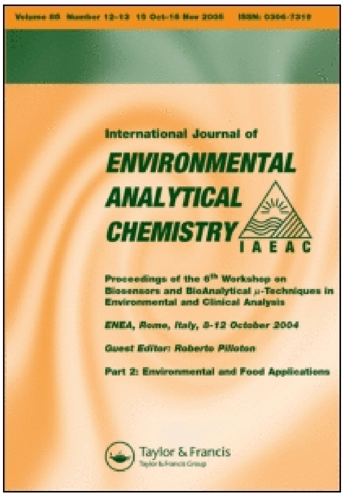

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Calcutta Pollutants: Part III. Toxic Metals in Dust and Characterisation of Individual Aerosol Particles

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Calcutta Pollutants:

Part III. Toxic Metals in Dust and Characterisation of Individual Aerosol Particles

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The concentration of eight heavy metals Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb on dust of street, household, restaurant, top of leaves and five soil samples of Calcutta city are measured by Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The available metals of dust samples in 0.07 N (HCl) are also measured by AAS. The Electron Probe Micro Analysis (EPMA) is also made to characterize individual aerosol particles collected on Nuclepore membrane filter.

KEY WORDS: Toxic metals, aerosol particles, street dust, leaves, soil, AAS, ICP-AES, Nuclepore filters.

INTRODUCTION

During the past decade considerable attention was devoted to low levels of environmental exposure to heavy metals mainly lead and cadmium and their possible implication to human health. Metal deposition in the body is assumed to be cumulative in nature, there

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are many routes by which metals may enter the body. Continuous inhalation of toxic compounds present in the atmospheric particles may cause chronic pulmonary diseases.[1–5] A common route by which metals may enter the body is in the ingestion of street dust[6,7] and household dust.[8] It has been reported[9] that for young children lead in dust carried to mouth by the hands or on objects sucked or placed in the mouth may contribute around half the total intake of the metals. It has been reported[7] that for city children a significant source of uptake of metals is from street dusts and children living in cities have high concentrations of toxic metals in their blood.[10,11]

In our earlier publications[12,13] we have discussed the environmental condition of city of Calcutta with respect to heavy metals and polyaromatic hydrocarbons (PAH) on aerosol particles in winter[12] and the concentration of a few toxic metals in sewage and sludge in use for fisheries and agriculture.[13] The concentration of metals and PAH found in air particulate during winter is high.[12] However the metal concentration in sewage and sludge is lower than in many other countries. The world health organisation (WHO) has reported[14] that Calcutta has the highest TSP value. Since the TSP value is very high in Calcutta, the dust deposition value should also be expected to be very high and since the significant uptake of metals may take place through dust, a study of heavy metals in dust is felt necessary.

In this present paper we will report a few toxic metals, Pb, Cd, Ni, Mn, Cr, Zn, Cu and Co concentration in dust of various origin from Calcutta city and also we will characterise the individual particles of aerosol collected on Nuclepore filter by a low volume sampler. The dust samples were analysed by two instrumental techniques: atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). To avoid matrix interference in AAS, specially for graphite furnace AAS a chelate extraction procedure as described for sewage sludge[13] was adopted.

An EPMA (electron probe microanalysis) study was made to characterise individual aerosol particles.

EXPERIMENTAL

Analysis of toxic metals in dust

Collection of dust Dust samples were collected from (a) streets, (b) houses, (c) restaurants and (d) top of leaves. Five soil samples were also collected at a depth of 15 cm below the surface. The places of collection were close to the sites used for collection of aerosol for X-ray fluorescence analysis of metals and polyaromatic hydrocarbon. These places were B.B.D.-Bag (BBDB), Park Street (PK), Gariahat (GH), Esplanade (ES) and Shyambazar (SB). The location and characteristics of these places were described elsewhere,[12] while collection of samples care was taken of flaking paints and direct metal contamination.

