Concentrations, enrichment and predominant sources of Sb and other trace elements in size classified airborne particulate matter collected in Tokyo from 1995 to 2004†

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APM was collected and trace elements existing in the particles were monitored since May 1995 in this study. APM sample was collected separately by size ($d < 2$ μm, 2–11 μm and > 11 μm) on the roof of the university building (45 m above ground) in the campus of Faculty of Science and Engineering, Chuo University, Tokyo, Japan, using an Anderson low volume air sampler. The collected sample was digested by HNO_3, H_2O_2 and HF using a microwave oven, and major elements (Na, Mg, Al, K, Ca and Fe) were measured by ICP-AES, and trace elements (Li, Be, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba and Pb) were measured by ICP-MS. It was observed that the APM concentration was higher between the winter and the spring, compared to during the summer. The enrichment factor was calculated for each element in each set of APM ($d < 2$ μm, 2–11 μm and > 11 μm). Seasonal trends of enrichment factors were examined, and the elements were classified into 3 groups according to the common seasonal behavior. It is likely that the elements in the same group have common origins. Toxic pollutant elements (Sb, Se, Cd, Pb and As) were found in small particles with d of <2 μm in concentrated levels. Antimony (Sb) had the highest enrichment factor, and the results suggested that Sb level in APM was extremely high. The origins of Sb were sought, and wastes from plastic incineration and brake pad wears of automobiles were suspected. Each set of APM ($d < 2$ μm, 2–11 μm and > 11 μm) was classified by the shape, and the shape-dependent constituents of a single APM particle were quantitatively measured by SEM-EDX. High concentration of Sb was found in APM <2 μm and square particles. Particles less than 2 μm and square shaped particles were major particles produced by actual car braking experiments. From these experimental results it was concluded that the source of Sb in squared APM <2 μm is considered to be from brake pad wear.

Introduction

Airborne particulate matter (APM) has become a serious problem for air pollution just like SO_x and NO_x. There are a variety of sizes in APM in the atmosphere. Soil dust particles are coarse particles that have larger d of 10 μm and are removed by nose hair and membrane in the nasal cavity. On the other hand, particles with d less than 10 μm are delivered into the bronchial tube and lung by indrawn breath, but particles with d between 2 and 10 μm can be coughed out at a bronchial tube. However, particles with d less than 2 μm are easily taken into the bronchial branch and deposited deep inside the lung, and can cause lung function disorder, endocarditis, declining sperm count and so on.[1] According to epidemiological research conducted in 6 cities in the United States, there was a good correlation between the mortality rate and the concentration of fine particles less than 2.5 μm.[2] Epidemiological research conducted in Europe and Asia also showed a good correlation between the mortality rate and the concentration of fine particles, therefore, the effect of APM to human health is a serious concern.[3,4] Moreover, not only the health effects to adults, but also correlation of mortality rate to infants and children are also anticipated.[5]

Since APM has a long residence time, it can be transported over long distances depending upon the atmospheric circulation. Larger particles are removed from the atmosphere within

several days by natural precipitation or by being washed away by rain,[6] but smaller particles can stay within the atmosphere for several weeks. Thus small particles are likely to travel with the atmospheric current, and affect the surrounding environment.[7,8] Such APM pollution is therefore a global concern.

Under these backgrounds, size classified APM has been collected in the mega-city of Tokyo every month since 1995,

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and the concentration of total APM and trace elements were monitored. Similar monitoring has been conducted in the United States,[9] the Czech Republic[10] and Australia,[11] but it is very rare that the monitoring has been conducted for more than 10 years.[12] In this study, trace elements in size classified APM collected in the mega-city of Tokyo were measured and the sources of the APM pollution were investigated.

Experimental

Sampling

APM was collected at the rooftop (approximately 45 m above ground) of a building in the Chuo University campus, located in Bunkyo-ku, Tokyo, Japan. An Anderson low volume air sampler (AN-200; Tokyo Dylec Co., Japan) using the cascade impactor principle was used to collect APM by size. In this study, APM was separated in 3 groups: $d < 2$ μm, 2–11 μm and >11 μm, and each group of APM was collected on a quartz fiber filter (Pallflex 2500 QAT-UP; Pallflex Products Co., USA).

