Characteristics of Nanoparticulate Matter Collected in Tokyo Metropolitan Area: Focusing on Particles Containing Heavy Metals

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1. Introduction

Our research group has performed long-term monitoring of size-classified Airborne Particulate Matter (APM) in Tokyo since 1995 [1]. The averaged enriched factors of major elements such as Na, Fe were high in coarse particle, whereas those of toxic trace elements such as As, Se, Cd, Sb and Pb were extremely enriched in fine APM (PM2.5). Especially, Sb is tremendously enriched in fine APM, and large anthropogenic emission sources had been implied. Our previous study demonstrated a number of edge-shaped fine APM contained high concentration of Sb, which inferred brake abrasion dusts generated from friction of brake pads are one of the major atmospheric Sb sources [1]. Based on this background, we sampled size-classified APM at urban and roadside sites in Tokyo metropolitan area, and the characteristics of the nanoparticulate matter fraction such as shape and elemental composition were investigated by bulk analysis using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and single particle analysis using a Scanning Electron Microscope equipped with Energy Dispersive X-ray spectroscopy (SEM-EDX).

2. Single particle measurement of fine APM (PM2.5) collected at roadside and ambient sites in Tokyo

Field sampling of fine APM (PM2.5) was performed simultaneously in urban and road side atmosphere in central Tokyo, and then shape and elemental composition of single APM was measured by SEM-EDX. From the shape distribution of fine APM by SEM, each shape of fine APM distribute almost equally in the urban atmosphere, whereas edge-shaped and cotton-like APM dominated at the roadside atmosphere. Edge-shaped and cotton-like APM are generated by mechanical abrasion and coagulation of nano-sized particles, respectively. Consequently, automobile originated APM such as brake dusts and road dusts generated by mechanical abrasion and coagulated diesel exhaust particles are considered be dominant sources of fine APM in roadside atmosphere.

From the elemental analysis by EDX, high concentration of Sb was found in spherical and edge-shaped APM in urban atmosphere. Our previous study showed that brake pads contain few % of Sb [2], and thus many of edge-shaped APM were considered to be originated from mechanical abrasion of brake pads. The other possible major source of Sb is incineration of plastic materials which are major use of Sb in Japan [3]. The spherical APM containing high Sb is presumably associated with incineration of plastic materials.

In the roadside atmosphere, high concentration of Sb was found in edge-shaped and cotton-like fine APM. The major sources of was edge-shaped APM containing high Sb is

considered to be brake abrasion dusts. The possible sources of cotton-like APM are coagulation of nano-sized brake abrasion dusts and microparticulation of gaseous Sb. A lead electrode plate in most starter battery contain up to 2.5 % Sb, and SbH_3 will be generated while charging a starter battery, particularly at the end of charging or upon overcharging [4]. Consequently, edge-shaped and cotton-like fine APM in the roadside atmosphere are mainly originated from automobile related emission sources such as brake abrasion dusts and coagulated particles containing volatile Sb in a starter battery.

3. Bulk analysis and single particle measurement of size classified APM collected at a roadside site in Tatebayashi

In order to investigate characteristics of nanoparticulate matter in high size resolution, field sampling was performed in Tatebayashi, a suburban city of Tokyo metropolitan area, by using a low pressure impactor (13 classes, Particle size range: 0.06 μm – 11 μm). Then, elemental distribution of size classified APM was investigated by bulk analysis using ICP-MS. APM showed a characteristic bimodal profile in which peaks were found in coarse (3.6 – 5.2 μm) and fine (0.5 – 0.7 μm) fractions. The coarse fraction of APM was well agreed with the elemental ratios of Cu/Sb and Ba/Sb in brake dusts [5]. On the other hand, the fine fraction was well agreed with the elemental ratios of Cd/Sb and Pb/Sb in waste fly ash [5]. Furthermore, shape and elemental mapping of coarse and fine APM were similar to those of brake dusts and fly ash, respectively. Consequently, it was suggested that micron-sized APM containing high concentration of Sb is mainly originated from brake abrasion dusts, and nano-sized APM containing high concentration of Sb is mainly originated from waste fly ash.

4. Conclusions

From the field investigation of size-classified APM in Tokyo metropolitan area, APM containing high Sb, one of toxic heavy metals, could be characterized by bulk analysis using ICP-MS and single particle analysis using SEM-EDX. In the urban atmosphere, spherical and edge-shaped APM containing high Sb are considered to be mainly originated from plastic materials from incinerators and breke abrasion dusts, respectively. In the roadside atmosphere, automobile related APM such as brake dusts and nano-sized particles generated by nucleation of SbH_3 from a starter battery are major sources of APM containing high Sb.

(References)

[1] N. Furuta et al., *J. Environ. Monitor.*, **7**. 1155-1161 (2005).
[2] A. Iijima et al., *Atmos. Environ.*, **41**, 4908-4919 (2007).
[3] Japan Oil, Gas and Metals National Corporation, *2006 Material flow of mineral resource* (2007).
[4] M. Kentner et al., *Int. Arch. Occup. Environ. Health*, **67**, 119-123 (1995).
[5] A. Iijima et al., *Environ. Chem.*, **6**, 122-132 (2009).

