

Partitioning between soluble and insoluble fractions of major and trace elements in size-classified airborne particulate matter collected in Tokyo†‡

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Airborne particulate matter (APM) is a major air pollutant, and the effect on human health of fine APM (PM_{2.5}) deposited deep inside the lungs has recently become a serious concern. Moreover, soluble constituents may leach from APM, and intensify some health disorders. To identify the soluble chemical constituents of APM, size-classified APM was sampled in central Tokyo, and the elemental compositions of the water-soluble, acid-soluble and insoluble fractions were investigated. The extraction procedure was validated by calculating the mass balance of soluble and insoluble fractions of a standard APM reference material (NIST SRM 1648). Among the major elements, Fe and Ti in APM of all size classes and K in coarse APM were distributed primarily in the insoluble fraction and were inferred to be present as oxides or silicates, whereas Na and Mg in all size classes and K in fine APM were primarily in the water-soluble fraction and were inferred to be have originated mainly from sea salt. Among the trace elements, Zn and Cd in the fine APM ($d < 2 \mu\text{m}$) had large enrichment factors, indicating an anthropogenic origin, and were distributed primarily in the water-soluble fraction. When fine anthropogenic APM enters into the lungs, leached toxic elements, such as Cd, may adversely affect health. The higher the bonding energy of the monoxide molecule of the element was, the higher its distribution ratio was in the water-soluble fraction. Therefore, many metallic elements in APM were inferred to be present as oxygen-bonded compounds.

Introduction

Airborne particulate matter (APM) is recognized as a major air pollutant, along with nitrogen and sulfur oxides. From the viewpoint of adverse effects resulting from the inhalation of particulate matter, APM is usually classified according to its aerodynamic diameter, and the atmospheric concentrations of size-classified APM are regulated by the environment quality standards. Coarse particles with aerodynamic diameter $d > 10 \mu\text{m}$ are mainly derived from natural sources and those that are breathed in are typically filtered out in the nose and throat. On the other hand, particles with $d < 10 \mu\text{m}$ (PM₁₀) can be delivered into the bronchial tubes and cause health problems; thus, the government regulatory agencies in many countries have enacted an environmental standard for PM₁₀. In 1972, the Environment Agency of Japan enacted an environment quality standard for suspended particulate matter (100% of particles with $d < 10 \mu\text{m}$).¹ Since then, epidemiological studies in the United States, Europe, and Asia have shown a

remarkable correlation between the mortality rate of a population and the concentration of fine particles with $d < 2.5 \mu\text{m}$ (PM_{2.5}) in the air.^{2–4} As a result, the effect of PM_{2.5} on human health has become a serious concern. In 1997, the US Environmental Protection Agency established a new air quality standard for PM_{2.5}.⁵ Many researchers in Japan are currently investigating the atmospheric behavior of PM_{2.5},⁶ and the Ministry of the Environment of Japan is considering establishing an environmental quality standard for PM_{2.5} soon.

The above-mentioned standards deal with the atmospheric concentration of APM, but not with its chemical composition. However, the elemental composition and the concentrations of chemical species in APM should be scrutinized to assess in more detail the effect of APM on human health. Many studies have observed carcinogenic or cumulative toxic substances, such as polycyclic aromatic hydrocarbons and toxic metallic elements, to be constituents of APM, especially fine APM.^{7–9} Our research group has performed long-term monitoring of size-classified APM in Tokyo since 1995,¹⁰ which has demonstrated that fine APM, with $d < 2 \mu\text{m}$, is extremely enriched in toxic elements, such as As, Se, Cd, Sb, and Pb. When fine APM containing toxic substances is inhaled deep into the lungs, some of the constituents may leach from the APM, thus exacerbating some health disorders. Indeed, it has been reported that reactive oxygen species, such as the hydroxyl radical, are produced by the Fenton reaction with Fe(II) and Cu(II) in fine particles.^{11,12}

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Many studies have investigated the organic, metallic, and ionic components of size-classified APM. In addition to these bulk composition measurements, results of elemental and speciation analyses of the water-soluble fraction have recently been reported for many locations around the world.^{12–20} However, the mass balance between the bulk APM composition and the sum of the water-soluble and insoluble fractions has been investigated by only a few studies.²¹ Moreover, the dominant factors influencing the partitioning of trace elements between water-soluble and insoluble fractions have not been extensively elucidated. In this study, we first investigated the mass balance of major and trace elements fractionated into water-soluble, acid-soluble, and insoluble fractions by using a standard APM reference material. Then, we investigated the partitioning of the major and trace elements between soluble and insoluble fractions of size-classified APM collected in central Tokyo. Using the obtained results, we evaluated the chemical species in APM that are readily incorporated into the human body. Finally, we elucidated the physical properties influencing the solubilities of APM constituents.

