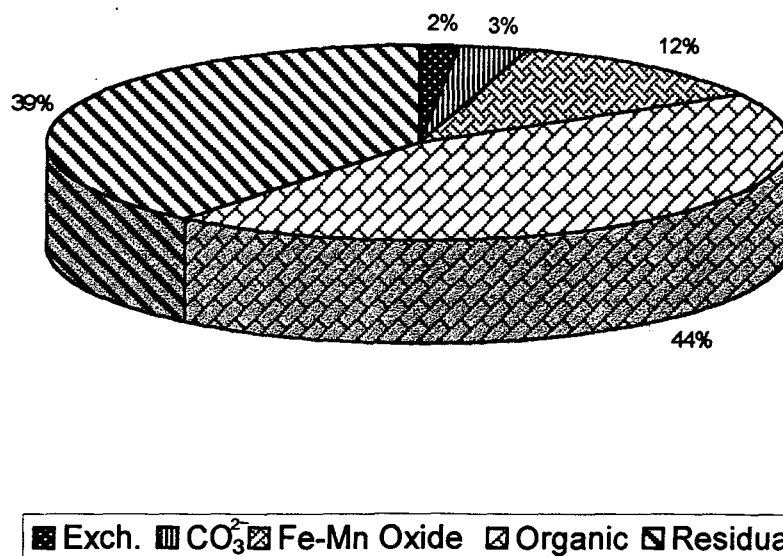Legend: ■ Exch. ▥ CO$_3^{2-}$ ▨ Fe-Mn Oxide ▨ Organic ◨ Residual

Table 5.6d. Percentage distribution of Nickel in different fractions in street dust.

S.N.	Exchangeable fraction	CO$_3^{2-}$ bound	Fe-Mn Oxide bound	Organic fraction	Residual fraction
W4	13.18 (17.79)	7.60 (10.26)	8.54 (11.53)	7.67 (10.35)	63.00 (85.00)
W7	1.24 (45.08)	20.89 (760.0)	54.96 (2000.0)	17.50 (636.89)	5.41 (196.76)
W9	10.75 (19.67)	4.83 (8.85)	23.01 (42.12)	13.37 (24.47)	48.04 (87.94)
W11	8.47 (15.91)	6.46 (12.14)	37.45 (70.35)	11.77 (22.12)	35.85 (67.35)
W12	10.14 (18.26)	5.96 (10.73)	14.25 (25.65)	17.52 (31.53)	52.13 (93.82)
KB2	8.76 (18.73)	12.50 (26.73)	19.70 (42.12)	18.60 (39.76)	40.44 (86.47)
KB4	9.70 (16.85)	12.68 (22.02)	23.57 (40.94)	16.12 (28.00)	37.93 (65.88)
KB9	6.44 (18.26)	13.59 (38.49)	29.81 (84.47)	31.06 (88.00)	19.10 (54.12)
KB11	6.01 (23.44)	23.49 (91.67)	43.05 (168.0)	11.70 (45.65)	15.75 (61.47)

* Values in parenthesis are concentrations in ppm

Table 5.6e. Percentage distribution of Chromium in different fractions in street dust.

S.N.	Exchangeable fraction	CO$_3^{2-}$ bound	Fe-Mn Oxide bound	Organic fraction	Residual fraction
W4	0.09 (10.73)	0.07 (8.56)	4.31 (508.42)	0.73 (85.74)	94.80 (11193.50)
W7	0.49 (10.42)	0.27 (5.77)	7.28 (155.50)	1.87 (40.00)	90.09 (1924.50)
W9	0.20 (11.04)	0.16 (8.87)	4.94 (268.32)	0.81 (43.88)	93.88 (5095.92)
W11	0.18 (10.73)	0.27 (16.31)	9.03 (540.59)	0.77 (46.20)	89.75 (5374.38)
W12	0.08 (9.49)	0.16 (19.10)	4.45 (525.74)	0.66 (77.98)	94.65 (11193.50)
KB2	5.53 (9.80)	2.03 (3.60)	13.83 (24.50)	5.51 (9.77)	73.09 (129.46)
KB4	1.43 (10.11)	0.51 (3.60)	8.75 (61.71)	2.70 (19.07)	86.60 (610.77)
KB9	1.29 (10.11)	0.62 (4.84)	2.74 (21.40)	1.05 (8.22)	94.30 (737.62)
KB11	5.08 (10.42)	1.91 (3.91)	11.95 (24.50)	5.14 (10.54)	75.92 (155.62)

