

Atmospheric Deposition of Metals Associated with Air Particulate Matter: Fractionation of Particulate-Bound Metals Using Continuous-Flow Sequential Extraction

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ABSTRACT: The fractionation and elemental association of some heavy metals in air particulate matter from two different sources, a smelter and heavy vehicle traffic, were investigated using a continuous-flow sequential extraction procedure. Air particulate matter (a combination of wet and dry deposition) was collected monthly for one year and was analyzed by a four-step continuous-flow sequential extraction procedure employing a modified Tessier scheme. Examination of crustal enrichment factors (EF_{crust}) suggested that the Cd, Zn and Pb in the air particulate matter were predominantly of anthropogenic origin. Total Pb deposition in the dry season was found to be higher than that in the wet season, and may be attributed to soil dust. However, the fractional distribution of metals between forms did not differ between seasons. The results showed that the reducible phase (Fe/Mn oxides) was the largest fraction of Pb in air particulate matter from both the smelter and heavy traffic sites. The overlain metal extraction profiles demonstrated a close elemental association between Al and Pb in the acid-soluble phase of air particulate matter. In the reducible fraction, Pb was found to dissolve earlier than Fe indicating that Pb could occur adsorbed onto Fe oxide surfaces in the air particulate matter.

KEYWORDS: air particulate matter, continuous-flow sequential extraction, enrichment factor.

INTRODUCTION

Air particulate matter, together with associated metal contaminants, can be formed as the result of both natural and anthropogenic processes. Typical natural sources are the sea, giving rise to saline particles, or wind-blown dust derived from the land. Human activity produces air particulate matter as a result of industrial activities, traffic emissions and combustion processes. In particular, mining and smelting activities are important sources of heavy metals in the environment. For example, lead smelters are one of the most important sources of Pb pollution in the environment. Another source of Pb, still important in some countries, is the combustion of leaded gasoline. Lead is a toxic element and is dangerous to human health even at relatively low levels. Knowledge of the bulk concentrations of metal contaminants is essential for an assessment of ecosystem risk. Lead contamination in the vicinity of smelters is mainly airborne and represents a long-term pollution effect on the environment.

Environmental risk assessment of metals associated with air particulates has usually been based on the total

concentrations of the metals. This can provide information on the degree of contamination, however, the mobility of metals in the environment depends not only on their total concentration but also on the associations and forms present in the solid phase by which they are bound. These forms include the following broad categories: soluble; exchangeable; carbonate-bound; Fe and Mn oxide-bound; organic matter-bound and residual¹. Understanding the mode of occurrence of metals in air particulates is essential for the environmental assessment of this form of contamination.

One approach to the study of the distribution of metals among these physicochemical phases is the use of phase-selective chemical extractions involving multiple extracting reagents². The reagents employed in sequential extractions have been chosen on the basis of their selectivity and specificity towards particular physicochemical forms. Sequential extraction techniques are widely used to fractionate metals in solid samples on the basis of the leachability/extractability of different metal forms^{3,4}.

In our previous work, a continuous-flow extraction system has been developed to perform chemical

speciation by sequential extraction of both metals⁵ and nonmetals⁶ in solid materials. Compared with batch extraction systems, the procedure is rapid, has less risk of contamination, has the possibility of further automation, and is easy to perform. The system has also been found to have less problems of readsorption due to the shorter extraction times required⁷. In addition, the extractogram (a graphical plot of concentration versus extraction volume) offers additional information about chemical association of metals in the solid phases.

This study aims to investigate the use of a continuous-flow sequential extraction system to determine the fractionation of metals in air particulate matter. Another objective was to use the extractograms obtained from the dynamic extraction system for interpretation of elemental associations in the various air particulate fractions. Results obtained from this work should improve our understanding of the forms and elemental associations of metals in air particulate matter.