Experimental

Sampling of size-classified APM

APM was collected on the rooftop (approximately 45 m above the ground) of a building on the Chuo University campus (Fig. 1). The geographical location of the sampling site is the same as that of our long-term monitoring.¹⁰ The Chuo University campus is in central Tokyo, and the sampling site is approximately 50 m from an arterial roadway (R254). The traffic density on the R254 is approximately 1680 cars h⁻¹ during the daytime on weekdays.²² This value was approximately 4 times as much as the national average. Therefore, the area around the sampling site is a typical urban, heavy traffic area. Most vehicles on the R254 are gasoline-powered automobiles, which accounted for approximately 60% of the total traffic.²² Because the sampling site was high above the ground, effects of soil and road dusts blown up by wind are expected to be small.

An Andersen low-volume air sampler (AN-200; Tokyo Dylec Co., Tokyo, Japan; flow rate, 28.3 L min⁻¹) was used to collect size-classified APM ($d < 2 \mu\text{m}$; = 2–11 μm ; and $> 11 \mu\text{m}$), and each size class of APM was collected on a different quartz fiber filter (80 mm in diameter; Pallflex 2500

QAT-UP; Pallflex Products Co., East Hills, NY, USA). The filters were kept in a desiccator for at least 3 days before the weight of the collected APM was measured.

APM was collected during 4 sampling periods (2–26 November 2004, 1–25 April 2005, 19–30 August 2005, and 17–28 October 2005). During each sampling period, the flow rate of the low-volume air sampler was checked once a day.

APM extraction procedure

The entire extraction procedure is shown in Fig. 2. Each collected APM sample was fractionated into water-soluble, acid-soluble and insoluble fractions.

The entire quartz fiber filter with the collected APM sample and 40 ml of ultrapure water (Milli-Q Element; Japan Millipore Co., Tokyo, Japan; resistivity $> 18.2 \text{ M}\Omega \text{ cm}$) were placed in a polytetrafluoroethylene (PTFE) vessel, and the sample was completely immersed in the water. The extraction was performed by using a thermostat shaker (MCS-150; AS ONE Co., Osaka, Japan) for 24 h at 25 °C and 120 shakes per minute. After extraction, the sample was filtered through a nitrocellulose membrane filter (0.45 μm pore size; HAWP04700; Japan Millipore Co.) and separated into water filtrate (water-soluble fraction) and residue (water insoluble). After the pH of the water filtrate was measured, 1 μl of concentrated HNO₃ (70%, Ultra Pure Chemicals; Kanto Chemical Co. Inc., Tokyo, Japan) was added to prevent adsorption onto the wall of the storage vessel, and then ultrapure water was added to make a total volume of 50 ml. The solution was then transferred and stored in a polypropylene (PP) vessel.

The residues of the November 2004 and April 2005 samples were extracted with 0.1 M HNO₃, which was prepared by dilution of concentrated HNO₃ with ultrapure water. The extraction and sample preparation procedures were the same as those used for the water extraction described above. Each residue was separated into acid filtrate (acid-soluble) and further residue (insoluble). The sample amounts of August 2005 and October 2005 were too small for the extraction with 0.1 M HNO₃ to be performed.

After the final residue sample was dried at the room temperature, the sample was placed into a PTFE vessel and digested by 3 ml of HF (50%, semiconductor grade; Daikin Industries Co. Ltd., Osaka, Japan), 6 ml of concentrated HNO₃, and 1 ml of H₂O₂ (30%, Ultra Pure Chemicals; Kanto Chemical Co. Inc.) in a microwave digesting equipment (Microwave Labstation MLS-1200 mega; Milestone s.r.l., Sorisole, Italy), which is the same acid digestion method that we used previously.¹⁰ HF was evaporated by heating the sample solution at 230 °C on a hot plate, and 0.1 M HNO₃ was added to make the total sample volume 50 ml. The sample was then transferred to a PP vessel for storage. The operating conditions of the microwave digestion are shown in Fig. 2.