* Values in parenthesis are concentrations in ppm

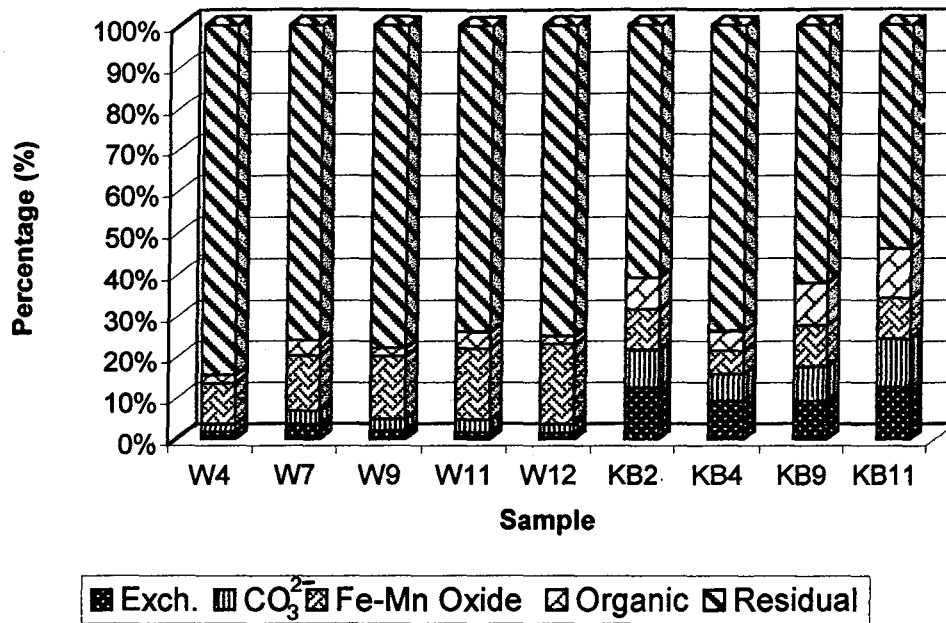**Fig.5.6a. Percentage Distribution of Nickel in Different Fractions**

Legend: ■ Exch. $\boxed{\text{III}}$ CO_3^{2-} ☒ Fe-Mn Oxide ☒ Organic ☒ Residual