MATERIALS AND METHODS

Sampling Sites

The study sites are an area surrounding a small lead smelter located in Saraburi province, approximately 110 km north of Bangkok, Thailand and a heavy traffic area in central Bangkok, Thailand. The smelter has been operating for the last 10 years and its main activity is to recycle lead from old batteries. The criterion for the location of monitoring stations of air particulate matter was that each site should be clear of shelter from the wind and not overhung by electricity cables or tall trees. For sampling at the lead smelter site, three sampling locations were chosen at distances of 2 km, 1 km and 300 m from the smelter. The site in central Bangkok was located in one of the busiest traffic junctions (near Victory Monument). At each site, atmospheric deposition of particulates and metals was monitored for a period of one year. At all sites, duplicate samplers were installed within 20 m of each other.

Design of Air Particulate Collectors

Passive air particulate collectors provide a relatively simple method for monitoring dust particles deposited by both dry and wet deposition. The plastic cones used as collectors were constructed from polyethylene funnels and were 25 cm in diameter with an internal depth of 12.5 cm. The edges of the plastic funnels were cut in a zigzag shape to discourage birds from perching and thus minimize contamination from bird excreta (Fig. 1). At each monitoring site, the plastic funnels were mounted on posts 1.6-1.8 m above ground level to avoid contamination by saltating soil particles. The tubing connecting the plastic funnels to the receiving bottles, and the bottles themselves, were shielded with

black plastic sheeting to prevent algal growth. Rainfall and particles passively deposited into the plastic funnel were collected in a 4-L bottle which was replaced monthly. A known volume of high purity water was used to flush particles out of the plastic funnel down the tube into the bottle at the time of sample collection. After collection and transport to the laboratory, samples were filtered through a glass microfibre filter (Whatman GF/B (Maidstone, UK), 47 mm diameter, 1 micron particle retention) and the sample volume determined. The pH of the samples was also measured. The particulate matter retained on the filter was then subjected to continuous flow extraction, and the filtered solutions containing soluble constituents were analysed separately.

The volume of samples for wet season months (June-October) was quite consistent at approximately 3 L, and in dry season months at approximately 0.1 L. Air particulates in August were chosen to represent the wet season, and air particulates in March, the dry season. These two months were selected because they are in the middle of the wet and dry seasons, respectively, and less likely to be affected by instability of changing weather.

Chemicals and Apparatus

All chemicals used were of analytical grade. Multi-



Fig 1. The photograph of an air particulate collector.

element stock solution for ICP-MS (AccuStandard, Inc. CT, USA) was used for the preparation of standard solutions. An inductively coupled plasma quadrupole mass spectrometer (ICP-QMS, Perkin Elmer ELAN 6000) was used for the elemental determination of air particulate extracts.

Fractionation Scheme

A modified Tessier sequential extraction scheme² was carried out using the following solutions:

Step 1 (F1): 0.01 M $\text{Mg}(\text{NO}_3)_2$ (exchangeable fraction)

Step 2 (F2): 0.11 M CH_3COOH (acid soluble fraction; carbonate or specifically sorbed)

Step 3 (F3): 0.01 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ adjusted to pH 2 with HNO_3 , 85°C (reducible fraction; Fe/Al/Mn oxide-bound)

Step 4 (F4): 8:3 v/v (30% H_2O_2 :0.02 M HNO_3), 75°C (oxidizable fraction; organic-bound)

Step 5 (F5): Aqua Regia (residue fraction)

Continuous-Flow Extraction System

Extraction Chamber

An extraction chamber was designed to allow containment and stirring of air particulate samples. Extractants could flow sequentially through the chamber and leach metals from the targeted phases. The chambers and their covers were constructed from borosilicate glass to have a capacity of approximately 10 mL. The outlet of the chamber was furnished with a glass microfibre filter GF/B (47 mm diameter, 1 μm particle retention, Whatman, Maidstone, UK) to allow dissolved matter to flow through. Extractant was pumped through the chamber using a peristaltic pump (Micro tube pump, MP-3N, EYELA, Tokyo Rikakikai Co. Ltd.) at varying flow rates using tygon tubing. Heating of the extractant in steps 3 and 4 was carried out by passing the extractant through a glass heating coil approximately 120 cm in length, which was placed in a water bath. The flow extraction setup is shown in Fig. 2.