Determination

Major elements (Na, Mg, Al, K, Ca and Fe) in samples were determined with ICP-OES (SPS-5100; SII NanoTechnology Inc., Tokyo, Japan), and trace elements (Li, Be, Ti, V, Cr, Mn,

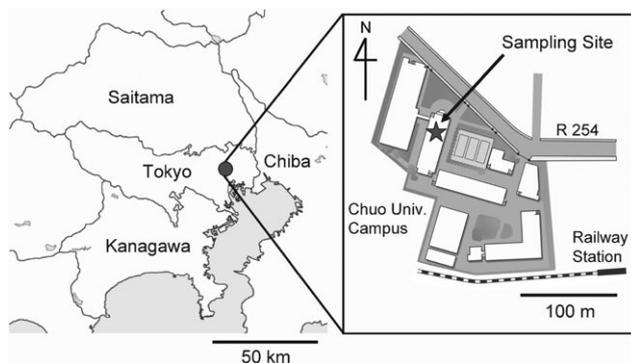


Fig. 1 Geographical location of the sampling site.

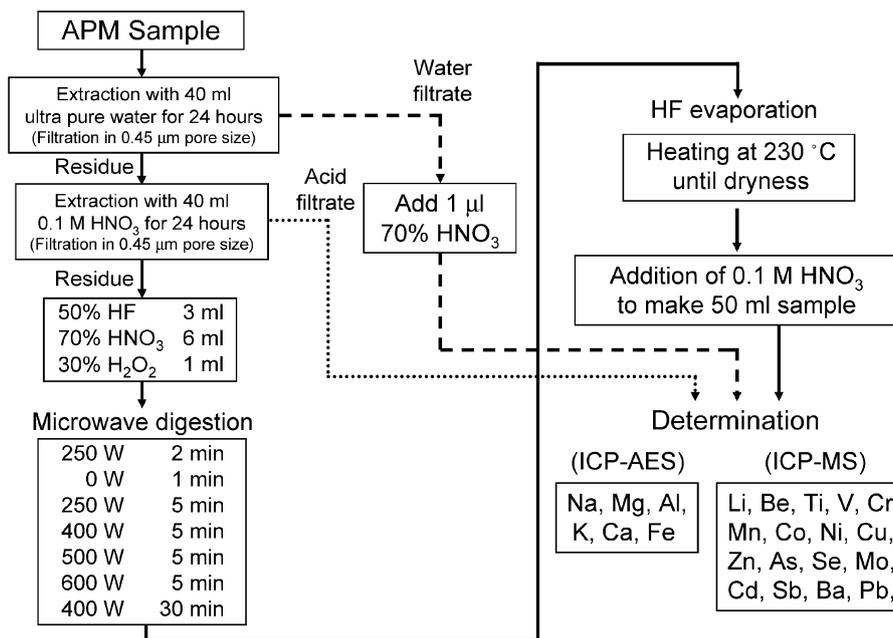


Fig. 2 The entire procedure of extraction and acid digestion treatments. Water soluble, - - - ->; Acid soluble,>; Insoluble, ———>.

Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba and Pb) with ICP-MS (HP4500; Yokogawa Analytical Systems Inc., Tokyo, Japan).

For the determination of major elements, multi-element standard solutions (0, 1, 5, 10 and 30 $\mu\text{g ml}^{-1}$) were prepared by dilution of commercially available single-element standards (1000 $\mu\text{g ml}^{-1}$ AAS grade; Kanto Chemical Co. Inc.) with 0.1 M HNO_3 . For the determination of trace elements, multi-element standard solutions (0, 1, 5, 10, 50, 100 and 300 ng ml^{-1}) were prepared by dilution of a commercially available 20-element standard (XSTC-384, 10 $\mu\text{g ml}^{-1}$ in 2% HNO_3 ; SPEX CertiPrep Inc., Metuchen, NJ, USA) with 0.1 M HNO_3 . For internal standard calibration in the ICP-MS analysis, In and Re standards (1000 $\mu\text{g ml}^{-1}$ AAS grade; Kanto Chemical Co. Inc.) were spiked into both sample and standard solutions, and the internal standard concentrations were finally adjusted to 100 ng ml^{-1} .

