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INVESTIGATION OF PB, ZN, MN, NI, CO AND CR IN INSOLUBLE DUSTFALL

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Dust samples collected from different locations in urban areas of Peshawar were analyzed for lead, zinc, manganese, nickel, cobalt and chromium using atomic absorption spectrophotometric technique. Elemental concentrations of the studied elements did not vary significantly at different sample locations. A comparison of the elemental contents with the local soil was also made. Soil, road dust, vehicle exhaust, metallic corrosion, tire wear, zinc compounds in rubber material, galvanized material, weathering and corrosion of building material are some of the possible sources of heavy metal pollution in Peshawar. Peshawar can be considered as one big urban centre with high population and traffic density.

Key words: Heavy metals, Dustfall, Pollution.

Introduction

In developing countries, rapid industrialization and urbanization without environmental control has resulted in heavy metal contamination of communities. Peshawar, the provincial capital of North West Frontier Province (N.W.F.P.) Pakistan has no exception. Heavy metals alongwith other pollutants are discharged into the atmosphere through industrial activities, automobile exhaust, refuse burning, man-made activities, pesticide use in agriculture etc. It has now been well established that aerosol and deposited dusts in urban areas contain substantial amounts of many potentially toxic trace metals in comparison to those found in non-urban areas (Philip *et al* 1980). Thus people residing in urban areas are exposed to larger amounts of potentially hazardous elements than their counterparts.

Dusts often contain elevated concentrations of trace metals. In some instances the dusts may represent a significant source of pollution especially when rain water runoffs remove a large part of the dust and its associated metals. Dust is now recognized as a significant source of heavy metals in the urban environment as well as an important source of heavy metal intake by young children due to its inadvertent ingestion (Duggan and William 1977; Harrison *et al* 1981). Human beings, animals and plants take in heavy metals through air, water and food. It has been reported that plants are more sensitive to pollution than animals or man. Injury to vegetation caused by heavy metals has been well documented as a result of many botanical and chemical investigations during the past hundred years (Yousafzai *et al* 2001). Dust by itself retards the growth of road side plants by affecting photosynthesis (Hussain *et al* 1994).

There have been a considerable number of studies on the concentrations of heavy metals in falling dust, street dust, soil dust, the vast majority being carried out in the developed countries with long histories of industrialization, extensive road building and use of leaded gasoline (Fergusson and Kim 1991; Smirnioudi *et al* 1997; Gelinas and Schmit 1998; De Miguel *et al* 1999; Zhang *et al* 1999). However, very few studies have been made in developing countries such as India, Bahrain, Saudi Arabia etc. (Chakraborti and Raeymaekers 1988; Madany *et al* 1990; Modaihsh 1997).

In Pakistan, little attention has been paid to the atmospheric pollution in general and dustfall/trace metal pollution in particular. Very small data on pollutant metal concentration is available for a few cities of Pakistan (Yousafzai *et al* 1991; Faridullah and Khan 1996; Choudhary and Tanisely 1998). The objective of this investigation is to assess the concentrations of trace metals namely Pb, Zn, Mn, Ni, Cr and Co in urban areas of Peshawar; no study has been so far made in these areas.

Experimental

Dustfall samples were collected in accordance with a standard method (Robert 1966). A plastic bucket of about 22-24 cm mouth diameter, 20-22 cm base diameter and 25 cm height was secured in a bucket shaped iron cage mounted on a metallic pole. A metallic strip (one edge of which was cut like a saw) was wrapped around the bucket so that the saw like teeth protruded above the mouth of the bucket. The whole assembly is generally called dustfall collecting apparatus/ collector as shown in Fig 1.