Sample preparation

APM sample and filter were put into a Teflon vessel, and was digested by HNO_3 (70% EL grade; Kanto Chemical Co. Inc., Japan), H_2O_2 (30% EL grade; Kanto Chemical Co. Inc., Japan) and HF (50% for semiconductor; Daikin Industries Co. Ltd., Japan) using a microwave digesting equipment (Microwave Labstation MLS-1200 mega; Milestone s.r.l., Italy). HF was evaporated by heating the sample solution on a hot plate, and pure water (Milli-Q Element; Japan Millipore Co., Japan) was added to make a 50 ml sample.

Measurement

The ICP-AES (JY24; Jobin Yvon, France) was used to analyze major elements (Na, Mg, Al, K, Ca and Fe), and the ICP-MS (HP 4500; Yokogawa Analytical Systems Inc., Japan) was used to analyze trace elements (Li, Be, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba and Pb). The shapes of APM collected and the constituents of a single particle by size were measured by SEM-EDX (JSM-5600LVB-JED-2200, JEOL, Japan).

Results and discussion

Total APM concentration

Fig. 1 describes the seasonal trend of APM concentration for each size, and the total of all 3 sizes. In order to sample 1000 m³ of air per sample, each sample was collected at 28.3 l min⁻¹ for 25 days, and therefore samples were analyzed on a monthly
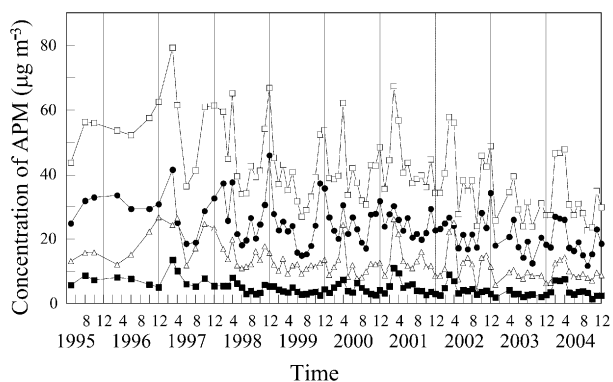
Fig. 1 Long-term trends of the concentration changes of size classified APM in the atmosphere (μg m⁻³). —□—; total, —●—; <2 μm, —△—; 2–11 μm and —■—; >11 μm.

Table 1 Analytical results[a] of NIST SRM 1648 (urban particulate matter)

	Found (%)	RSD (%)	Certified (%)
Na	0.42 ± 0.01	2.2	0.43 ± 0.002
Mg	0.78 ± 0.02	2.1	0.8[b]
Al	3.40 ± 0.05	1.8	3.42 ± 0.11
K	1.00 ± 0.01	0.8	1.05 ± 0.01
Ca	5.72 ± 0.10	1.7	—
Fe	3.91 ± 0.05	1.2	3.91 ± 0.10

	Found/μg g⁻¹	RSD (%)	Certified/μg g⁻¹
Li	25.50 ± 0.2	0.7	—
Be	ND		—
Ti	4114 ± 83	2.0	4000
V	137.7 ± 0.8	0.6	127 ± 7
Cr	387.9 ± 7.1	1.8	403 ± 12
Mn	820.1 ± 6.0	0.7	786 ± 17
Co	17.70 ± 0.04	0.2	18[b]
Ni	78.36 ± 0.2	0.3	82 ± 3
Cu	551.3 ± 8.9	1.6	609 ± 27
Zn	4249 ± 38	0.9	4760 ± 140
As	122.3 ± 1.0	0.8	115 ± 10
Se	26.74 ± 0.6	2.1	27 ± 1
Mo	18.75 ± 0.6	3.3	—
Cd	70.24 ± 0.7	0.9	75 ± 7
Sb	46.84 ± 0.6	1.4	45[b]
Ba	758.7 ± 3	0.4	737[b]
Pb	6228 ± 60	1.0	6550 ± 80

[a] ± Values were derived from the analysis of 3 samples. [b] Reference value. ND: not detected.

basis. Sample and data have been collected since May 1995, and this paper summarizes results obtained until December 2004.