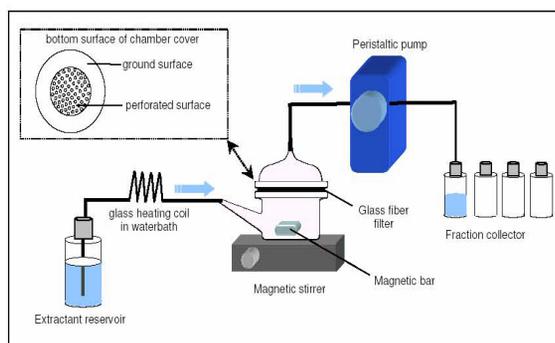


Fig 2. The set-up of the continuous-flow extraction system.

Extraction Procedure

Since it was impossible to remove air particulate matter from the filters collected from the samplers without loss of material, the whole central portion of the filter through which the solution had passed was cut from the filter and transferred to a clean extraction chamber. Following addition of a magnetic bar, a glass microfibre filter was then placed on the outlet followed by a silicone rubber gasket, and the chamber cover was securely clamped in position. The chamber was connected to the extractant reservoir and the collector vial using tygon tubing and placed on a magnetic stirrer. The magnetic stirrer and peristaltic pump were switched on to start the extraction. The extracting reagents continuously flowed through the chamber to effect sequential extraction. The extract passing the membrane filter was collected at 30 mL volume intervals to obtain six subfractions for each extractant. Extraction was carried out until all four extraction steps were completed. Elemental concentrations in extracts were determined by ICP-QMS.

Dissolution of Residues

A closed-vessel microwave digestion system (Milestone model MLS-1200 Mega, Bergamo, Italy) was used for pseudo-total digestion of air particulate matter residues. Residues from the extraction chamber were transferred to the digestion vessels together with concentrated HNO_3 (4 mL) and 37% HCl (2 mL). The vessel was then tightly sealed and subjected to microwave digestion. After cooling, the digested solutions were made up to volume in volumetric flasks before ICP-QMS measurements. The total amounts of metals associated with the particles were determined by summation of metals in exchangeable, acid soluble, reducible, oxidizable and residual fractions.

Quality Control

Analytical quality assurance was addressed by undertaking duplicate analysis of all extracted solutions. Blank analysis was performed frequently and every time a change of reagents or materials was used.

RESULTS AND DISCUSSION

Total Metal Deposition and Enrichment Factors

The samples were obtained in this study using sample collectors modified from Gray et al.⁸ as described in section 2.2. The material collected would have resulted from a combination of both wet and dry deposition processes. Total metal deposition was calculated from a combination of the amounts of soluble metals, as determined in the original sample filtrates, and the amounts of metals determined in the various particulate matter fractions. At each sampling, at all

four sites, solution and air particulate samples from both duplicate samplers were analyzed. The volume and pH of the rainwater harvested by the samplers, together with total metal depositions (solution plus particulate) are shown in Table 1.

In the dry season, harvested rainwater ranged from 1.6 to 13.2 mm month⁻¹, and from 52 to 70 mm month⁻¹ in the wet season. The rainwater pH was around 8 in the wet season and varied from 4 to 7 in the dry season. The higher pH of rainwater harvested in the wet season was attributed to activities including biomass burning which produces oxides of Ca, Mg and K to neutralize the acidity of rainwater. In the wet and dry seasons, photochemical processes, driven by sunlight presumably cause oxidation of SO₂ and NO_x to give acidic rainwater⁹.

Pb, Cd and Zn are the most common toxic metal contaminants in air particulates because they appear in gasoline, car components, oil lubricants and are widely used in industry. Sources of metal contamination in air particulates have been reviewed¹⁰. Table 1 shows that the concentration of Pb in air particulate matter adjacent to the lead smelter area (L1) is distinctly elevated and decreases with distance from the smelter in both dry and wet seasons, implicating the lead smelter as the point source of contamination. The highest Zn content was obtained at sampling site L4, most likely originating from traffic-related sources (vehicle tyres).