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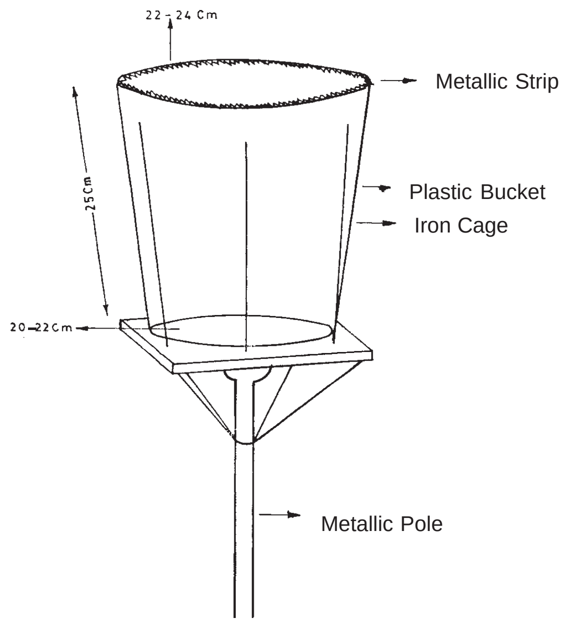

Fig 1. Dustfall collector

Dustfall collectors were installed at four locations in urban areas of Peshawar on the roof of the buildings along road side at height of 25-30 feet from ground level (at Government Higher Secondary School GHSS No.1 Peshawar Cant; GHSS No.1 Peshawar City; on main gate of PCSIR Laboratories Peshawar and at a petrol pump near new bus stand Peshawar). After a period of one calendar month, collected to 30 ± 2 days, the collectors were taken off, covered with plastic lid and brought to the laboratory. The contents of the collectors were filtered through ordinary sieve (20-25 mesh) to remove extraneous matter like leaves, insects, twigs and stones if any. The filtrate was further filtered through Whatman filter paper No.41 or 42. The filter paper with residue was dried at 105°C. The weight thus obtained was the insoluble dustfall at Peshawar. The average monthly rate of dustfall at Peshawar was 27.65±6.75 tons km^{-2} per month (Faridullah *et al* 2002). Data on meteorological conditions was obtained from Meteor. Observatory (1993-98).

Analytical measurements. A combination of HNO_3+ $HClO_4$ was used as extractant, HNO_3 being the best extractant for toxic metals (Choudhary and Tanisely 1998). To 0.5 gm of dried homogenized sample, 2 ml HNO_3 and 0.5 ml $HClO_4$ was added in a digestion flask and heated at 65°C till the dissolution of the sample (about 30-40 min.). The temperature was gradually increased to 250°C. Complete drying of the residue was achieved at the temperature of 300-350°C. The flask was cooled. Then 0.1ml HNO_3 and deionized water was added and filtered to remove any residue. The volume was made in 25 ml flask. Blanks were prepared by taking 0.1ml HNO_3 and diluted to 25 ml with deionized water. All the glassware were extensively soaked in dilute HNO_3 and rinsed with deionized water. The analyses were performed by Hitachi Z-8000 atomic absorption spectrophotometer with Zeeman correction in flame mode.

Results and Discussion

The monthly average rate of dustfall at Peshawar is given in Table 1. The overall average rate of dustfall at Peshawar from 1993-98 was 27.65 ± 6.75 tons km^{-2} per month (Faridullah *et al* 2002). The average metal concentrations ($\mu g\ g^{-1}$) with standard deviations are summarized in Table 2. The values reported are the average of triplicate determinations and are presented in Fig 2. Sampling locations are shown in Fig 3. All the sampling sites were located on main G. T. Road on which all types of vehicles pass the whole day. Table 3 shows the average climatic conditions of Peshawar.

The concentrations of chromium, manganese and zinc at the four sites are very close to each other (Table 2) due to locations of all on main G. T. Road with the same number of vehicles passing through all of them. About 4000-5000 vehicles/hour pass through the study points. It is seen from Table 2, that high concentrations of Pb, Co and Ni were recorded at PCSIR Laboratories area. This may be due to traffic held up at traffic signals, high number of vehicles and large number of automobile workshops in the surrounding area. Furthermore, this location is at a few kilometers from industrial estate area of Peshawar. The lowest value of lead 334.00 ($\mu g\ g^{-1}$) was found in city area probably because this location is quite open. In fact the amount of pollutant at ground level depends upon the amount emitted, dispersed