Street dusts were collected by gently sweeping the street by a brush until sufficient samples had been collected. The dust was then swept into a dust pan and transferred to a polyethylene bag. Household dusts, dusts from restaurant and from top of leaves were collected by a soft-brush. Samples were dried at 80 °C for 24 hours and sieved to exclude material larger than 30 mesh. They were then kept in a desiccator before weighing.

Determination of "total" metal

Samples of dust and soils (1–2 gms) were digested with concentrated nitric/hydrochloric acid as described in our sewage sludge treatment.[13] Harrison *et al.*[15] Duggan *et al.*[7] also used this acid mixture for dust analysis. In certification of heavy metal contents in soil, aquaregia treatment has also been reported by the Commission of European Community.[16] After making the final solution to a volume (50 ml) with dilute hydrochloric acid, an aliquot was extracted by the chelating agent (a mixture of APDC and Na.DDTC). The detail about the instrumentation and the whole procedure for determination was described in our earlier publication.[13] Cobalt, lead, manganese, nickel and cadmium were determined by graphite furnace AAS and zinc and copper by flame AAS. These elements along with chromium were also analysed by ICP-AES. Chromium was determined directly by ICP-AES only, since the chelate extraction procedure was not found suitable. The blank was measured under the identical condition.

Determination of "available" metal

About 1.0 gm of dust was extracted with 0.07 N hydrochloric acid according to the method described in Pencils & Graphic Instruments (safety) Regulations.[17] The extracted metals were determined by only AAS as described for total metal.

Analysis of standard sediment sample NBS(1645)

Since we could not get a standard reference dust sample, we have analysed a standard sediment to judge the suitability of our dissolution procedure by HNO_3/HCl.

RESULTS AND DISCUSSION

The concentration of the total and available metal in various dust samples are presented in Table 1. The importance of study of available metal was reported by Duggan and Williams.[7] By the term "available" metal they meant the metal which is soluble in hydrochloric acid at the concentration existing in the stomach and which is hence mobile and available for adsorption into the blood stream.

Table 2 presents the analysis of the standard sediment sample (NBS-1645) under identical condition the dust and soil samples were treated and analysed. The results show that the recovery is about 25% lower for chromium and 10–15% lower for Cd, Pb, Ni, Cu, Zn and Mn. Thus our results may be 25% underestimated for chromium and 10–15% for other metals. This HNO_3/HCl procedure was adopted for more simplicity and also suggested by several other workers for dust and soil samples.[7,15,16]

The results from Table 1 shows that the studied heavy metals concentration in the dust are higher when compared to the soil of the same region. In all the samples analysed the ratio of total extractable are within the range 1.1–2.2. The higher lead concentration in street dust is expected due to added alkyllead compounds to gasoline which is the major cause of lead in the environment.

Zinc and cadmium concentration in street dust may be due to fragmentation of car tyres. Shaheen[18] pointed out that one of the main causes of higher concentration of metal in street dust is the wear and tear of motor vehicles.

Table 3 presents a comparative data of heavy metals on Calcutta street dust and household dust with the London and Lancaster,

Table 1 Concentrations of total and extractable metals by AAS and ICP-AES in various dust and soil samples ($\mu g\ gm$)[a]