Fig.5.6b. Average Partioning Pattern of Nickel

6% 5% 12% 5% 72%

Legend: ■ Exch. $\boxed{\text{III}}$ CO_3^{2-} ☒ Fe-Mn Oxide ☒ Organic ☒ Residual
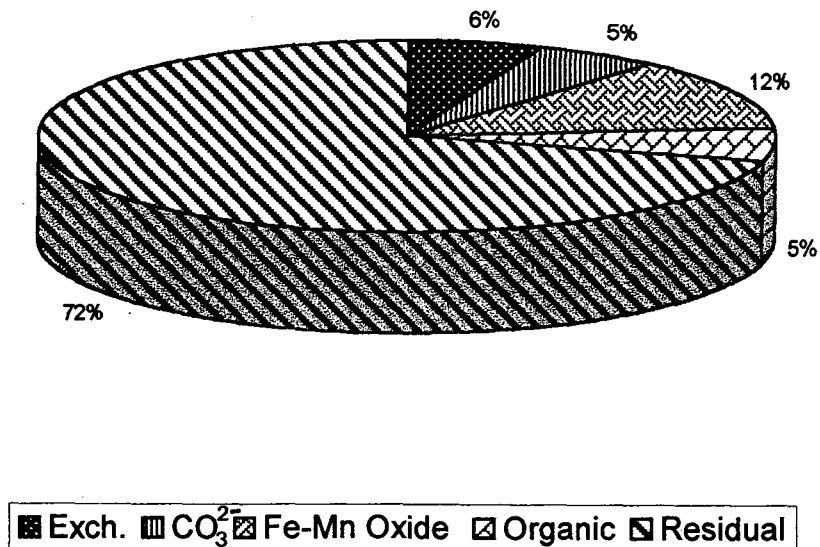
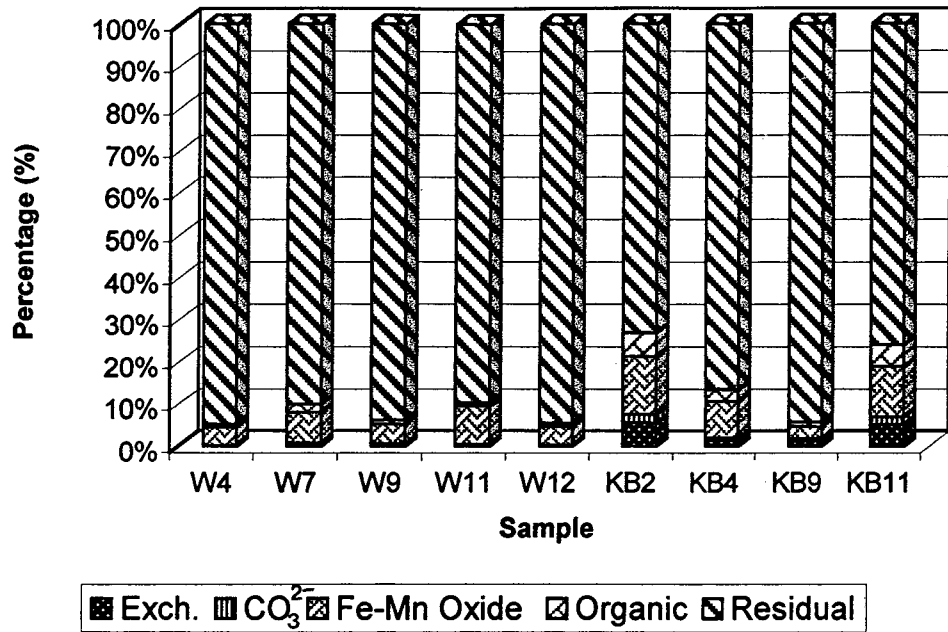Fig.5.7a. Percentage Distribution of Chromium in Different Fractions

Fig.5.7b. Average Partioning Pattern of Chromium

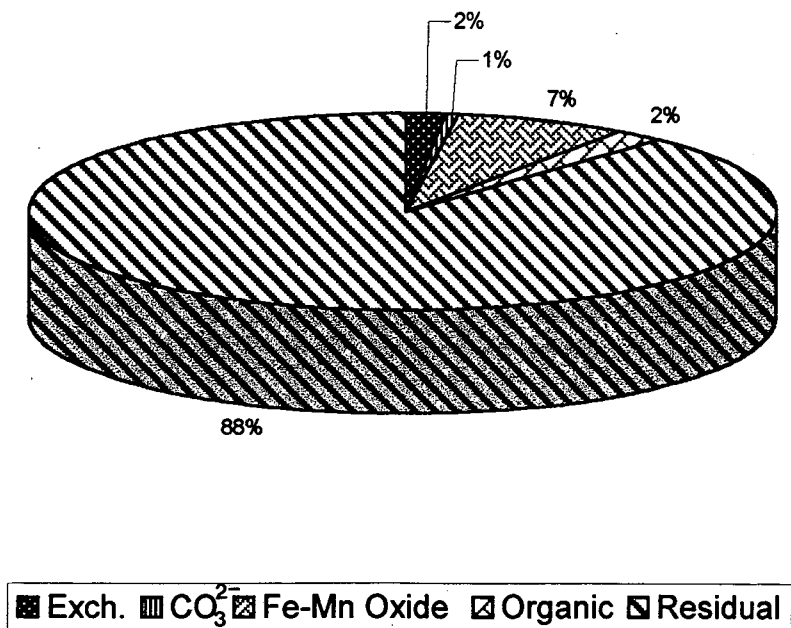## Table 5.6f. Percentage distribution of Lead in different fractions in street dust.