Table 1

Average monthly rate of dustfall at Peshawar (tons km^{-2}.month)*

Month/ Location	PCSIR Labs. area	GHSS No.1 Cant.	GHSS No.1 City	Bus stand area
January	17.60	21.60	15.52	23.00
February	18.03	22.84	17.00	26.96
March	22.05	26.29	20.93	29.29
April	25.96	29.67	23.98	34.55
May	31.47	37.90	28.17	42.90
June	35.28	43.54	31.28	47.77
July	30.66	37.50	26.08	42.94
August	28.68	37.07	24.38	40.54
September	24.73	31.60	23.71	37.17
October	21.93	27.85	20.38	31.22
November	20.22	25.75	17.76	28.20
December	17.84	24.65	15.14	24.15

* Average of six years data.

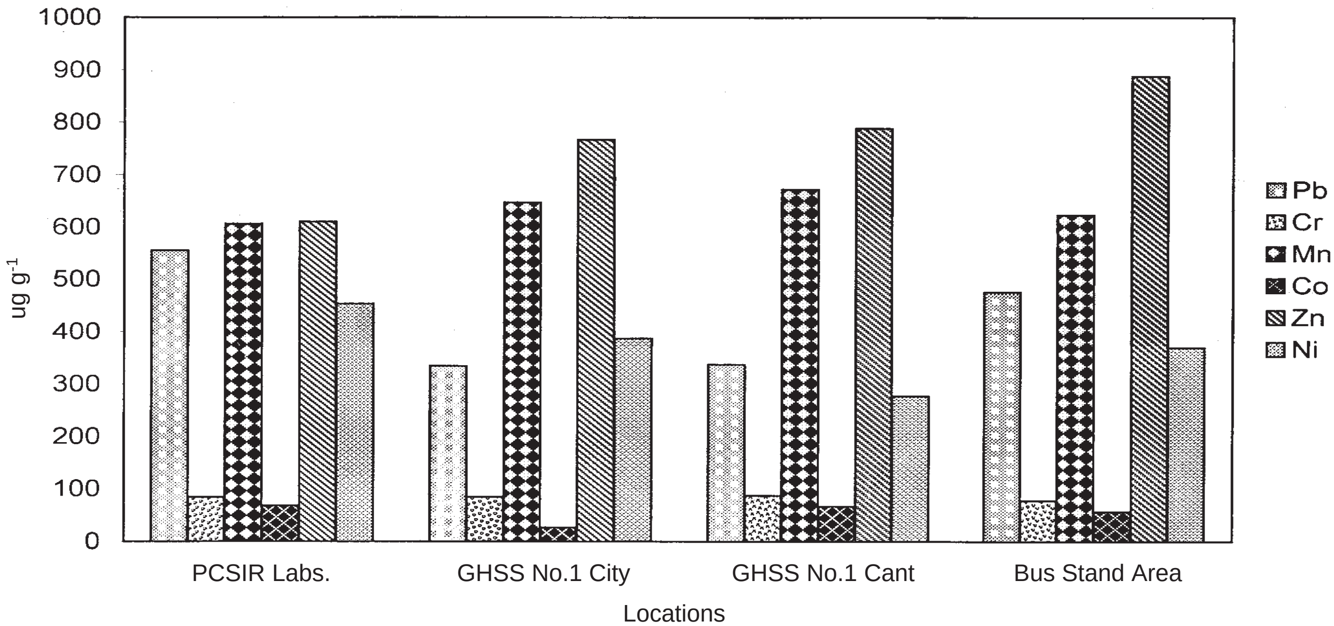

Fig 2. Average trace metal concentration (ug g^{-1}) in insoluble dustfall.

and diluted by the atmospheric currents thus the pollution spreads to a larger area.

The concentration of Zn was very high in all the samples. Zinc in some lubricating oils forms as an important component of many zinc coating additives such as antioxidant Zn-dithiophosphate and also in the tyres of motor vehicles. Elements such as Zn, Cr, Ni are produced due to wear and tear in the car (Fergusson and Kim 1991). This suggests that automobiles form is the major polluting source of many trace metals. Highest value of Cr was found at the cantonement area. This could be attributed to the lead chromate in yellow lines. A more probable source of Cr could be the attrition of chrome-plating and alloys in motor vehicles.