Metals		*Street dust*				*Household dust*				*Restaurant dust*				*Dust on leaves*				*Soil*			
		No	*Range*	*Mean*	*S.D.*	*No.*	*Range*	*Mean*	*S.D.*	*No.*	*Range*	*Mean*	*S.D.*	*No.*	*Range*	*Mean*	*S.D.*	*No.*	*Range*	*Mean*	*S.D.*
Cr	Total	5	(60–180)	(130)	(28)	10	(40–160)	(110)	(19)	5	(31–148)	(96)	(17)	4	(33–160)	(101)	(18)	5	(19–67)	(41)	(16)
Mn	Total	5	(460–1130)	(660)	(310)	10	(248–656)	(503)	(140)	5	(270–798)	(585)	(180)	4	(460–570)	(494)	(40)				
		5	520–1320	700	351	10	270–855	581	210	5	340–980	668	260	4	520–627	574	45	5	(120–514)	(368)	(151)
	Extractable	5	330–840	488	140	10	185–590	360	83	5	180–520	390	107	4	270–380	310	18				
Co	Total	5	(8–22)	(13)	(4)	10	(7–14)	(10)	(3)	5	(7–18)	(13)	(4)	4	(8–17)	(12)	(3)				
		5	11–27	18	6	10	10–18	13	3	5	9–22	15	5	4	10–19	15	3	5	(7–11)	(9.0)	(2)
	Extractable	5	4–11	8	2	10	5–9	7	2	5	3–9	7	2	4	2–8	5	2				
Ni	Total	5	(39–74)	(52)	(22)	10	(41–71)	(56)	(14)	5	(37–89)	(69)	(21)	4	(51–69)	(59)	(8)				
		5	26–68	48	20	10	30–60	45	12	5	27–82	58	23	4	43–60	51	7	5	(30–44)	(36)	(6)
	Extractable	5	19–48	31	12	10	19–38	31	7	5	11–33	21	7	4	13–33	22	5				
Cu	Total	5	(183–320)	(239)	(44)	10	(173–268)	(209)	(24)	5	(210–370)	(304)	35	4	(206–280)	(248)	(30)				
		5	210–380	267	59	10	190–286	235	30	5	230–400	338	69	4	255–300	258	35	5	(46–188)	(81)	(61)
	Extractable	5	160–360	188	40	10	110–196	177	26	5	180–270	219	19	4	160–240	186	13				
Zn	Total	5	(490–1130)	(870)	(181)	10	(520–1100)	(906)	(96)	5	(820–2016)	(1121)	(392)	4	(440–1070)	(820)	(154)				
		5	560–1320	910	203	10	593–1212	1003	161	5	980–2360	1394	566	4	480–1160	860	163	5	(122–550)	(230)	(180)
	Extractable	5	380–870	670	(160)	10	470–1011	800	69	5	780–1896	1094	360	4	398–290	710	147				
Cd	Total	5	(10–30)	(13)	(8)	10	(7–23)	(11)	(7)	5	(12–22)	(11)	6	4	(8–16)	(11)	(4)				
		5	8–24	11	7	10	5–18	9	6	5	6–17	9	5	4	7–11	8	23	5	(4–6)	(5)	(0.5)
	Extractable	5	3–13	8	4	10	2–8	6	2	5	3–8	6	2	4	2–6	4	1				
Pb	Total	5	(1210–3063)	(1936)	(610)	10	(490–1060)	(870)	(130)	5	(930–1740)	(1400)	(290)	4	(670–1020)	(830)	(139)				
		5	1360–3280	2086	752	10	580–1120	960	170	5	1124–1990	1600	360	4	724–1123	928	170	5	(30–310)	(267)	(44)
	Extractable	5	840–1980	1340	320	10	302–660	510	70	5	601–980	760	110	4	300–610	480	69				

[a]The ICP-AES results are in brackets and AAS results without bracket. Hydrochloric (0.07 N) extractable results are from AAS only. Soil samples were measured by ICP-AES and for total only.

Table 2 Analysis of NBS standard sediment no. 1645[a] (μg/gm)

No *NBS* *1645*	*Cr*	*Mn*	*Co*	*Ni*	*Cu*	*Zn*	*Cd*	*Pb*
NBS	2.96±0.28	785±97	n.a.	45.8±2.9	109±19	1720±169	10.2±1.5	714±28
Ours	—	703±82	10.6±1.2	40±2.6	96±13	1599±149	8.6±1.3	610±19
	(2.08±0.17)	(690±76)	(9.9±0.9)	(42±2.5)	(94±11)	(1562±130)	(8.7±1.4)	(599±17)

[a]Results without bracket is by AAS and results with bracket is by ICP-AES. Chromium result is in %.