S.N.	Exchangeable fraction	CO$_3^{2-}$ bound	Fe-Mn Oxide bound	Organic fraction	Residual fraction
W4	13.18 (17.79)	7.60 (10.26)	8.54 (11.53)	7.67 (10.35)	63.00 (85.00)
W7	1.24 (45.08)	20.89 (760.0)	54.96 (2000.0)	17.50 (636.89)	5.41 (196.76)
W9	10.75 (19.67)	4.83 (8.85)	23.01 (42.12)	13.37 (24.47)	48.04 (87.94)
W11	8.47 (15.91)	6.46 (12.14)	37.45 (70.35)	11.77 (22.12)	35.85 (67.35)
W12	10.14 (18.26)	5.96 (10.73)	14.25 (25.65)	17.52 (31.53)	52.13 (93.82)
KB2	8.76 (18.73)	12.50 (26.73)	19.70 (42.12)	18.60 (39.76)	40.44 (86.47)
KB4	9.70 (16.85)	12.68 (22.02)	23.57 (40.94)	16.12 (28.00)	37.93 (65.88)
KB9	6.44 (18.26)	13.59 (38.49)	29.81 (84.47)	31.06 (88.00)	19.10 (54.12)
KB11	6.01 (23.44)	23.49 (91.67)	43.05 (168.0)	11.70 (45.65)	15.75 (61.47)

*Values in parenthesis are concentrations in ppm

Table 5.7. Average percentage values of metals in different fractions in street dust.

Metal	Exchangeable fraction	CO$_3^{2-}$ bound	Fe-Mn oxide bound	Organic fraction	Residual fraction
Cd	27.16	22.31	8.86	2.90	38.76
Cr	1.60	0.67	7.47	2.14	88.12
Cu	1.68	2.94	12.08	44.26	39.04
Ni	5.90	5.49	12.31	5.36	70.94
Pb	8.30	12.00	28.26	16.15	35.29
Zn	2.66	20.87	45.64	11.14	19.69

All values are in percentages.