The elements nickel, manganese and cobalt are generally used in our daily life. Ni as metal and its alloys are used for Ni-coating or nickel plating of articles. Being an important constituent of explosives, manganese is released into the air through fire-display and several types of crackers used at different occasions. The multiuse of manganese (metal alloys, dry batteries cell, feed additives, pigments, chemical deter-

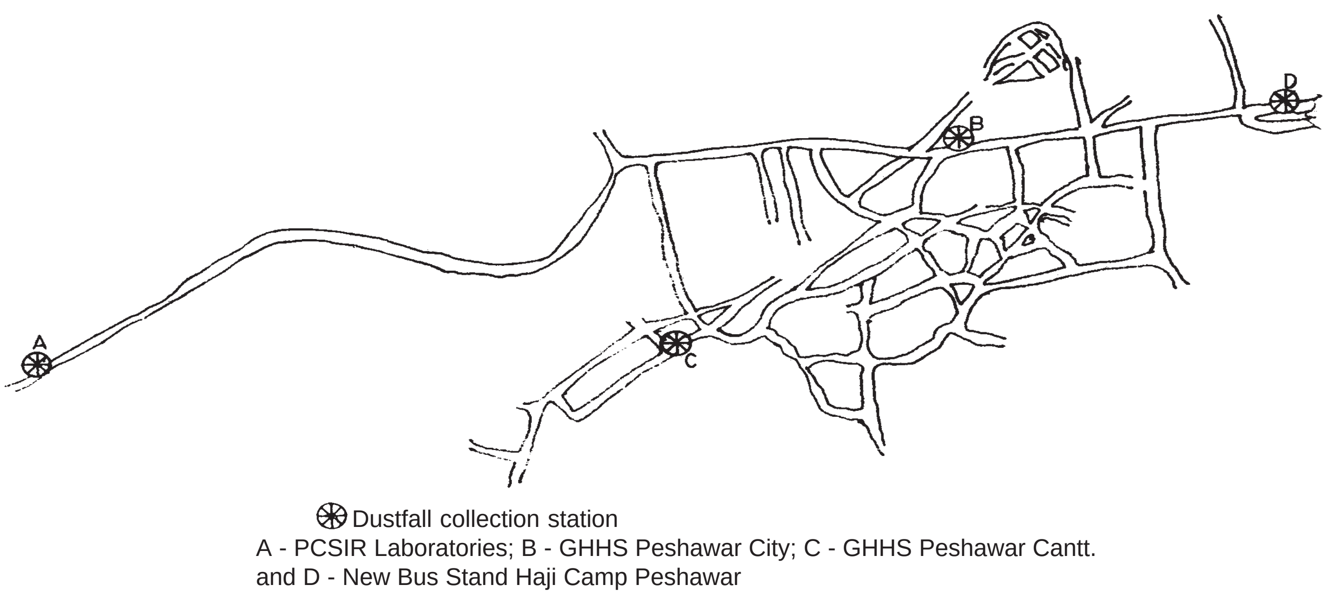

Fig 3. Map of Peshawar.

Table 2
Average trace metal concentration ($\mu g\ g^{-1}$) in insoluble dustfall

Metals	PCSIR labs. area	GHSS No.1 City area	City GHSS No.1 Cant. area	Bus stand area
Pb	504-581 (555± 196.17)	150-400 (334±167.55)	170-400 (337±89.85)	406-540 (476±62.82)
Cr	45-104 (84±22.01)	40-123 (85±35.89)	37-124 (87±49.47)	40-128 (78±33.50)
Mn	557-654 (606± 66.28)	600-690 (647±84.95)	630-706 (672±33.14)	531-754 (623±58.50)
Co	33-136 (68±26.50)	10-55 (27±5.66)	32-113 (67±42.29)	14-95 (57±8.77)
Zn	460-936 (610±339.31)	493-1050 (767±247.40)	671-887 (788±130.37)	634-1153 (888±322.47)
Ni	98-856 (453±140.29)	116-600 (387±247.40)	96-450 (277±221.84)	88-809 (370±58.50)