Total Pb depositions at locations L1 and L2 were substantially higher in the dry compared with the wet season, in spite of the much higher rainfall in the latter. This may be related to a greater deposition of wind-blown dust material in the dry season. Nriagu¹¹ has indicated that wind-blown dusts are a major source of Pb emissions worldwide.

Trace metals in aerosols are derived from a variety of sources including the earth's crust, the oceans, the biosphere, and a number of anthropogenic processes. The degree to which a trace metal in an aerosol is enriched, or depleted, relative to a specific source can be assessed to a first approximation using an enrichment factor (EF_{crust})¹². The enrichment factor

(EF_{crust}) of an element in an aerosol sample is defined as

$$EF_{crust} = \left(\frac{(C_{xatm}/C_{Alatm})}{(C_{xcrust}/C_{Alcrust})} \right)$$

where (C_{xatm}) and (C_{Alatm}) are the concentrations of the atmospheric trace metal and Al, respectively, and (C_{xcrust}) and (C_{Alcrust}) are their concentrations in average crustal material. The enrichment factor (EF_{crust}) was determined in this study based on the total depositions of trace elements and Al relative to their average crustal concentrations as reported by Mason and Moore¹³.

As an approximate guide, values of EF_{crust} lower than 10 (in effect 10 times the level of samples with no enrichment) are believed to have originated from normal weathering of crustal material. Values of EF_{crust} larger than about 10¹ are referred to as enriched elements and may have some sources other than crustal weathering, possibly anthropogenic. The higher the value of EF_{crust}, the more likely that an anthropogenic source is involved.

The high enrichment factors (10¹ – 10³) for Pb, Cd and Zn suggest a substantial anthropogenic input for these three metals. Not only the lead smelter, but also vehicular exhaust emission was a major source of Pb contamination. Pb is still persistent in road dust from earlier vehicular exhaust emission before leaded gasoline was banned, because of its long residence time in the environment¹⁴. Similar to earlier reports^{10,15}, particulate Zn in ambient air probably has its origin from automobile sources, i.e., wear and tear of vulcanized rubber tyres, lubricating oil and corrosion of galvanized vehicular parts. Cadmium is being emitted mainly from industrial activities and industrial and domestic wastes related with paints and batteries. In contrast, iron (Fe) shows no enrichment (EF_{crust} ≈ 1) and EF_{crust} for Al by definition is 1.0. The metals Pb, Cd and Zn are all relatively volatile metals, and because they are readily transported in air, have been referred to as atmosphere elements¹⁶. Previous studies have reported the accumulation of Pb and Cd in the soil

Table 1. Rainwater volumes, pH and total metal depositions (g ha⁻¹ month⁻¹) for representative dry and wet season months (n=2).

Location	Rainfall		pH of		Pb		Cd		Zn	
	(mm month ⁻¹)		rainfall							
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
L1	1.6	52.0	8.04	7.25	78.51 ± 64.50	10.26 ± 7.25	0.41 ± 0.33	0.91 ± 0.00	106.2 ± 34.92	116.7 ± 33.73
L2	2.0	65.2	8.51	7.57	8.25 ± 1.83	0.92 ± 0.083	1.25 ± 0.17	0.34 ± 0.17	71.3 ± 36.25	70.9 ± 5.83
L3	2.2	67.8	8.06	6.14	0.22 ± 0.008	0.26 ± 0.092	1.16 ± 0.00	0.33 ± 0.25	54.0 ± 22.33	52.4 ± 9.20
L4	13.2	70.3	8.34	4.59	2.84 ± 0.33	2.42 ± 1.04	1.42 ± 0.33	0.17 ± 0.00	110.2 ± 25.00	233.3 ± 51.53

L1, L2, L3: 0.3, 1 and 2 km from lead smelter, respectively.
L4: Heavy traffic area.