The instrumental detection limits of ICP-OES and ICP-MS were $<0.005 \mu\text{g g}^{-1}$ and $<0.15 \text{ng g}^{-1}$, respectively. Most of the elements determined in this study were above the detection limit. Because only a few data for Se in APM with $d > 11 \mu\text{m}$ were below the detection limit, we excluded these data from the data set.

Results and discussion

Validation of the extraction procedure

To confirm the validity of the extraction procedure, a standard APM reference material (NIST SRM 1648; National Institute of Standards and Technology, Gaithersburg, MD, USA) was fractionated by using the procedure described, and the elemental compositions of water-soluble and insoluble fractions were measured (Table 1). The acid-soluble fraction was not measured in this experiment. For all elements with certified or reference values, the total concentrations in the water-soluble

and insoluble fractions were in a good agreement with the certified or reference values, within a relative error of 15%. Therefore, we inferred that artifacts, such as contamination or loss of the sample during extraction and microwave digestion, were negligible. Morsellia *et al.* previously investigated the mass balance of 7 elements (V, Cr, Ni, Cu, Zn, Cd and Pb) in NIST SRM 1648.²¹ Our study extended to all of the certified and reference values listed in NIST SRM 1648.

Partitioning between soluble and insoluble fractions of size-classified APM

The size-classified APM samples obtained during the 4 sampling periods were fractionated, and then the elemental compositions of water-soluble, acid-soluble, and insoluble fractions were measured. The total concentrations of the elements in the soluble and insoluble fractions are listed in Table S1 (in the electronic supplementary information).[†] The concentrations shown in Table S1 were corrected by using filter blank values. The elemental concentrations of the blank filters, except for Mo, were less than 10% of the elemental concentrations in the size-classified APM sample. Therefore, the blank values did not largely affect the APM analytical values. The Be concentration in APM of all size classes was exceptionally low, and a considerable amount of Mo was present in a blank filter. Therefore, the data on Be and Mo are omitted from the following discussions. Minimum, maximum, median, and mean concentrations of the elements in size-classified APM obtained during our long-term monitoring in Tokyo¹⁰ from May 1995 to December 2006 are shown in Table S2 (in the electronic supplementary information).[‡] All total element concentrations obtained by the extraction experiments (Table S1[†]) were between the minimum and maximum long-term values, and they were of a similar order of magnitude to the long-term median and mean values

Table 1 Elemental mass concentrations of water-soluble and insoluble fractions obtained by the extraction experiment for a standard APM reference material (NIST SRM 1648)

		Water-soluble	Insoluble	Found ^b	Certified
Major (wt%)	Na	0.072 ± 0.010	0.43 ± 0.02	0.50 ± 0.02	0.43 ± 0.002
	Mg	0.123 ± 0.032	0.65 ± 0.03	0.78 ± 0.03	0.8 ^c
	Al	0.006 ± 0.001	3.43 ± 0.09	3.44 ± 0.09	3.42 ± 0.01
	K	0.113 ± 0.024	0.99 ± 0.03	1.10 ± 0.03	1.05 ± 0.01
	Ca	1.48 ± 0.20	4.29 ± 0.15	5.77 ± 0.20	—
	Fe	N.D. ^a	3.81 ± 0.05	3.81 ± 0.05	3.91 ± 0.10
Trace/μg g ⁻¹	Li	0.454 ± 0.106	24.8 ± 0.5	25.2 ± 0.6	—
	Be	0.011 ± 0.005	2.17 ± 0.04	2.18 ± 0.05	—
	Ti	0.935 ± 0.194	3830 ± 102	3830 ± 102	4000 ^c
	V	3.02 ± 0.81	127 ± 2	130 ± 2	127 ± 7
	Cr	1.21 ± 0.27	361 ± 8	362 ± 8	403 ± 12
	Mn	109 ± 28	618 ± 25	727 ± 24	786 ± 17
	Co	1.59 ± 0.49	14.3 ± 0.2	15.8 ± 0.4	18 ^c
	Ni	N.D. ^a	69.1 ± 1.2	69.1 ± 1.2	82 ± 3
	Cu	57.3 ± 13.9	454 ± 8	511 ± 8	609 ± 27
	Zn	1400 ± 349	2990 ± 199	4390 ± 175	4760 ± 140
	As	11.7 ± 2.9	104 ± 1	116 ± 3	115 ± 10
	Se	3.39 ± 1.05	21.9 ± 0.6	25.3 ± 1.2	27 ± 1
	Mo	0.334 ± 0.534	50.4 ± 5.5	50.8 ± 5.0	—
	Cd	17.3 ± 4.6	48.7 ± 2.9	66.0 ± 3.1	75 ± 7
	Sb	0.924 ± 0.480	43.0 ± 2.0	44.0 ± 2.2	45 ^c
	Ba	4.80 ± 1.24	751 ± 16	756 ± 16	737 ^c
	Pb	94.4 ± 25.4	5500 ± 309	5600 ± 306	6550 ± 80

^a ND: not detected. ^b Soluble + insoluble. ^c Reference.