Table 3 Comparison of the results of total metals in street and household dust of Calcutta with London and Lancaster (UK) (conc. μg/gm)

Metals	*Mean Value*											
	Street dust						*Household dust*					
	No. of samples	*Calcutta*	*No. of samples*	*London*	*No. of samples*	*Lancaster*	*No. of samples*	*Calcutta*	*No. of samples*	*London*	*No. of samples*	*Lancaster*
Cr	5	130	—	—	13	29	10	110	—	—	4	31
Mn	5	680	—	—	—	—	10	542	—	—	—	—
Co	5	15	—	—	13	9.1	10	10	—	—	4	8.5
Ni	5	50	—	—	13	35	10	50	—	—	4	43
Cu	5	253	65	115	13	143	10	224	683	208	4	221
Zn	5	890	65	513	13	534	10	954	683	1324	3	1170
Cd	5	12	65	4.0	13	4.6	10	10	683	7.7	4	10.7
Pb	5	2011	65	1354	13	1880	10	915	683	1007	4	716

UK.[19] The higher concentration of Calcutta is observed in this comparative study. We have made a limited study and only few samples of each kind and mainly close to the main street. A thorough study should be made to know the actual impact of the heavy metals to the people of Calcutta.

Electron probe microanalysis of individual particles

Sampling and sample preparation For electron probe microanalysis (EPMA) of individual particles, the air particulates were collected with a low volume sampler at a flow rate of about 5.0 1/min and about 1.5 m above the ground. Particles were collected on polycarbonate membrane filter (Nuclepore Corporation, California) with 0.45 μm pore size and 47 mm diameter. A filter holder from Schleicher and Schüll, Dassel, West Germany was used. Approximately 1 m^3 of air was sampled on each filter during almost peak traffic hours from 8 a.m.–12 noon and from 4 p.m. to 8.0 p.m. The places of collection were BBD-Bag (BBDB), Park Street (PK), Gariahat (GH), Esplanade (ES) and Shyambazar (SB).

From the loaded Nuclepore filter, an area of 1 cm^2 was cut, which was immersed in a cuvet containing 4.0 ml *n*-hexane under ultrasonic agitation. The particles were removed from the filter and brought into suspension. After one minute of ultrasonic treatment, the filter piece was removed and the suspension was immediately filtered on a 0.45 μm Nuclepore filter, which was dried afterwards with clean air in a laminair flow hood. Next, the filter was mounted on a plane polythene slab with a double face scotch tape. To prevent electrostatic charging under the electron beam, the filter surface was coated with a carbon layer of 40 nm thickness.

EXPERIMENTAL

The automated electron probe characterization of the aerosol particles was performed with a JEOL JXCA 733 Superprobe, which is equipped with a Tracor Northern TN2000 periphery controlled by an LSI 11/23 computer. The I/O devices are a TN4000 colour display and a line printer. Data can be stored on diskette or on magnetic tape. A TN1310 interfaces the computer system and the controls of electron beam sample stage movements on the electron probe.

Automated measurements were performed with an electron energy of 25 KeV and a beam current of 1 nA. For each particle X-rays were collected for 20 s, implying a detection limit of 1% for most K peaks in the X-ray spectrum, when the continuum background intensity was subtracted. During the analysis, the image magnification was 1000 ×, limiting the size of the smallest detectable particle to 0.2 μm.

After analysis, the totality of collected data was transferred to a VAX 11/780 computer where a qualitative analysis allows to assign elements to the detected peaks. A data matrix, containing n samples described by m variables then represents the results of the analysis. By application of a standardless ZAF-correction,[20] modified for particle effects,[21] X-ray intensities were converted into elemental concentrations.