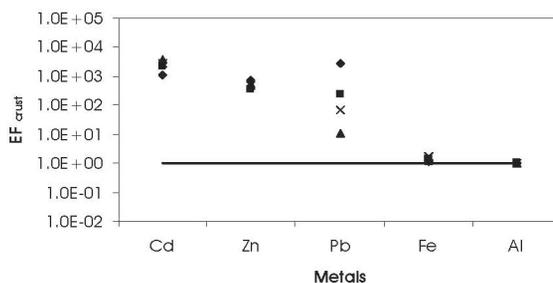
surrounding the smelter^{17,18}.

Fractionation of Metals in Air Particulate Samples

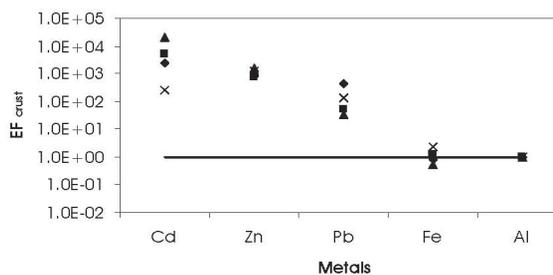
For Pb and Zn, concentrations of these metals in the filtered solutions obtained from the air samplers were all below detection limits, i.e. all of the Pb and Zn were associated with the air particulate matter. In the case of Cd, for three samples (L2 and L3 wet season, L4 dry season) some Cd was detected in the water-soluble fraction, equivalent to depositions of between 0.42 and 1.24 g Cd ha⁻¹ month⁻¹, and accounting for between 23 and 84% of the total Cd deposition for those samples. For the other samples, all of the Cd was associated with the air particulate matter.

Information on the fractionation of metals in air particulate matter is essential for considering their mobility, mechanisms of transformation and also their environmental risk. The fractionation of Pb, Cd and Zn in air particulate matter has been studied previously using sequential extraction procedures^{1,19,20}. These studies found that Pb was strongly associated with carbonate and Fe-Mn oxide phases.

Metal fractionation data for the four sites is shown in Table 2. However, it should be noted that for sites L2 and L3 in particular, the concentrations of metals in several fractions were close to the detection limits. The samples from the most contaminated sites (L1 and L4) provide the most complete sets of data. For these sites,



(a) Dry season



(b) Wet season

- ◆ L1: 300 m from lead smelter
- ▲ L3: 2 km from lead smelter
- L2: 1 km from lead smelter
- × L4: heavy traffic area
- no enrichment factor

Fig 3. Mean EF_{crust} values for metals (Pb, Cd, Zn, Fe and Al) deposited at different sites (L1-L4).

Table 2. Fractional distribution of metals in representative air particulate matter from dry and wet seasons as determined using a continuous-flow sequential extraction procedure.