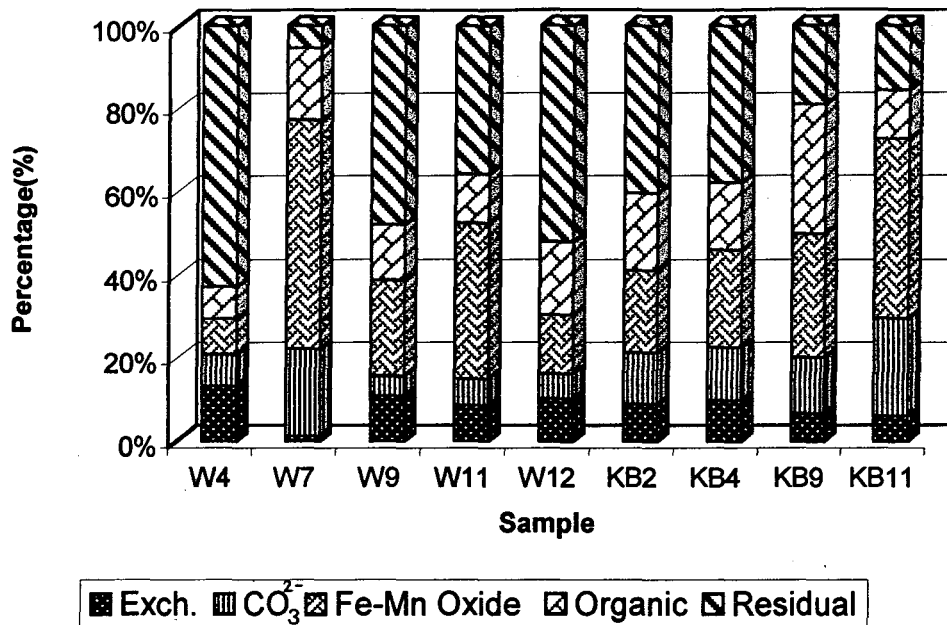## Fig. 5.8a. Percentage Distribution of Lead in Different Fractions
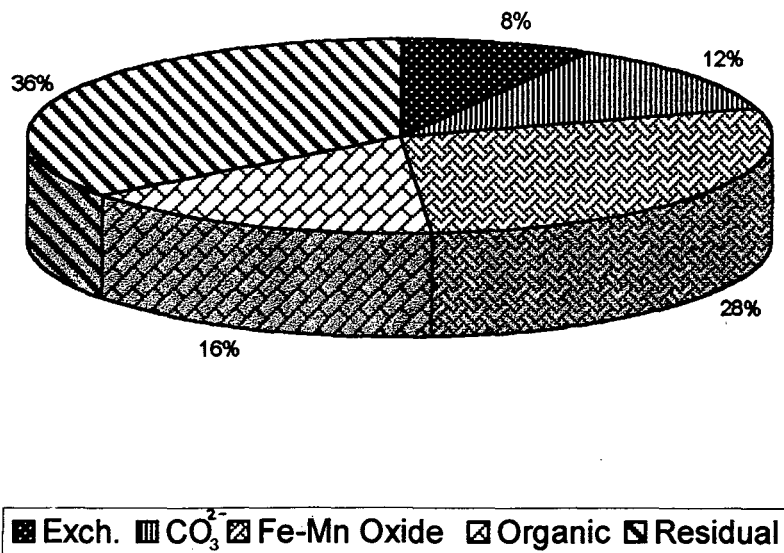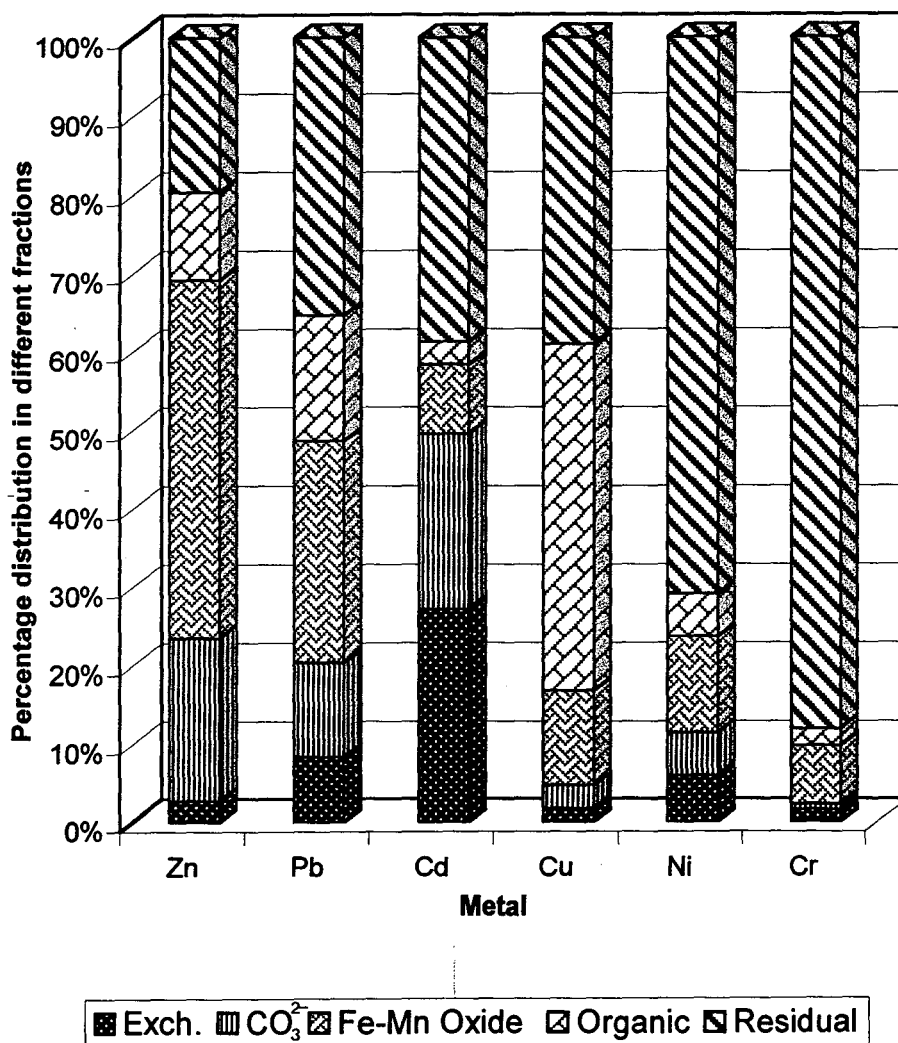

Fig.5.8b. Average Partioning Pattern of Lead

Fig.5.9. Comparison of metal distribution(% values) in different fractions

The results of sequential extraction for different metals are described in terms of % distribution in each fraction in Table 5.5a.to 5.5f. which show a certain similarity between the speciation pattern for street dust samples, irrespective of their wide range of metal levels and different sampling areas.

This is perhaps not surprising that street dusts to a large extent are made up of soil material (Fergusson and Ryan, 1984; Hopke et al., 1980; Fergusson et al., 1986) and hence their chemical speciation might be expected to be similar with soils.

Cadmium

The Cd association with different fractions followed the order: residual > exchangeable > carbonate > Fe-Mn oxide bound > organic. Ma and Rao (1997) obtained similar order for Cd speciation in polluted soils.