(Table S2†). The elements listed in Table S1 can be grouped into those which were present predominantly in coarse ($d > 11$ or $= 2\text{--}11$ μm; Na, Mg, Al, Ca, Fe, Be, Ti, Co, Ba, Cr and Cu) or fine ($d < 2$ μm; V, As, Se, Cd and Pb) particles or those present in similar concentrations in both the coarse and fine particles (K, Li, Mn, Ni, Zn, Mo and Sb). We observed a similar grouping of the elements in our long-term monitoring results (Table S2†). Therefore, the elemental concentrations in the size-classified APM used for the extraction experiment were typical values for central Tokyo.

The pH ranges of the water filtrate before addition of 0.1 M HNO₃ were 3.8–4.0, 4.4–4.5, and 5.0–5.1 for APM with $d < 2$ μm, $= 2\text{--}11$ μm, and > 11 μm, respectively. Because the pH range of the water filtrate of blank samples ($n = 3$) was 4.8–4.9, large amounts of acidic substances, such as secondarily formed sulfate and nitrate, were likely present among the smaller particles ($d < 2$ μm).

The distribution ratios of the major elements in the water-soluble, acid-soluble, and insoluble fractions of size-classified APM sampled during 1–25 April 2005 are shown in Fig. 3. In all particle size groups, approximately 80% of the total element concentrations of Al and Fe were in the insoluble fraction. Major elements in the Earth's crust in order of relative crustal abundance are O, Si, Al, Fe,²³ and aerosols derived from soil comprise both coarse and fine particles.²⁴ Furthermore, our long-term monitoring demonstrated that the major elements mainly originated from natural sources.¹⁰ Considerable portions of the Fe and Al in APM were insoluble because Fe and Al are present as insoluble oxides or silicates in soil dust. Although the other major elements, besides Fe and Al, were primarily distributed in the water-soluble fraction, we observed some important distinguishing features. In all APM size groups, 70–90% of Ca and Na was in the water-soluble fraction, whereas in the coarse (> 11 μm) and fine (< 2 μm)

particle groups, 50% of Mg was in the insoluble fraction. Furthermore, 60% of K was in the insoluble fraction of the coarser particle groups (> 2 μm), whereas 75% of K was in the soluble fraction of the fine particles. It has been reported that

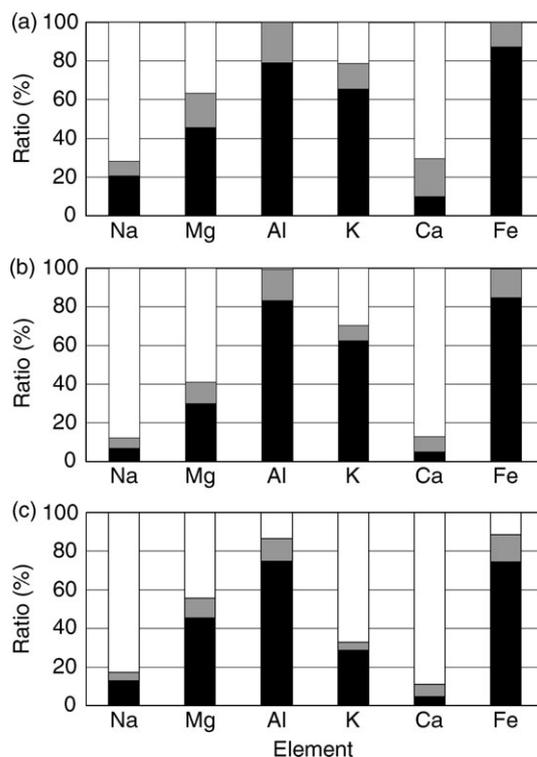


Fig. 3 Distribution ratios of the major elements in the water-soluble, acid-soluble, and insoluble fractions of size-classified APM sampled during 1–25 April 2005. (a) $d > 11$ μm, (b) $d = 2\text{--}11$ μm, (c) $d < 2$ μm. Water-soluble, □; Acid-soluble, ■; Insoluble, ■.