In Tokyo, APM with d smaller than 2 μm was most concentrated, and was followed by APM with d between 2 and 11 μm, and then larger than 11 μm. Scrutiny of the size classified data reveal seasonal variation. For APM less than 2 μm, high concentration was observed in the winter (from December to February) and low concentration was observed in the summer (from June to August). Two reasons can be considered in this seasonal change. One is climate reason. There is more rain in the summer than in the winter in Tokyo and APM less than 2 μm can be washed away by rain. Another reason is that radiative cooling causes an inversion layer during the winter, and APM is kept in lower atmosphere because the atmosphere mixing is drastically reduced. For APM between 2 and 11 μm, high concentration is observed in the spring (May and April). In these months, flower seeds of cedar and cypress are spread and yellow sands are transported from China by a strong western wind. For APM larger than 11 μm, clear seasonal variation cannot be observed.

Concentrations and enrichment factors of elements in APM

To confirm that the analytical procedures are correct, a standard reference material of airborne particulate matter, SRM 1648 (Urban Particulate Matter) was measured. The analytical results are listed in Table 1. The analytical results were in a good agreement with the certified values within analytical error.

Elemental analysis was performed for the collected APM samples using ICP-AES and ICP-MS for each month. The concentrations obtained from May 1995 through December 2004 are summarized in Table 2 in the units of μg g⁻¹ and ng m⁻³. The analytical results are the average value of data obtained. Seasonal trend of elemental concentration was investigated for each size of APM. For APM <2 μm, there is a

Table 2 Long-term monitoring results of major and trace elements in size classified APM (1995.5–2004.12)

Element	Elemental abundances in Earth crust[a]/μg g⁻¹	APM (<2 μm)			APM (2–11 μm)			APM (>11 μm)		
		/μg g⁻¹	/ng m⁻³	EF	/μg g⁻¹	/ng m⁻³	EF	/μg g⁻¹	/ng m⁻³	EF
Na	24 500	7540	173	5.5	48 000	558	7.5	21 400	95.7	2.3
Mg	13 900	1580	37.3	1.8	11 500	146	2.9	9780	46.2	1.8
Al	78 300	5580	135	1.0	25 600	332	1.0	39 100	187	1.0
K	28 200	8090	193	6.2	10 100	131	1.4	7340	35.6	0.8
Ca	28 700	6050	141	3.5	37 700	461	4.4	58 900	267	4.6
Fe	35 400	9880	229	4.9	41 400	506	4.0	42 900	205	2.9
Li	30	8.9	0.22	5.5	14.4	0.20	1.6	11.0	0.059	1.1
Be	2.0	0.2	0.01	1.5	0.8	0.01	1.3	0.8	0.004	1.0
Ti	4700	427	10.3	1.5	2170	28.2	1.5	2620	12.5	1.4
V	95	208	4.63	473	105	1.3	44.9	96.2	0.468	28.6
Cr	70	113	2.58	31.7	283	3.3	14.6	356	1.49	11.8
Mn	690	683	16.3	19.6	1030	12.8	5.2	1060	5.00	3.8
Co	12	5.8	0.14	8.9	15.2	0.2	4.3	16.9	0.081	3.4
Ni	44	143	3.19	64.6	142	1.65	11.7	239	0.93	12.2
Cu	30	478	11.9	341	1080	13.2	133	527	2.35	43.3
Zn	60	5050	121	1770	4210	50.8	250	2120	9.16	83.5
As	1.7	68.0	1.60	781	32.5	0.43	65.8	10.2	0.049	15.6
Se	0.09	56.5	1.30	12 300	14.6	0.19	628	3.48	0.017	90.8
Mo	1.0	72.0	1.64	1370	85.4	1.00	304	79.3	0.394	172
Cd	0.1	46.5	1.17	9710	15.3	0.21	546	4.28	0.019	102
Sb	0.2	199	4.93	20 900	188	2.29	4330	53.0	0.227	634
Ba	590	232	5.22	7.0	1170	13.7	6.9	585	2.59	2.4
Pb	15	1570	39.2	2190	709	9.67	171	277	1.26	44.0

[a] Cited from ref. 14.

trend that the concentration of major elements is high in the summer and low in the winter, and on the contrary, the concentration of trace elements in APM <2 μm is generally low in the summer and high in the winter. As an exception, Ni, Cr and V show high concentration in the summer and low in the winter. For APM between 2 and 11 μm, there is a trend that the concentration of both major and trace elements is low in the summer and high in the winter. For APM >11 μm, any seasonal change could not be recognized in the concentration of both major and trace elements.