Fraction	Metal deposition in air particulate fractions (g ha ⁻¹ month ⁻¹)							
	L1		L2		L3		L4	
	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Lead								
F1	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)
F2	5.25 ± 4.50	0.42 ± 0.25	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)	0.50 ± 0.00	ND (<0.04)
F3	61.92 ± 61.50	6.25 ± 8.08	ND (<0.16)	ND (<0.16)	ND (<0.16)	ND (<0.16)	1.67 ± 0.17	1.25 ± 0.33
F4	9.67 ± 2.75	1.42 ± 2.00	6.75 ± 2.17	ND (<0.04)	ND (<0.04)	ND (<0.04)	ND (<0.04)	0.17 ± 0.17
F5	1.67 ± 1.17	2.17 ± 0.92	1.50 ± 0.33	0.92 ± 0.083	0.22 ± 0.008	0.26 ± 0.092	0.67 ± 0.17	1.00 ± 0.08
Sum	78.51 ± 64.50	10.26 ± 7.25	8.25 ± 1.83	0.92 ± 0.083	0.22 ± 0.008	0.26 ± 0.092	2.84 ± 0.33	2.42 ± 1.04
Cadmium								
F1	ND (<0.01)	ND (<0.01)	ND (<0.01)	ND (<0.01)	ND (<0.01)	ND (<0.01)	ND (<0.01)	ND (<0.01)
F2	0.33 ± 0.33	0.83 ± 0.08	ND (<0.0003)	ND (<0.0003)	ND (<0.0003)	ND (<0.0003)	1.25 ± 0.08	ND (<0.0003)
F3	ND (<0.002)	ND (<0.002)	1.08 ± 0.17	0.17 ± 0.17	1.08 ± 0.08	0.33 ± 0.25	ND (<0.002)	ND (<0.002)
F4	ND (<0.001)	ND (<0.001)	ND (<0.001)	ND (<0.001)	ND (<0.001)	ND (<0.001)	ND (<0.001)	ND (<0.001)
F5	0.08 ± 0.00	0.08 ± 0.00	0.17 ± 0.00	0.17 ± 0.00	0.08 ± 0.08	ND (<0.003)	0.17 ± 0.00	0.17 ± 0.00
Sum	0.41 ± 0.33	0.91 ± 0.00	1.25 ± 0.17	0.34 ± 0.17	1.16 ± 0.00	0.33 ± 0.25	1.42 ± 0.33	0.17 ± 0.00
Zinc								
F1	2.1 ± 2.92	4.1 ± 5.83	ND (<0.12)	1.2 ± 1.67	ND (<0.12)	0.7 ± 0.92	ND (<0.12)	2.8 ± 4.00
F2	25.5 ± 21.17	22.0 ± 2.90	ND (<0.22)	ND (<0.22)	ND (<0.22)	ND (<0.22)	38.5 ± 11.00	6.8 ± 5.33
F3	8.2 ± 11.58	1.1 ± 1.50	ND (<0.08)	ND (<0.08)	ND (<0.08)	ND (<0.08)	34.3 ± 8.83	9.3 ± 3.75
F4	2.1 ± 3.00	2.2 ± 3.08	10.0 ± 1.17	ND (<0.25)	3.8 ± 5.33	4.0 ± 5.58	6.6 ± 1.25	7.4 ± 2.25
F5	68.3 ± 44.50	87.3 ± 54.17	61.3 ± 35.08	69.7 ± 4.25	50.2 ± 17.00	47.7 ± 0.17	30.8 ± 43.67	207.0 ± 39.92
Sum	106. ± 34.92	116.7 ± 33.73	71.3 ± 36.25	70.9 ± 5.83	54.0 ± 22.33	52.4 ± 9.20	110. ± 25.00	233.3 ± 51.53

ND: Not detectable.
 L1, L2, L3: 0.3, 1 and 2 km from lead smelter, L4: Heavy traffic area.
 F1: Exchangeable, F2: Acid soluble, F3: Reducible, F4: Oxidizable, F5: Residue fractions.

it was observed that Pb occurred predominantly in the reducible fraction, with much smaller amounts occurring in the acid-soluble, oxidizable and residual fractions. There was no Pb in the exchangeable fraction. The predominance of Pb in the Fe-Mn oxide (reducible) fraction is in broad agreement with previous reports for air particles^{1,19,20} and soil dusts^{15,21}. The adsorption of Pb cations onto the Fe-Mn oxide phase is considered as a reasonably universal fixation process.

Cadmium occurred predominantly in the in acid soluble or reducible phases, while the highest proportions of Zn occurred mainly in the residual phase. Zinc in this fraction is unlikely to be easily released under natural conditions, however at sites L1 and L4 there were also reasonable amounts of Zn present in the acid-soluble fraction.

Elemental Associations of Lead in Air Particulate Samples Based on Extractograms

For investigation of elemental associations, comparison of extractograms obtained from continuous-flow sequential extraction can be used (graphic plots of metal concentrations in subfractions versus subfraction number) It is possible to evaluate the elemental associations in the various extracted solid phases by comparing the details of peak profiles and peak shapes of overlain extractograms.

The distribution and chemical associations of Pb and major elements (Al and Fe) in air particulate matter for contaminated air particulate samples (300 m from lead smelter and heavy traffic area) can be evaluated using the extractograms shown in Fig. 4. Chemical associations of Pb in air particulate matter were not studied at sampling sites L2 and L3 because of the low concentrations of Pb in each fraction (Table 2).