Further data analysis can be performed by the DPP software (Data Processing Package),[22] including unvariate statistics, different clustering algorithms principal component analysis and other data handling facilities.

RESULTS AND DISCUSSION

Since the sample preparation for the five samples was carried out in an identical way, the loading on the analyzed Nuclepore filters is a relative measure for the particle concentration in the sampled air. No severe differences in filter loading occurred, as shown in Table 4, but the ESP and SB sample show the highest loadings. At these filter loadings, the mean distance between the particles on the filter varied between 20 and 40 μm. In these conditions, there was practically no particle agglomeration so that indeed single particles were analyzed.

The distribution of the equivalent diameters for all the analysed particles show maxima in the submicron range, with a long tail toward larger diameters (Figure 1). The size distributions of aerosol particles sampled in urban environments, described by Post *et al.*[23] (Phoenix aerosol, USA) or by Bloch *et al.*[24] (Antwerp aerosol, Belgium) show the same typical shape as those from our measurements.

Table 4 shows the lists of detected elements in each sample;

Table 4 List of detected elements on each sample

Sample	*Number of analysed particles*	*Number of particles mm^2 of filter*	*Detected elements*
BBDB	852	716	Na, Mg, Al, Si, P, S, Cl, Ca, Ti, Cr, Ni, Mn, Fe, Cu, Zn, Ba, Pb
PK	852	591	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb
GH	800	916	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Fe, Cu, Zn, Pb
ES	852	1273	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Ba, Pb
SB	852	1312	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Ni, Mn, Fe, Cu, Zn, Pb

between 14 and 17 different elements occur, with an elemental concentration higher than 1%.

The mean composition of the particles for the principal elements was calculated for the size classes: 0–0.5, 0.5–1, 1–2, 2–3, 3–4, $5 < \mu$m. The results are plotted in Figure 2.

The largest part of the particles contains silicates or alumino silicates. They originate from wind blown soil dust or were released from coal burning processes as fly ash particles. Some particle types were found such as Ca, Fe, containing particles with small amounts of Ti, Ba or Zn and with a diameter larger than 5 μm. These particle types were also reported by Mattigod[25] who ascribed them to fly ash particles from US sub-bithuminous coal.

In the silicate group, quartz like particles represent between 9 and 16% of the analysed particles. They sometimes contain elements as Al, K, Ca, Ti or Cr. About 50% of all the particles are alumino-silicates of K, Ca or Fe while all have a comparable diameter. Remarkable is that sulfur containing silicates have a higher mean diameter than the silicates without sulfur. This can be explained by a sulfate layer on the surface of these particles. Indeed, most particles belonging to this particle type besides of the silicate component contain comparable amount of Ca and S. On the filters were also found very small particles with a pure sulfur spectrum. Due to their