Table 2 Mean enrichment factors of trace elements in size-classified APM obtained during the long-term monitoring in Tokyo (May, 1995–December, 2006)

Elements	Enrichment factor		
	<2 μm	2–11 μm	>11 μm
Li	8.7	2.5	1.8
Ti	1.7	1.8	1.5
V	38.5	3.7	2.4
Cr	16.2	7.8	6.3
Mn	17.5	4.9	3.5
Co	4.2	2.1	1.6
Ni	46.7	8.8	8.8
Cu	335	148	46.7
Zn	1480	227	74.7
As	715	62.0	15.0
Se	8670	454	68.1
Cd	8490	506	94.6
Sb	12 200	3790	399
Ba	6.6	6.7	2.3
Pb	1930	157	41.1

Na, Mg, and K in APM collected in central Japan are derived mainly from sea salt.¹⁵ Therefore, the large amount of Na in the water-soluble fraction may have been derived from NaCl in the APM. In the size-classified APM, the elemental ratios Mg/Na and K/Na were 0.29–0.48 and 0.22–1.06, respectively, whereas these ratios in sea salt are 0.12 and 0.03, respectively.²⁵ The larger Mg/Na ratio in APM than in sea salt suggests that some of the water-soluble Mg may be derived from MgCl₂, and that the other insoluble Mg was derived from soil dust. The K/Na ratio, particularly in the coarse particles (>11 μm), was considerably larger than that in sea salt, and the proportion of K in the insoluble fraction of the coarse particles was large. Therefore, K in the coarse particles is likely derived from insoluble compounds in soil.

The distribution ratios of the trace elements in the water-soluble, acid-soluble and insoluble fractions of size-classified APM sampled during 1–25 April 2005 are shown in Fig. 4. From the viewpoint of particle size, the proportions of most trace elements in the water-soluble fraction tended to increase with decreasing APM diameter. Smaller APM particles have a larger specific surface area, and as a result the extraction efficiency is expected to be relatively higher for smaller APM particles.

The mean enrichment factor (EF) values of trace elements in the size-classified APM obtained during our long-term monitoring in Tokyo¹⁰ from May 1995 to December 2006 are shown in Table 2. The EF is an index of the contribution from anthropogenic sources and is defined as the element/Al ratio in atmospheric aerosol samples divided by the element/Al ratio in crustal rock (based on the average crustal composition at 0–40 km depth).²³ An element with an EF close to 1 likely originated from natural sources, whereas an element with an EF much larger than 1 likely has been enriched from anthropogenic sources. The elements listed in Table 2 can be divided into three major groups: elements (Li, Ti, Co and Ba) with EF less than 10, which presumably originated from natural sources; elements (V, Mn, Cr and Ni) with moderately high EF, possibly indicating some contribution from anthropogenic source; and elements (Cu, As, Zn, Se, Cd, Sb, and Pb) with