The enrichment factor is a value that compares the concentration in the APM and Earth crust (see in the second column of Table 2), and is calculated using the following equation:[13]

$$EF = [M(APM)/Al(APM)]/[M(Crust)/Al\,(Crust)]$$

where M(APM): concentration of M in APM and M(Crust): concentration of M in Earth crust.[14] When the enrichment factor of an element is close to 1, it is likely that this element originates from natural sources, and when the enrichment factor is larger than 1, it is likely that the element was enriched by artificial or human sources. In Table 2, the enrichment factors are shown as well as the concentration in the units of μg g⁻¹ and ng m⁻³.

Na, Mg, Al, K, Ca, Fe, Li, Be, Ti, Co and Ba were found in high concentrations in APM with d of >11 μm and 2–11 μm, but were found in low concentrations in APM with d < 2 μm. The enrichment factors of these elements are single figure values for all sizes, and they are likely to have been generated naturally. However, other elements were found in higher concentrations in APM with d < 2 μm than the larger APM. The enrichment factor becomes larger as the APM size becomes smaller, and toxic elements such as Zn, As, Se, Mo, Cd, Sb and Pb were highly enriched in APM with d < 2 μm. The calculated enrichment factor for Sb was extremely high (20 900), and this means the atmosphere is highly polluted by Sb. In a recent study of airborne particles back to ca. 15 000 years, the average enrichment factor (calculated using Sc as the reference element) for Sb in pre-industrial periods (5320–8030

years BP), was 4.8 ± 1.4.[15] Therefore, the net enrichment factor of Sb in contemporary airborne particles in Tokyo is estimated to be ca. 5000 at maximum values.

Similarities of seasonal trends of the enrichment factors

In this study, trace elements in APM have been monitored since May 1995, thus the seasonal trend of the concentration and enrichment factor of each element can be verified. There were elements that showed a similar seasonal trend, and it was suspected that the elements that behave in a similar manner have a similar source of origin. Seasonal trend of trace elements in APM with d of less than 2 μm were evaluated, and the elements were grouped into 3 types according to the similarity of seasonal trend; (group 1: Na, K, Ca and Fe), (group 2: V, Cr and Ni) and (group 3: Cu, Zn, Mn, As, Se, Cd, Sb and Pb). Figs. 2(a)–(c) plot the seasonal trends of each group of elements. Fig. 2(a) plots the seasonal trend of group 1 taking the enrichment factors of Ca (left) and Fe (right) for y-axis. Elements in group 1 have fairly low enrichment factors, therefore, they appear to originate from natural sources. Fig. 2(b) plots the seasonal trend of group 2 taking the enrichment factors of V (left) and Ni (right) for y-axis. The enrichment factors of group 2 are moderate; V: 473, Cr: 31.7 and Ni: 64.6 (Table 2), and they are seen in concentrated levels during the summer (from June to August). These elements are known to be released from the combustion of fossil fuel, and it is suspected that these elements are emitted from the coastal line of Tokyo Bay where the heavy and chemical industries are, and the seasonal wind carries the particles from the southeast toward the northwest, close to where Chuo University is located. Fig. 2(c) plots the seasonal trend of group 3 taking the enrichment factor of Sb (left) and Pb (right) for y-axis. The enrichment factors of group 3 are extremely large, and their pollution levels are very serious. The pollution levels of these elements are high throughout the year, and they seem to be concentrated between autumn and winter (from October to December). In Japan, there is least precipitation during this season, and the northwest seasonal wind blows from the
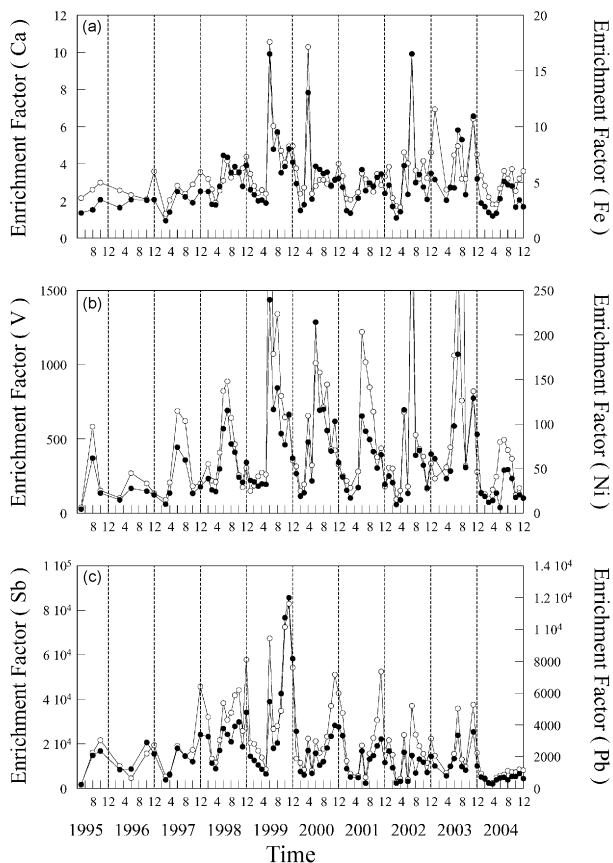
Fig. 2 Seasonal trends of enrichment factors for trace elements in APM with $d < 2$ μm. (a) Group 1: seasonal trend of Ca (—○—) and Fe (—●—). (b) Group 2: seasonal trend of V (—○—) and Ni (—●—). (c) Group 3: seasonal trend of Sb (—○—) and Pb (—●—).