Table 3
Average climatic data of Peshawar

Months	Temperature°C		Humidity %	Wind direction	Rainfall (mm)	Wind velocity
	Maximum	Minimum				$km\ h^{-1}$
January	16.98	1.62	29.83	NW	11.74	2.61
February	19.12	3.89	31.19	NW	34.66	3.14
March	21.85	8.51	35.56	NW	69.97	3.25
April	26.86	12.89	32.97	SW	63.31	3.40
May	34.67	18.72	27.62	SW	21.26	4.18
June	38.60	22.38	32.35	S	16.42	4.47
July	36.12	24.90	51.09	SW	78.62	4.85
August	28.81	24.57	49.88	NW	43.64	4.46
September	33.85	21.00	39.47	NE	26.52	3.70
October	28.37	14.02	30.38	N	26.90	2.98
November	24.89	9.38	30.24	SE	82.00	2.74
December	20.71	2.76	30.89	SW	18.50	2.42

gents, fertilizers, coating welding rods etc.) enhance Mn concentration in the environment. The concentration of cobalt is very high at PCSIR Laboratories and cantonement area (68 and 67 $\mu g\ g^{-1}$) respectively. Definite source of cobalt is difficult to ascertain but most probably the use of cobalt in high speed steel, cemented carbides, high temperature alloys in industries and as a catalyst in various industrial processes contribute significantly to atmospheric pollution.

Average climatic conditions of Peshawar are given in Table 3. Climatic variables influence the severity of air pollution in general and dustfall in particular. These variables vary tremendously day to day, season to season and even from location to location. It is seen from Table 3 that all these variables have very wide month to month variation. The most common wind direction is from north to west followed by from south to west. Wind velocity is low in winter ranging from 2.61 to 2.74 $km\ h^{-1}$. It is high in summer (4.85 $km\ h^{-1}$). High and strong winds are dust raising in character. Average maximum temperature was recorded in the month of June (38.60°C) and average minimum, in the month of January (1.62°C).

The concentration of Pb, Zn, Mn, Ni, Cr and Co in the dust was compared with the concentration of these metals in soil of Peshawar. (Imdadullah *et al* 2001) reported the concentration ($mg\ kg^{-1}$) of Pb, Zn, Mn, Ni, Cr and Co in the soil of Peshawar to be 1.19, 17.39, 20.61, 5.71, 2.06 and 2.40 respectively. This suggests that heavy metals ultimately settle down on the earth as soil acts as a recipient of all types of wet and dry depositions from the atmosphere. Substantial amount of heavy metals is added to the soil through air. The elemental composition, pattern of distribution and possible sources of dust are not common to all urban environment, but vary according to the peculiarities of sites. However, for comparison the data on the concentration of heavy metals in dust of various other countries is presented in Table 4. It is observed that concentration of the studied metals are comparable to other countries. There are no significant differences in quantities of Zn, Mn, and Cr while Ni and Co are in much higher quantities as compared to other countries. In fact, dusts are very complex material. These are site specific. The variations are of great importance as they can give some ideas of the local factors which contribute to atmospheric dustfall.

Conclusion

Most of the roads in Peshawar are narrow with sides filled with mud. Fast moving vehicles when pass along them raise dust into the ambient air which remains suspended there for some time but ultimately settles on the ground. The waste material removed from sewerage line is usually piled up at the sides of the roads. Due to usual delay by the municipal authorities, in transportation of the sludge to dumping sites, there is persistent exposure of air to dried sludge. Heavy metal concentration in dust of Peshawar is comparable to the metal pollution in other countries. The major polluting sources of