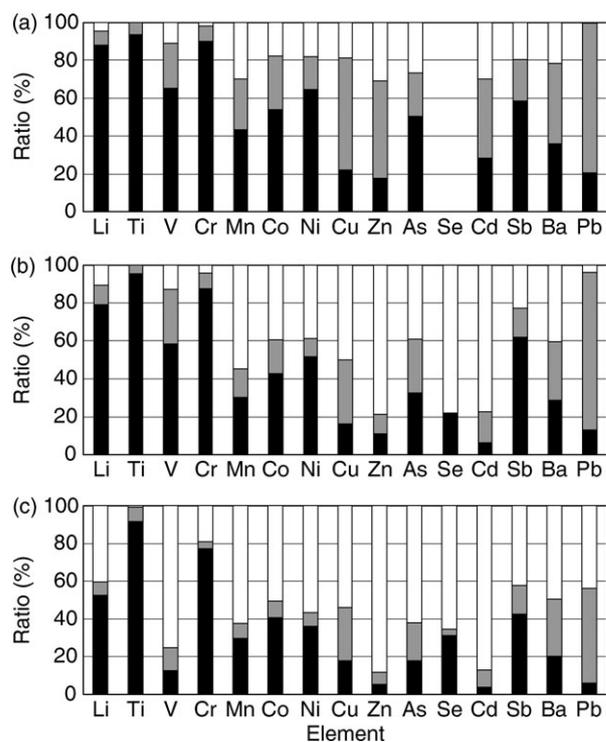


Fig. 4 Distribution ratios of the trace elements in the water-soluble, acid-soluble, and insoluble fractions of size-classified APM sampled during 1–25 April 2005. (a) $d > 11 \mu\text{m}$, (b) $d = 2\text{--}11 \mu\text{m}$, (c) $d < 2 \mu\text{m}$. Water-soluble, □; Acid-soluble, ■; Insoluble, ■.

very high EF (more than several hundred), indicating that they derived mainly from anthropogenic sources. In the third group, the EF values tended to be higher in the fine APM than in the coarse APM because the fine particles enriched in these elements are produced by combustion or mechanical abrasion in industrial processes. However, it is possible for fine particles enriched in these elements to be deposited onto coarse particles, or for coarse particles to consist of aggregates of enriched fine particles. Therefore, we observed some enrichment of these elements in the coarse APM.

More than 90% of Ti was observed in the insoluble fraction in all size groups of APM (Fig. 4), and because the EF of Ti is close to 1 in all sizes of APM, we considered that it originated mainly from natural sources. Like Al and Fe, Ti in APM is thought to be present as insoluble oxides (*e.g.*, TiO₂) and to originate from soil dust.¹⁵ The presence of insoluble Ti species can explain its considerably high distribution ratio in the insoluble fraction. The proportion of V in the water-soluble fraction of APM with $d < 2 \mu\text{m}$ was high (75%), whereas its proportions in APM with $d = 2\text{--}11 \mu\text{m}$ or $d > 11 \mu\text{m}$ were extremely low (10–15%). Other elements also showed a decreasing distribution ratio in the water-soluble fraction with increasing APM diameter (*e.g.*, Mn: 60% in $d < 2 \mu\text{m}$, 55% in $d = 2\text{--}11 \mu\text{m}$ and 30% in $d > 11 \mu\text{m}$; Ni: 60% in $d < 2 \mu\text{m}$, 40% in $d = 2\text{--}11 \mu\text{m}$ and 20% in $d > 11 \mu\text{m}$). However, the difference in the distribution ratio of V in the water-soluble fraction between $d < 2 \mu\text{m}$ and $d = 2\text{--}11 \mu\text{m}$ was exceptionally large. Heavy oil combustion is a major source of V in the Tokyo metropolitan area,²⁶ and the major chemical species of

V from such combustion are V_2O_5 and $VOSO_4$, which have relatively high water solubility.²⁷ Therefore, we assume that the chemical species of V in the fine APM were V_2O_5 and $VOSO_4$ that originated from heavy oil combustion, and that the chemical species of V in coarse APM differed from those in the fine APM. The proportions of Zn and Cd in the water-soluble fraction were remarkably high (80–90%) in APM with $d < 2 \mu\text{m}$ and $d = 2\text{--}11 \mu\text{m}$. In addition, the EF values of Zn (1480) and Cd (8490) in APM with $d < 2 \mu\text{m}$ were relatively high. Thus, these elements probably were derived largely from anthropogenic sources. Zn is recognized as a marker of tire material abrasion dust,²⁸ whereas incineration fly ash and fly ash from fusion furnaces are important sources of Cd in fine APM.²⁹ Since most Cd compounds are toxic to humans, when anthropogenic fine APM is drawn into the alveoli of the lungs, toxic elements such as Cd in the APM may leach out and adversely affect health.

All major and trace elements, except for Pb, had small distribution ratios in the acid-soluble fraction. Pb, however, had high distribution ratios (50–80%) in the acid-soluble fraction of APM of all sizes. The leaching efficiency of Pb from waste rock from mining operations has been previously reported to be high when pH is 1.0–3.0.³⁰ We thus inferred that the acid-soluble Pb in APM originated from acid-soluble substances of anthropogenic origin.