Eurasian Continent. Therefore the increase may be due to particles that traveled to Tokyo with the winds.

Estimation of sources of Sb from quantitative analysis of various samples

Sb concentration in APM with $d > 11$ μm was 53.0 μg g^{-1}, 2–11 μm was 188 μg g^{-1} and <2 μm was 199 μg g^{-1}, and the enrichment factors were 634, 4330 and 20 900, respectively, thus Sb was found to be enriched in all sizes of APM. In APM with $d < 2$ μm, Sb concentration was found to be 3 times higher than that of As, which is the same group in the periodic table. Arsenic (As) pollution is known to originate from combustion of oil waste and coal.[16] On the other hand, Sb pollution has recently started to receive attention,[17] but the levels of enrichment at such high concentrations had not been reported yet. In Japan, antimony sulfide is used for flame resisting auxiliaries and imported in massive amounts, such as 20 000 tons per year in 2000. Recently, the use and import of Sb has been gradually decreasing,[18] but still at a very high level. Fig. 3 demonstrates this situation for APM <2 μm. There are two reasons for the decrease of the Sb concentration (ng m^{-3}) in APM <2 μm. One is the decrease of the total APM concentration, as shown in Fig. 1. The other reason is the decrease of the use and importing of Sb in Japan. Sb compounds are used to make incombustible and thermal resistant plastic products and as recycled fiber, brake pads for automobiles *etc*. There is a possibility that antimony trioxide is produced during a process of heating, which is an abiding concern because antimony trioxide is known as carcinogenic.[19]

In recent years, Tokyo has started to separate and collect rubbish by type, however, there are still cases where plastic rubbish is being incinerated. Several typical materials such as
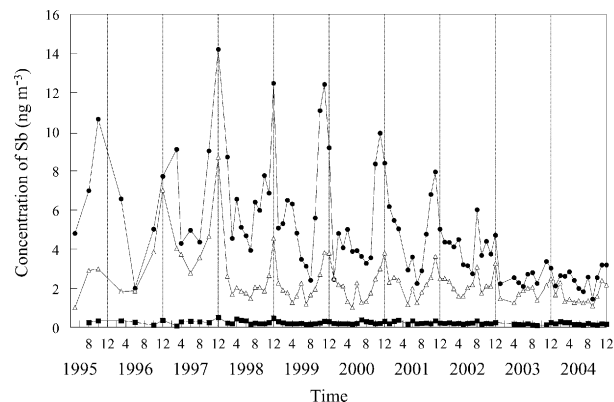
Fig. 3 Long-term trends of the concentration changes of Sb in size classified APM (ng m^{-3}). —●—; <2 μm, —△—; 2–11 μm and —■—; >11 μm.