Table 4

Some typical metal concentrations in dust samples in various countries mg g^{-1}

Country	Place/site	Pb	Zn	Ni	Cr	Mn	Co	Ref.
Pakistan	Peshawar	334-555 (425)	610-888 (763)	277-753 (372)	78-87 (83)	606-672 (637)	27-68 (55)	Present study
Saudi Arabia	Riyadh	66.8	141.8	26.0	-	319	20.6	Modiash, 1997
Bahrain	Various sites	290-1250 (697)	30-267 (151)	39-300 (125)	53-370 (144)	-	-	Madany *et al* 1990
U. K.	Lancaster	159-15000	160-3725	15-125	10-91	-	-	Schwar and Alexander 1988
Greece	Various sites	65-259	75-241	52		-	-	Yassoglou *et al* 1987
Nigeria	Various sites	40-243	12-48	1-3	23-26	-	-	Ndiokwere 1984
Netherlands	Near smelter	25-2667 (761)	05-16 (1.5)					Keizer *et al* 1982
Hong Kong	Play ground	302	1517	-	-	-	-	Wong and Mak 1997
New Zealand	Christ church	887-1070	-	-	-	-	-	Fergusson and Ryan 1984
Malaysia	Kualalumper	2466	344	-	-	-	-	Ramlan and Badri 1989
Kenya	Various sites	23-950	-	-	-	-	-	Onayri *et al* 1991
Taiwan	Taipei	196	-	-	-	-	-	Chan and Chu 1984
England	London	30-17900 (345)	-	-	-	-	-	Day *et al* 1975
Egypt	Various sites	56-1850 (126)	-	-	-	-	-	Ali and Nasrullah 1985
Canada	Halifax	674-1919	-	-	-	-	-	Fergusson 1987
Equador	Various sites	19-970 (108)	44-1018 (218)	-	-	-	-	Hewitt and Candy 1990
Kuwait	Salmich	132	-	-	-	-	-	Malik *et al* 1985
U.S.A.	Various sites	82-13800 (900)	-	-	-	-	-	Philip *et al* 1980

many trace metals are automobile, man-made activities, soil road dust, metallic corrosion, galvanized material, tire wear and zinc compounds in rubber materials and to a very small extent, industrial activities. The concentration of the studied metals at the four locations is almost the same. All the locations have the same climatic conditions.

References

Ali M A, Nasrullah M M 1985 Internl Conf Athens, Lekkas (ed) *CEP Consultants, Edinburgh* **2** pp 559-561.

Chakraborti D, Raeymaekers B 1988 Calcutta pollutants: Toxic metals in dust and characterization of aerosol particles. *Intern. J Environ Anal Chem* **32** 121-133.

Chan H H, Chu S S 1984 Chemical association of lead, cadmium, copper and zinc in street dusts of Taipei Taiwan. *J Chin Agri Chem Soc* **22**.

Choudhary M H Z, Tanisely D A 1998 Comparison of extractants for toxic metals in dust causing environmental pollution and their analysis in close and open system. *J Chem Soc Pak* **20**(4) 251-253.

Day J P, Hart M, Robinson N S 1975 Lead in urban street dust. *Nature* 253, 343.

De Miguel E, Llamas J E, Chacan E, Mazadiego L F 1999 Sources and pathways of trace elements in urban environment. *Sci Total Environ* **235**(1-3) 355-357.

Duggan M J, Williams S 1977 Lead in dust in city streets. *Sci Total Environ* **7** 91.

Faridullah K, Khan S A 1996 Investigation of heavy and toxic metal in dustfall of Islamabad (Pakistan) region. *Bangladesh J Sci Ind Res* (BJSIR) **31**(2) 107-115.

Faridullah K, Shakila B, Ghauri E J, Mushtaq A 2002 Air Pollution in Peshawar(Rate of dustfall). *Pak J Sci Ind Res* **45**(1) 1-6.

Fergusson J E, Ryan D E 1984 The chemical composition of street dust from large and small urban areas related to city type, source and particle size. *Sci Total Environ* **34** 101.

Fergusson J E 1987 Significance of the variability in analytical results for lead, copper, nickel and zinc in street dust. *Can J Chem* **34** 101.

Fergusson J E, Kim N D 1991 Trace elements in street and house dusts, sources and speciation. *Sci Total Environ* **100** 125.