In the nonresidual fraction the highest % of Cd (27%) was associated with the exchangeable fraction, which is in agreement with the findings of Elsokkary and Lag (1978), Miller and McFee (1983), Kuo et al. (1983) and Hickey and Kittrick (1984) in soils and Harrison et al. (1981) and Gibson and Farmer (1984) in street dusts.

On an average 22.31% of Cd was present in carbonate phase, which is consistent with the findings of Hickey and Kittrick (1984), Ramos et al. (1994) and Gibson and Farmer (1984). Enhanced significance of carbonate fraction in the present study is probably a consequence of the more alkaline nature of the sample. At higher pH the substitution of Cd^{2+} for Ca^{2+}in the calcite and precipitation of $CdCO_3$ is expected (Lindsay, 1979; Miller and McFee, 1983).

The minor role of organic fraction in the speciation of Cd, as noted in present study (2.9%), is commonly found in river sediments (Forstner and Whittman, 1979), street dusts (Harrison et al., 1981) and soils (Miller and McFee, 1983; Kuo et al., 1983; Hickey and Kittrick, 1984 and Ramos et al., 1994); however, this contrasts with

the findings of Gupta and Chen (1975). The study of Keefer et al., (1984) and Sposito et al., 1976 also suggest that Cd has a very low organic complexation and if present, is not tightly bound. The high % of Cd in residual fractions was also observed by Ma and Rao (1997) and Ramos et al., (1994).

The amount of Cd determined as sum of exchangeable and carbonate fractions, was often more than 50% of the total and are highly mobile and Cd-organic complexes if present are only loosely bound and they are easy to remove. These characteristics plus the known hazards to human health suggest that more frequent examination of the level of this element in dust may be necessary to determine the potential health hazards to the residents living near contaminated areas.

Copper

The amount of Cu in each fraction followed the order: organic > residual >> Fe-Mn oxide >>carbonate > exchangeable. Similar order of distribution was obtained by Ramos et al., (1994).

High contents of Cu in the residual fraction are often described in soils (Shuman, 1979; McLaren and Crawford, 1973; Hickey and Kittrick, 1984; Ramos et al., 1994) and dusts (Harrison et al., 1981).

Although there were considerable variations in the proportions of Cu present in different fractions, but its association in the nonresidual fraction was dominated by organic phase (44.26%) with Fe-Mn oxide bound (12.08%), carbonate (2.94%) and exchangeable (1.68%) of secondary importance.

Exchangeable fraction accounted for a very low percentage of Cu and varied from 0.4 to 4.1% with an average of 1.68%. This is in agreement with the previous works of Gupta and Chen (1975) for sediments; Ma and Rao (1997), Elsokkary and Lag (1978), Miller and McFee (1983), Ramos et al. (1994) and McLaren and Crawford (1973) for soils and Fergusson and Ryan (1984) and Hamilton et al. (1984) for

street dusts. Exchangeable Cu was quite low probably due to strong specific (covalent) interaction of Cu with organic matter and other surfaces (McLaren and Crawford, 1973).

The presence of Cu in organic fraction (44.26%) is in strong agreement with that observed in soil (Shuman, 1979; McLaren and Crawford, 1973; Miller and McFee, 1983; Kuo et al., 1983; Miller et al., 1986; Hickey and Kittrick, 1984; Gibson and Farmer, 1986; Baker, 1990; Levy et al., 1992; Ramos et al., 1994 and Ma and Rao, 1997), sediments (Pardo et al., 1990) and street dusts (Harrison et al., 1981; Gibson and Farmer, 1984; Fergusson and Ryan, 1984 and Hamilton et al., 1984). The presence of Cu in organic fraction is supported by the high formation constants of Cu - organic complexes (Stumm and Morgan, 1981; Irving and Williams, 1953). SEM / EDX analysis done by Adamo et al, (1996) on polluted soils also confirms the strong association of Cu with organic matter.

Except Cu no other metal was in significant association with organic fraction and a significant correlation was found between the %organic matter and the % of Cu in the organic fraction.

Fe-Mn oxide bound form (12.08%) was the second important nonresidual fraction. LeRiche and Weir (1963), Jenne (1968) and McLaren and Crawford (1973) each indicated that adsorption may be an important control of Cu levels. The high surface area and adsorbing capacity of Fe-Mn oxides coupled with the ability of Cu to replace Fe^{2+} in some Fe oxides (Taylor, 1965) may be responsible for such adsorption.