For the contaminated air particulate matter at the lead smelter site (L1), although the Pb occurred

predominantly in the reducible phase, Pb and Al had similar dissolution patterns within the acid soluble phase in both wet and dry seasons (Fig. 4: 1a and b). This indicates a close association between Pb and Al in the acid soluble phase of contaminated air particulate matter. In contrast, in the reducible phase, the Pb peak was found to increase rapidly early in the fraction, preceding the bulk of the Fe (and Al) dissolution in this phase. This has been taken as an indication that the Pb is mostly adsorbed on oxide (Fe/Al) surfaces; the results being very similar to the extractograms of soil samples collected at the same site¹⁷. The air particulates are probably therefore derived mainly from wind-blown dust at the site.

Extractograms for contaminated air particulate matter from the heavy traffic area site (L4) also show associations of Pb with the Fe/Al oxide phases (Fig. 4: 2a and b). Therefore, irrespective of the source of the contamination, the extractograms appear quite similar.

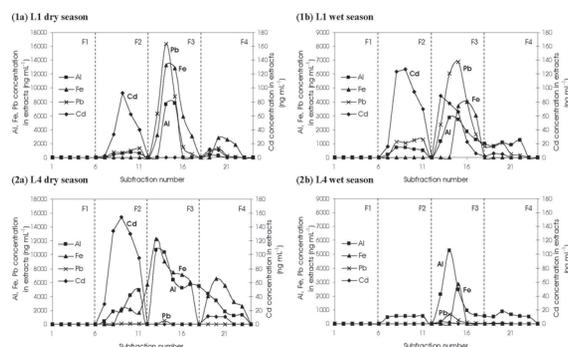


Fig 4. Extractograms for air particulate matter obtained using the continuous-flow sequential extraction procedure for contaminated air particulate: L1 in the dry season (1a) and L1 in the wet season (1b), L4 in the dry season (2a) and L4 in the wet season (2b).

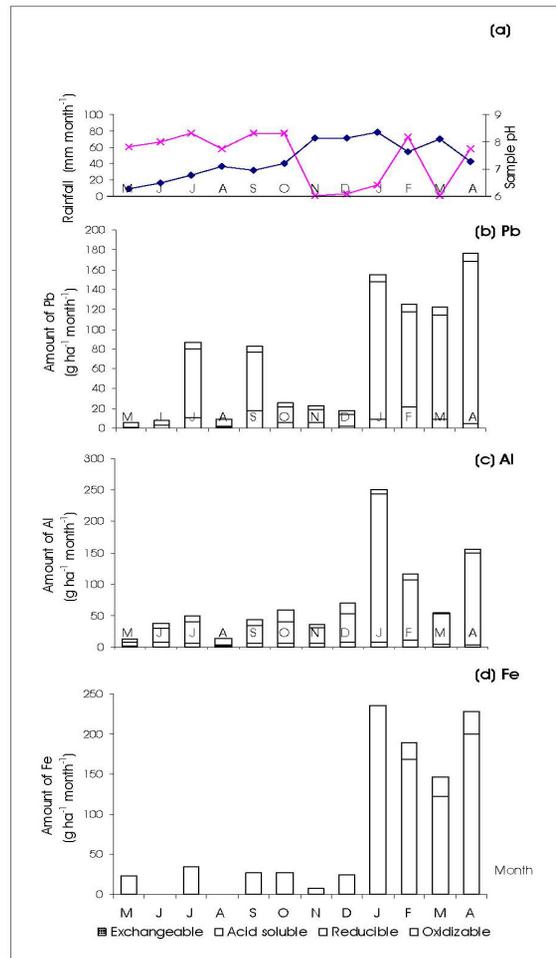


Fig 5. Monthly rainfall data (a) and fractional distribution of Pb (b), Al (c), and Fe (d) for air particulate matter collected near a lead smelter (site L1).