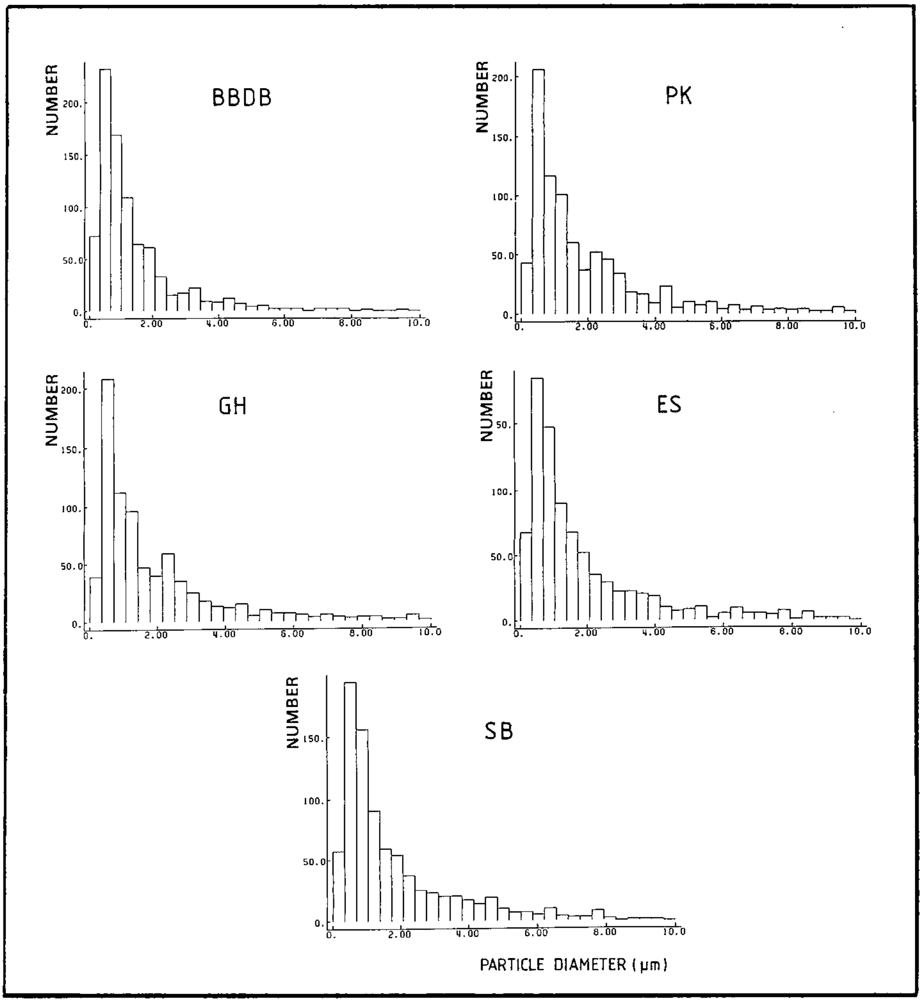

Figure 1 Distribution of the equivalent diameter of particles analyses on Nuclepore filter.