Overall Cu was largely associated with the last three chemical fractions (95%) as also reported by Hickey and Kittrick (1984).

Nickel

The residual fraction was by far the most important fraction for Ni (70.94%). These results are consistent with the observation of Gupta and Chen (1975) and Tessier et al. (1980), which suggested

that a majority of Ni in soils and sediments was detrital in nature. Ma and Rao (1997), Hickey and Kittrick (1984), Levy et al. (1992), Belzunce-Segarra (1997) and Barona et al. (1999) also observed very high percentage of Ni in residual fraction. Norrish (1975) has indicated that silicates during weathering commonly occlude Ni. Bruemer et al. (1988) suggested that the large proportion of Ni in residual fraction might be because Ni^{2+} has the highest field stabilisation energy of the common divalent metals and thus has high potential to be enriched in clay minerals. Adamo et al. (1996) confirmed by SEM / EDX analysis of polluted soils that Ni alone or in association with Fe oxides was often included in silicate matrices of the spherical particles.

Fe-Mn oxide bound was the next important fraction (12.31%) containing Ni, as also observed by Hickey and Kittrick (1984). Jenne (1968) has suggested that adsorption by Mn oxides controls Ni levels in soils. Using crystal field theory McKenzie (1972) concluded that substitution of Ni^{2+} for Mn in mixed valence Mn oxides might be responsible for much of adsorption. Ni was nearly equally distributed in exchangeable, carbonate and organic fractions.

Zinc

The distribution pattern in each fraction followed the order: Fe-Mn oxide bound > carbonate >= residual >> organic > exchangeable, which was also noted by Ramos et al. (1994). Majority of Zn was associated with Fe-Mn oxide fraction, which may be due to high stability constants of Zn oxides. Present study agrees with several other studies. The studies of Elsokkary and Lag (1978), Shuman (1979), Shuman (1985), Kuo et al. (1983), Miller and McFee (1983), Hickey and Kittrick (1984), Levy et al. (1992), Ramos et al. (1994) and Ma and Rao (1997) in soils, Gupta and Chen (1975) and Pardo et al. (1990) in sediments and Harrison et al. (1981) and Fergusson and Ryan in street dusts obtained the same results. The study of Shuman (1976,1977) show that Fe oxides adsorb considerable quantities of Zn and these oxides may also occlude Zn in the lattice structures.

Carbonate was the second most important nonresidual fraction for this element, containing approximately 21% of Zn, which is consistent with the findings of Hickey and Kittrick (1984) and Ramos et al. (1994) in polluted soils and Gibson and Farmer (1984) in street dusts. Presence of Zn in carbonate might indicate a pH suitable for metal precipitation. $CaCO_3$ may act as a strong adsorbent for heavy metals and could complex as double salts like $CdCO_3.ZnCO_3$.

Very little enrichment of Zn in the residual fraction was noted, as also observed by Hickey and Kittrick (1984). Very low percentages of total Zn in exchangeable fraction observed in present study are in agreement with Harrison et al. (1981), Hamilton et al. (1984) and Fergusson and Ryan (1984).

Chromium

The distribution pattern of Cr in different fractions was in the order: residual >>> Fe-Mn oxide bound > organic > exchangeable > carbonate. Similar order was reported by Usero et al. (1998) in marine sediments. Chromium was associated mainly (73%-94%) with the residual fraction in all the samples and relatively small amounts of Cr occur in the nonresidual fraction, which is supported by the study of Belzunce-Segarra (1997) and Gibbs (1973).

Lead

Lead in the street dust showed the order of association: residual > Fe-Mn oxide bound > organic > carbonate bound > exchangeable. The high percentages of lead in the residual fraction has been observed by many studies (Usero et al., 1998; Pardo et al., 1990; Belzunce-Segarra, 1997).

Except one sample (W7) having very high concentration of Pb (3670ppm), all the samples were showing similar pattern for Pb association in different fractions. This sample was having minimum (5%) of Pb in the residual fraction, which might be because of excessive enrichment of the sample with Pb and hence the lower % in

the residual fraction that mainly represents the metal associated with the primary and secondary minerals.