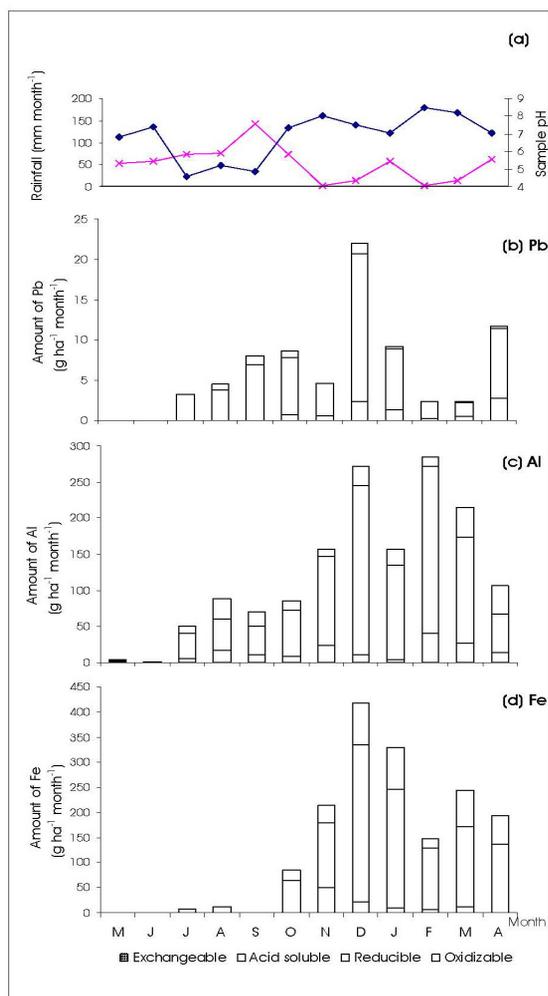


Fig 6. Monthly rainfall data (a) and fractional distribution of Pb (b), Al (c), and Fe (d) for air particulate matter collected near a heavy traffic area (site L4).

Monthly Fractional Distribution of Pb in Air Particulate Matters

Monthly data for the fractional distribution of Pb in air particulate matter are shown in Fig. 5-6. The data are shown together with rainfall (mm) and pH from May, 2004 to April, 2005.

At both sites, the fractional distribution of Pb, Al and Fe between chemical forms in contaminated air particulate matter was quite similar for all months, with no obvious differences between the dry and wet seasons. It can therefore be concluded that seasonal change does not affect the distribution of chemical forms of Pb, Al and Fe in air particulate matter. Considering the metal content of the particulate matter, it was clearly observed that total metal concentrations were higher in the dry compared with the wet months (Fig. 5 and 6). This was most clearly observed at sampling site L1. Soil aerosols normally make the largest contribution to

atmospheric pollution with Al and Fe as the most abundant metals acting as markers^{22,23}. In the dry season, wind-blown dusts are likely to be more abundant at both the smelter and heavy traffic sites with resulting deposition of particulate matter occurring by sedimentation or diffusion.

CONCLUSION

A continuous-flow sequential extraction system was used to study the fractionation and elemental association of metals in air particulate matter. For air particulate matter from the lead smelter and traffic-related dust examined in this study, Pb was predominantly present in the reducible fraction, with moderate amounts occurring in the oxidizable and residual fractions, and a small amount being associated with the acid soluble phase. Examination of extractograms showed close associations between Al and Pb in the acid soluble phase for the contaminated air particulate matter from the lead smelter. In contrast, in the reducible fraction, Pb appeared to dissolve earlier than Fe and Al suggesting that Pb is adsorbed on Fe/Al oxide surfaces in air particulate matter. Similar extractograms for soil collected from the same location suggests wind-blown dust to be the source of the particulate matter. Extractograms of Pb in particulate matter from a heavy traffic area also showed close associations of Pb with the major elements Al and Fe. Total Pb deposition in the dry season was found higher than in the wet season supporting the suggestion that soil dust is the predominant source of the atmospheric particulate matter. The fractional distribution of Pb, Al and Fe in particulate matter was very similar for both dry and wet seasons.

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