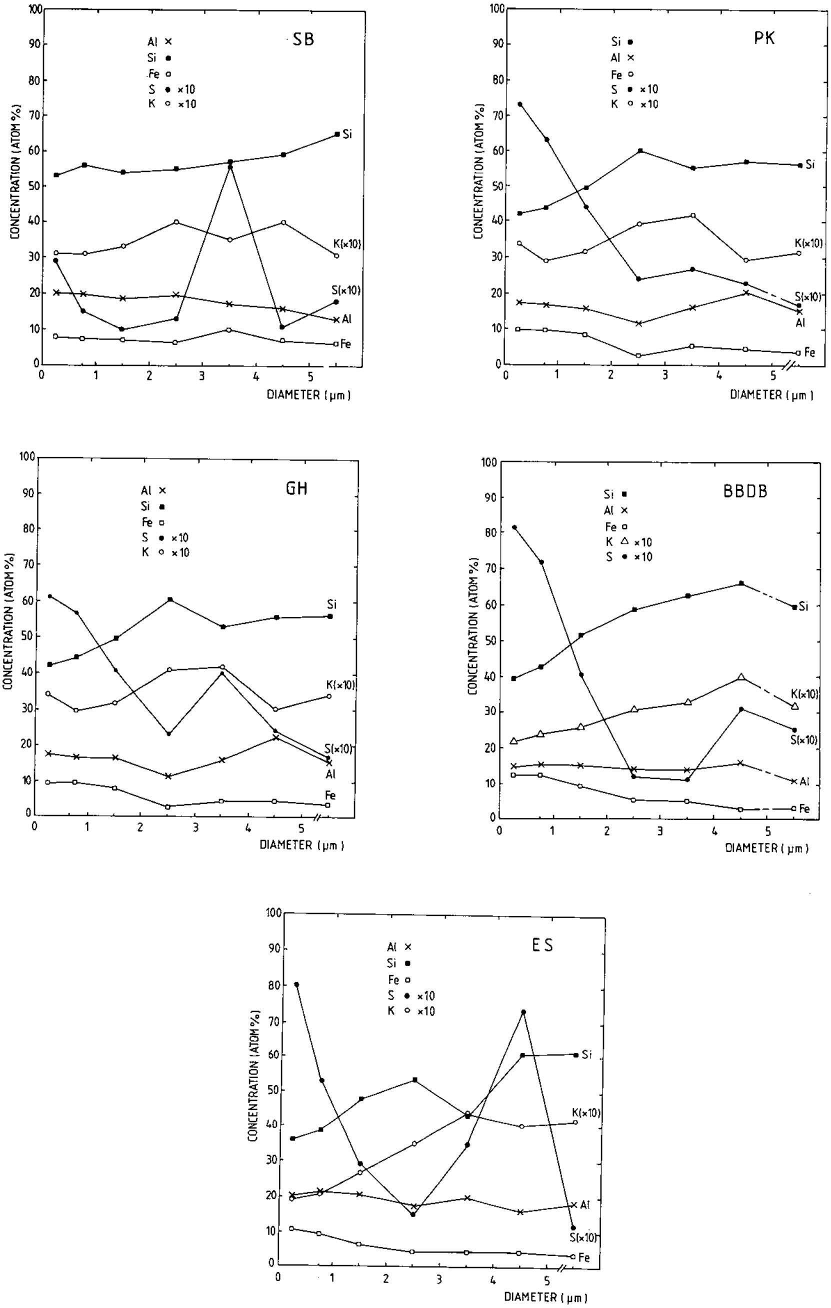

Figure 2 The mean composition of the particles for the principal elements.

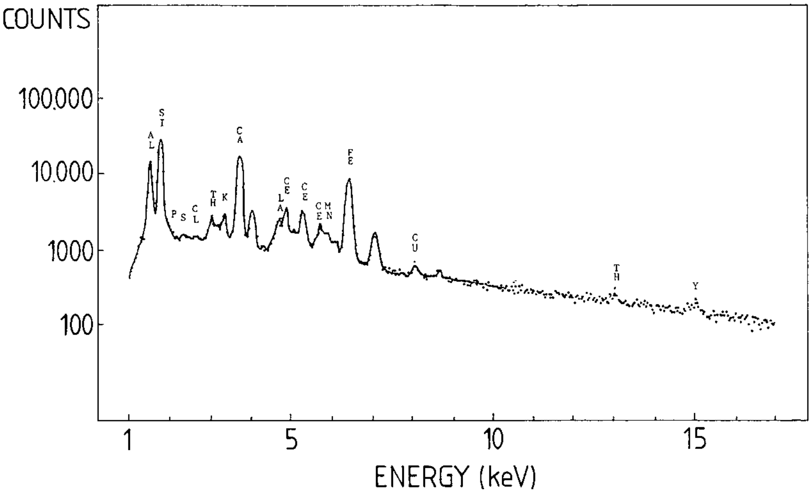

Figure 3 Typical spectrum of a particle showing the presence of Sr, Zr, Ta, Sn, Ce, La, Y and Th.

low thickness, they were not automatically detected during analysis. Only a few of these particles were counted in the submicron range. They contain most probably $(NH_4)_2SO_4$.

The diameter of heavy metal containing particles usually fall, in the submicron range. Besides pure Cr, Cu, Zn or Pb particles also quartz and alumino silicates contain these metals. This again is an indication for the presence of fly ash particles, since these metals were found to be present in fly ash with decreasing concentration with the particle diameter as was reported by Fisher *et al.*[26]

A few particle types showed the presence of Sr, Zr, Ta, Sn, Ce, La, Y and Th. A typical spectrum is shown in Figure 3. Only a few of them were found on the entire Nuclepore filter by inspection of the filter using the back scattered electron image. This image mode on the SEM allows to localize particles containing high atomic number elements among thousands of other particles.

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