The predominance of Pb in the Fe-Mn oxide fraction (28.16%) is in broad agreement with the observations of Pardo et al., 1990; Usero et al., 1998; Belzunce-Segarra et al., 1997), soils (Ramos et al., 1994; Levy et al., 1992) and street dusts (Hamilton et al., 1984; Gibson and Farmer, 1984; Fergusson and Ryan, 1984). The adsorption of Pb cations on the hydrous (amorphic) oxides of iron and Mn has been suggested as a reasonably universal fixation mechanism (Parks, 1965; Perdue, 1976).

Approximately 16% of Pb was in the organic fraction. The ability of lead to form organic complexes is known (Zimdahl and Skogerboe, 1976).

The average concentration of Pb in the carbonate fraction was (12%). $CaCO_3$ might act as a strong adsorbent for Pb and could complex as $CaCO_3.PbCO_3$.

The sequential extraction used in this study is useful to indirectly assess the potential mobility and bioavailability of the heavy metals in the street dusts. Assuming that the mobility of these metals is related to their solubility and geochemical forms, and that it decreases in the order of extraction sequence i.e. exchangeable > carbonate > Fe-Mn oxide bound > organic > residual. This order is just a generalisation and offers only qualitative information on metal mobility. Based on this information we can assume that metals in the nonresidual fraction, that is the sum of all the fractions except the residual, are more mobile than the metal associated with the residual fraction. Comparative trace metal affinities for different fractions are listed below.

Table 5.8. Comparative trace metal affinities for different fractions.

S.N.	Fraction	Comparative metal affinities
1	Exchangeable	Cd > Pb > Ni > Zn > Cu > Cr
2	Carbonate	Cd > Zn > Pb > Ni > Cu > Cr
3	Fe-Mn oxide bound	Zn > Pb > Ni = Cu > Cd > Cr
4	Organic	Cu > Pb > Zn > Ni > Cd > Cr
5	Residual	Cr > Ni > Cu > Cd > Pb > Zn

The environmental impact of sequential speciation categories depends on the ease of remobilization. The first two phases can release their metal loads by lowering the pH and are more mobile than the other phases, in this way taking first two phases the results can be ascertained in terms of mobility and hence the bioavailability. Based on this the order of comparative mobility of six metals was: Cd > Zn $\cong$ Pb > Ni > Cu > Cr.

Conclusion

Based on the observations on street dust samples collected from three different localities in Delhi, the following conclusions have been drawn:

The street dust samples collected from area A1 (Wazirpur Industrial Area) show alarmingly high concentrations of heavy metals, especially chromium, copper and nickel, which can lead to serious environmental hazards.

The concentrations of Pb and Cd do not show discernible variations between the three sites, indicating that no localised activity is mainly responsible for the concentrations of these two metals.

Only one sample (W7) shows very high lead concentration (3670ppm). The three samples from the adjacent grids had low concentrations of lead, indicating that high Pb concentration in this sample (W7) is because of some localised activity, which are the battery recharge centres and the spray painters. It is implied that the levels of metals in street dust can vary even at small distances.

No significant differences ($p < 0.05$) are observed in Zn levels between the industrial and heavy traffic sites, indicating that Zn can have its mixed origin, mainly from both the industrial and automotive activities.

Factor analysis and correlation analysis indicate a common source for the three metals i.e. chromium, copper and nickel, in street dust, which can only be industrial.

The present study on street dust indicates that the six metals examined are associated with various operationally defined chemical fractions as distinguished by sequential chemical extraction. Only cadmium is significantly associated with the exchangeable fraction, while for other metals exchangeable content is low. Appreciable portions of Cd (22.31%) and Zn (20.87%) are present in the carbonate bound fraction. Except copper no other metal is present substantially in the organic fraction. The Fe-Mn oxide bound fraction contains 45.64, 28.26, 12.31, 12.08, 8.86 and 7.47% of Zn, Pb, Ni, Cu, Cd and

Cr respectively. Ni (70.94%) and Cr (88.12%) are present mainly in the residual fraction.

Although very high levels of Cr and Ni are observed in the present study, very low percentages of these two metals in the nonresidual fractions indicate their limited environmental mobility.

Assuming that the metal mobility and bioavailability are related to their solubility and geochemical forms and that they decrease in the order of extraction sequence, the apparent mobility and potential bioavailability of these six metals in street dusts are:

Cd > Zn = Pb > Ni > Cu > Cr.

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