Gelinas Y, Schmit J P 1998 Estimation of the bulk atmospheric deposition of major and trace elements to a rural watershed. *Atoms Environ* **32**(9) 1473-1483.

Harrison R M, Laxen D P H, Wilson S J 1981 Chemical association of lead, cadmium, copper and zinc in street dust and roadside soils. *Environ Sci & Technol* **15**(11) 1378-1383.

Hewitt C N, Candy G B B 1990 Soil and street dust heavy metal concentrations in and around Cuenca, Equador. *Environ Pollut* **63** 129.

Hussain F, Shah Z, Sher Z, Saljooqi 1994 Airborne particulates and their effects on roadside wild trees of Peshawar city. *Sarhad J Agri* **1**(1) 91-97.

Imdadullah M, Khan N, Jamal M, Khattak R A 2001 Heavy metals (Cu, Fe, Mn, Zn, Cd, Co, Ni, Mo, Cr and Pb) status in some selected soils of Peshawar and Nowshera districts. *J Chem Soc Pak* **23**(1) 23-30.

Keizer M G, Hoohiemstra-Tielbeek M, Beltann F A M 1982 Contamination of soil and street dust with lead and cadmium near a smelter at Arnhem, Netherlands. *Neth J Agri* Sci **29** 227.

Madany I M, Ali S M, Akhtar M S 1990 Trace metal analysis of sewage sludge and soils in Bahrain. *Environ Intl* **16** 123.

Malik S R, Atari N A, Al-Mishwat A T 1985 Uses of nuclear technique and SSNTDs in the studies of lead pollution in Kuwait. *Water, Air and Soil Pollut* **25** 15.

Meteorological Observation, *Agri Univ Peshawar* 1993-1998.

Modiash A S 1997 Characteristics and composition of the falling dust sediments on Riyadh City, Saudi Arabia. *J Arid Environ* **36**(2) 211-223.

Ndiokwere C L 1984 Trace element analysis of airborn particulate matter in relation to air pollution in Benin city, Nigeria. *Environ Pollut* (Series B) **8** 133.

Onayri J M, Wandiga S O, Njenga G K , Nyatebe J O 1991 Lead contamination in street soils of Nairobi city and Mombasa Island, Kenya. *Bull Environ Contam Toxicol* **46** 782.

Philip K Hopke, Lamb R E, Watusch D F S 1980 Multielemental characterization of urban road way dust. *Environ Sci & Technol* **14**(2) 164.

Ramlan M N, Badri M A 1989 Heavy metals in tropical city street dust and roadside soils: a case study of Kuala Lumpur, Malaysia. *Environ Technol Lett* **10** 435.

Robert A R TR-2. 1966 Air Pollution Measurement Committee. *J Air Pollut Control Assoc* **16**(7).

Schwar M J R, Alexander D J 1988 Redecoration of external leaded paintwork and lead in dust concentrations in school playgrounds. *Sci Total Environ* **68** 45.

Smirnioudi V P, Thomaidis N S, Piperaki E A, Siskos P A 1997 Determination of trace metals in wet and dust deposition in Greece. *Fresenius Environ Bull* **6**(5-6) 331-336.

Wong J W C, Mak N K 1997 Heavy metal pollution in children playgrounds in Hong Kong and its health implications. *Environ Technol* **18**(1) 109-115.

Yassoglou N, Kosmas C, Asimakopulos J, Kallianou C 1987 *Environ Pollut* **47** 293.

Yousafzai A H K 1991 Lead and the heavy metals in the street dust of Metropolitan city of Karachi. *Pak J Sci Ind Res* **34**(5) 167-172.

Yousafzai A H K, Rais D, Farooq A, Kamran D 2001 Heavy metal accumulation in roadside vegetation of urban area of Karachi. *Pak J Sci Ind Res* **44**(1) 29-32.

Zhang H, D Ma, Q Xie. Chen X 1999 An approach to studying heavy metal pollution caused by modern city development in Nanjing. *China Environ Geology* **38**(3) 223-228.