cloth made of recycled fiber of polycarbonate (PC), fleece made of recycled fiber of polyethylene terephthalate (PET) and inflammable curtain material were analyzed. The analytical results are shown in Table 3.

Fly ash, cloth (PC), fleece (PET) and curtain samples contained 89.9, 102, 173 and 229 μg g^{-1} of Sb, respectively. This indicates that antimony sulfide is added to make chemical fabrics inflammable during the manufacturing process. The demand of fleece material made from recycled PET bottle fiber is growing for its high heat-retaining property and affordable price. There are many other plastic materials besides chemical fibers and clothing surrounding our life. It is likely that a lot of these other plastic products are also treated with antimony sulfide for flameproof properties, and therefore, when these products are incinerated, Sb is enriched inside the fly ash.

Because APM was sampled on the rooftop of a school building close to an arterial highway (national highway #254), it can be presumed that particles originating from

Table 3 Concentrations of elements in potential sources of pollution (incinerator)

| Element | Incinerator/μg g^{-1} | | | |
	Fly ash	Cloth (PC)[a]	Fleece (PET)[b]	Curtain
Na	26 200	64.8	56.9	180
Mg	21 400	0.0453	1.61	3.72
Al	82 600	0.577	ND	0.908
K	24 100	20.8	8.87	110
Ca	83 500	14.5	18.4	215
Fe	31 100	3.31	1.80	16.3
Li	ND[c]	ND	ND	ND
Be	ND	ND	ND	ND
Ti	9840	829	1670	10 900
V	74.5	ND	ND	ND
Cr	235	ND	ND	ND
Mn	689	0.112	0.245	21.4
Co	16.5	6.34	7.63	31.5
Ni	49.6	0.0798	ND	0.608
Cu	837	54.4	ND	1.84
Zn	2910	16.3	0.910	1.28
As	16.1	ND	ND	ND
Se	0.551	ND	ND	23.1
Mo	6.96	ND	ND	ND
Cd	7.77	ND	ND	ND
Sb	89.9	102	173	229
Ba	593	0.0884	0.137	1.04
Pb	349	0.140	0.145	1.85

[a] PC, PolyCarbonate. [b] PET, PolyEthylene Terephthalate. [c] ND, not detected.

Table 4 Concentrations of elements in potential sources of pollution (automobile)

| Element | Automobile/μg g^{-1} | | | | | | |
	Disk	Pad	Tire	DEP	Asphalt	Road dust (L)	Road dust (S)
Na	9.48	1030	318	1250	15 100	22 800	15 800
Mg	360	8020	ND	428	13 900	13 000	13 500
Al	1690	2710	522	ND^a	53 100	50 100	50 700
K	7.01	14 900	262	ND	14 700	13 600	12 900
Ca	19.8	11 900	654	8770	59 500	44 000	50 600
Fe	Major	Major	ND	ND	29 000	34 600	47 400
Li	ND	3.17	ND	ND	10.7	61.1	156
Be	ND	ND	ND	ND	ND	ND	ND
Ti	113	67 600	47.3	18.8	2510	2250	3830
V	96.8	118	ND	ND	101	62.7	97.8
Cr	784	42.9	0.85	36.0	147	251	649
Mn	7200	246	0.76	ND	680	6670	814
Co	34.9	3.91	0.53	ND	11.6	9.95	21.8
Ni	244	44.5	6.34	31.6	63.3	75.3	540
Cu	412	42 000	0.81	122	32.5	61.9	574
Zn	4.93	1250	6390	1340	159	566	1610
As	25.4	ND	1.47	ND	5.15	7.94	5.94
Se	ND	ND	0.82	ND	ND	ND	ND
Mo	64.7	2.16	ND	981	1.68	7.93	14.7
Cd	ND	ND	0.35	ND	ND	ND	ND
Sb	157	13 900	ND	ND	1.35	8.37	31.5
Ba	14.5	1200	2.36	149	344	483	530
Pb	1.14	22.8	6.96	17.7	39.0	109	257