Seasonal variation in the partitioning of elements between soluble and insoluble fractions

We compared seasonal variation in the partitioning of elements between soluble and insoluble fractions (Fig. 5). The distributions of major elements in the three fractions of APM with $d < 2 \mu\text{m}$, sampled during 2–26 November 2004, 1–25 April 2005, 19–30 August 2005 and 17–28 October 2005, showed remarkable seasonal variation (Fig. 5). The proportion of Mg in the water-soluble fraction was highest in October (70%) and lowest in April (45%), and K showed a

similar distribution pattern. The reason for this seasonal variation is not clear. One of the possible sources of insoluble Mg and K, however, is yellow dust (*kosa*), an aerosol from the Asian continent. Yellow dust often arrives in Japan in spring, and Mg (1.57%) and K (1.94%) are major components.³¹ Insoluble Mg and K compounds in yellow dust may explain the higher proportions of these elements in the insoluble fraction in April. Among the other major elements, the proportions of Ca and Na were highest in the water-soluble fraction in October and lowest in that fraction in August, whereas the proportion of Fe in the water-soluble fraction was approximately constant year round.

We also observed notable seasonal variations in the distribution ratios of the trace elements in the water-soluble fraction. The proportions of Mn, Co and Ni were highest in this fraction in August (approximately 60%, 70%, and 80%, respectively) and lowest in November (20–40%). The proportion of Ba was highest in the water-soluble fraction in October (60%) and lowest in November (25%). Several factors may account for the high water-soluble Mn, Co, and Ni contents in summer. One possible factor is variation in the hygroscopicity of fine APM. In summer, more organic aerosols are produced by atmospheric oxidation of volatile organic carbons (VOCs) than during winter, because there are more daylight hours and a higher solar flux in summer. A recent field study of sub-micrometre organic aerosols in Tokyo showed that in summer, the ratio of water-soluble organic carbon to total organic carbon in aerosols peaked in the early afternoon,³² when the atmospheric oxidation of VOCs occurs. If these water-soluble organic species are deposited onto inorganic particles, then the hygroscopicity of APM may increase. Furthermore, in Tokyo, the relative humidity in summer is usually higher than that in winter, causing the hygroscopicity of APM to be increased in summer. Thus, high hygroscopicity of APM in summer may account for the high distribution ratios of some trace elements in the water-soluble fraction. The relative importance of this factor is not clear at present, and further investigation may

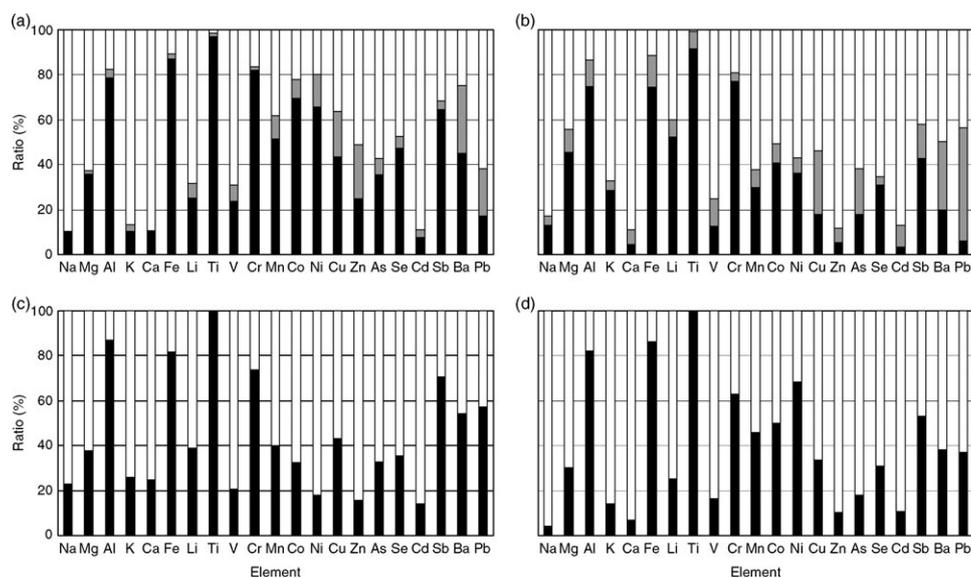


Fig. 5 Distribution ratios of the major and trace elements in the water-soluble, acid-soluble and insoluble fractions of APM with $d < 2 \mu\text{m}$. (a) November 2–26, 2004, (b) April 1–25, 2005, (c) August 19–30, 2005, (d) October 17–28, 2005. Water-soluble, □; Acid-soluble, ■; Insoluble, ■.

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