^{a} ND, not detected.

automobiles are excessively collected. Therefore, in order to investigate the origins further, the brake disk (disk), brake pad (pad), tire, diesel exhaust particles (DEP), asphalt and road dusts were also analyzed. Table 4 describes the results. For road dusts, coarse particles (L) were collected by using sieves of 48 and 100 mesh and fine particles (S) were collected by using a sieve of 100 mesh. Sb concentration in the brake disk and brake pad samples were 157 and 13 900 μg g^{-1}, respectively. It was observed that the brake pad contained a lot of Sb. The brake pad consists of backing material such as steel fiber, glass fiber, ceramic fiber *etc.*, combined by resin with the carbon black friction adjuster, brake noise adjuster and anticorrosive treatment. Because the pad is heated by friction with the disk, the antimony sulfide must be treated for heat-resistant properties. The brake pads are changed to new ones after 50 000–70 000 km drive, therefore, particles due to the brake pad wear are likely to be released into the atmosphere. It can be calculated the average of Sb emitted from brake pads is 1.24 g per car per year in Japan. Deterioration of brake disks is not as serious as brake pads because they are made of iron, so fewer particles are generated. The largest source of particles due to automobiles is the exhaust from diesel automobiles (DEP), however, Sb was not found from this sample. Gasoline, diesel oil, engine oil and other fuels including kerosene were also analyzed, but Sb was not detected in any of these fuels.
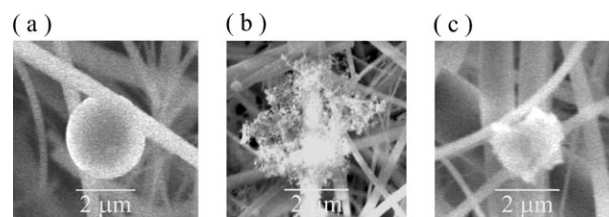
Estimation of sources of Sb from the shape and constituents of a single airborne particulate

From shapes of airborne particulates, it can be inferred that particles generated from mechanical wear out such as brake pad wear mostly shaped square and that particles generated from combustion process such as fly ash are mostly shaped spherical. In order to identify sources of APM collected in Tokyo, the size and shape distribution of particles was quantitatively measured by SEM. The results are shown in Table 5. Because of the SEM resolution, the fine particles discussed here range from 0.5 μm to 2 μm.

The observed shapes of fine particles are classified as spherical, cotton-like and square shapes (Fig. 4). Fractions of percentages of spherical, cotton-like and square shapes in 67 particles were 41.1, 31.6 and 27.3%, respectively. It is revealed that the fine particles are comparably distributed in each shape. In order to investigate what shaped fine particles abundantly contain Sb, the constituents of a single particle were measured by SEM-EDX. To calibrate the instrument SRM 1648 (Urban Particulate Matter) was used. The results are shown in Table 6. Among the analyzed fine particles, fraction of percentage of fine particles which abundantly contain Sb (> 50 μg g^{-1}) is approximately 70% for square particles whereas it is less than 30% for spherical or cotton-like particles. Moreover, the concentration of S besides Sb in square fine particles was higher than that of other shaped fine particles. Since S and Sb are used as brake pad materials, it is considered that fine

Table 5 Size distribution of APM collected at Chuo University and further classification of APM <2 μm by the shape

Size classification	Percentage (%) (n = 78)	Shape classification of APM (<2 μm)	Percentage (%) (n = 67)
0.5–2 μm	73.1	Spherical	41.1
2–11 μm	19.2	Cotton-like	31.6
>11 μm	7.7	Square	27.3

Fig. 4 SEM images of APM collected at Chuo University. (a) Spherical, (b) cotton-like and (c) square.

Table 6 SEM-EDX analytical results of a single APM particle collected at Chuo University ($n = 20$)

Trace elements in APM/μg g^{-1} [high Sb][a]				Trace elements in APM/μg g^{-1} [low Sb][b]			
	Spherical $n = 5$	Cotton-like $n = 5$	Square $n = 14$		Spherical $n = 15$	Cotton-like $n = 15$	Square $n = 6$
Na	7970	1490	3310	Na	3340	1250	5300
Mg	22 020	3520	3910	Mg	2270	1500	10 400
Al	41 300	7990	36 000	Al	37 610	8370	43 600
S	44 850	33 650	285 700	S	50 020	22 300	125 100
Cr	470	50	150	Cr	140	90	210
Ni	ND[c]	ND	ND	Ni	ND	ND	ND
Cu	390	170	240	Cu	230	220	420
Zn	18 320	2590	5400	Zn	4990	3850	9330
Cd	160	10	80	Cd	80	10	80
Sb	360	220	490	Sb	8	2	5
Ba	7210	180	300	Ba	590	270	80
Pb	ND	ND	ND	Pb	ND	ND	ND

[a] [High Sb], > 50 μg g^{-1}. [b] [Low Sb], < 50 μg g^{-1}. [c] ND, not detected.

Table 7 Size distribution of brake pad wear and further classification of particles with $d < 2$ μm by the shape

Size classification	Low load percentage (%) ($n = 147$)	High load percentage (%) ($n = 511$)
0.5–2 μm	70.7	68.9
2–11 μm	29.3	30.9
> 11 μm	—	0.2

Shape classification of particles < 2 μm	Low load percentage (%) ($n = 147$)	High load percentage (%) ($n = 511$)
Spherical	8.7	21.0
Square	91.3	79.0

particles rich in these elements are originated from brake pad wear. Although all squared fine particles are not originated from brake pad wear, this observation suggests that square particles may cause the enrichment of Sb in APM with $d < 2$ μm.

In order to investigate the shape of brake pad wear, a brake pad was rubbed off by a similar manner of actual vehicle travel, and the size and shape distribution of particles was investigated quantitatively. There are two conditions of abrasion. One is "low load" condition which is simulated as normal driving. The other is "high load" condition which is simulated as harsh braking. The size and shape distribution of particles in both conditions are shown in Table 7. Most of abraded brake pad wear in both conditions were fine (0.5–2 μm) and square particles. This observation is consistent with weight *versus* size distribution reported by Garg *et al.*[20] From these experimental results, it can be concluded that Sb in fine particles collected in the mega-city of Tokyo is significantly originated from brake pad wear of automobiles. These results are well consistent with that reported by Weckwerth.[21] He reported that high concentration of Sb was observed in particles sampled at roadside and the source of Sb was considered to be brake-lining of automobiles.

Conclusion

Several phenomena were found from monitoring APM by size ($d < 2$ μm, 2–11 μm, > 11 μm) since May 1995 in the mega-city of Tokyo. It was observed that APM < 2 μm was most abundant in Tokyo, and was followed by 2–11 μm, and then > 11 μm. APM was found in higher concentrations in the winter (from December to February). This is due to the low precipitation as well as the radiative cooling which causes an inversion layer, resulting in keeping APM in lower atmosphere during the wintertime. Toxic heavy metal elements such as As, Se, Cd, Sb and Pb were found in high concentration levels besides the major elements such as Na, Mg, Al, K and Ca, when APM was analyzed by size. By evaluating the enrichment factors of the analyzed elements, it became apparent that the atmosphere of Tokyo was seriously polluted by toxic heavy metal elements. The enrichment factors of each element showed seasonal trends. The correlation coefficient was calculated, and the elements could be grouped into 3 types according to the similarity of seasonal trend; (group 1: Na, K, Ca and Fe), (group 2: V, Cr and Ni) and (group 3: Cu, Zn, Mn, As, Se, Cd, Sb and Pb). Each group of elements is likely to have similar sources. Sb was most seriously polluted. It was found 3 times concentrated compared to As, which belongs to the same group in the periodic table. Fly ash from the combustion of plastic products and brake pads of automobiles are likely to be the contributory origins of Sb pollution. These products are treated with antimony sulfide, to be flame and heat resistant.

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