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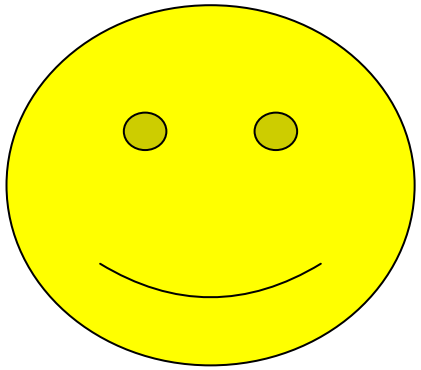

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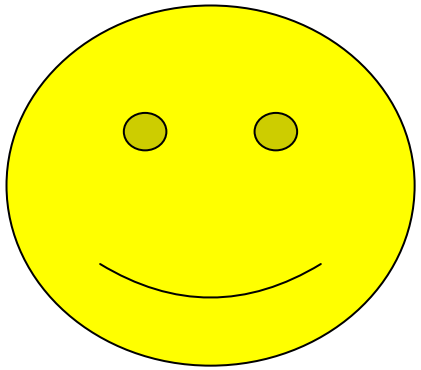

13th ETH-Conference on Combustion Generated Nanoparticles

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1. Objective of the study, measurement method of airborne particulate matter (APM)

Long-term Monitoring Results of Major and Trace Elements in Size Classified APM (1995.5 - 2007.3)

N. Furuta et al., *J. Environ. Monit.*, **7**, 1155-1161 (2005).
K. Sato et al., *J. Environ. Monit.*, **10**, 211-218 (2008).

Element	crust	APM (< 2 μm)			APM (2 - 11 μm)			APM (> 11 μm)		
	ng g⁻¹	μg g⁻¹	ng m⁻³	EF	μg g⁻¹	ng m⁻³	EF	μg g⁻¹	ng m⁻³	EF
Na	23600	7460	166	5.2	49300	565	7.6	21900	91.6	2.3
Mg	22000	1560	35.7	1.0	11500	141	1.8	9110	41.2	1.0
Al	79600	6370	146	1.0	26700	333	1.0	41400	184	1.0
K	21400	8050	187	6.5	10200	128	1.6	7500	33.9	0.9
Ca	38500	6760	151	2.6	38100	454	3.2	60800	257	3.4
Fe	43200	10000	226	3.7	41100	489	3.2	41600	187	2.2
Li	18	9.1	0.22	8.5	14.2	0.19	2.5	11.4	0.056	1.8
Be	2.4	0.2	0.01	1.3	0.8	0.01	1.0	0.83	0.004	0.8
Ti	4010	451	10.5	1.7	2200	27.5	1.8	2670	11.8	1.5
V	98	208	4.51	37.7	103	1.3	3.7	97.6	0.439	2.3
Cr	126	111	2.47	15.9	277	3.2	7.7	348	1.40	6.2
Mn	716	688	15.9	17.3	1030	12.5	4.9	1090	4.76	3.5
Co	24	5.8	0.13	4.1	15.6	0.19	2.1	17.4	0.077	1.6
Ni	56	139	3.04	45.8	137	1.57	8.7	222	0.83	8.6
Cu	25	440	10.3	330	1060	12.2	147	515	2.12	46.3
Zn	65	4920	114	1460	4260	50.1	225	2180	8.82	74.3
As	1.7	66.7	1.53	706	31.2	0.40	61.5	10.6	0.047	14.9
Se	0.1	57.3	1.28	8600	14.4	0.18	448	3.62	0.016	67.5
Mo	1.1	71.4	1.59	1140	88.4	1.01	275	87.0	0.384	164
Cd	0.1	42.1	1.03	8340	14.4	0.19	501	4.21	0.017	93.4
Sb	0.3	180	4.35	12000	181	2.14	3780	52.3	0.212	394
Ba	584	236	5.16	6.5	1150	13.3	6.7	581	2.42	2.3
Pb	14.8	1410	34.9	1890	645	8.50	155	264	1.13	40.6

- Elemental concentrations of major elements were high in coarse and those of trace elements were high in fine APM.
- Toxic elements such as As, Se, Cd, Sb and Pb were extremely enriched in fine APM (d < 2.1 μm).

Objective of this study

Bulk analysis of size classified APM by Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

→ Elemental composition distribution of nanoparticulates which is useful for source identification

Source information obtained from single particle measurement

Scanning Electron Microscope (SEM)	Energy Dispersive X-ray spectroscopy (EDX)
⇩	⇩
Shape	Elemental composition
• Spherical → Thermal • Edge-Shaped → Abrasion • Coagulated → Nano particles	(Marker elements) • Soil → Mg, Al, Ca • Diesel → C, N, S • Heavy Oil → V, Cr, Ni

Size classified APM including nanoparticulate was collected in Tokyo Metropolitan Area, and characteristics of the nanoparticulate matter such as shape and elemental composition were investigated in order to identify emission sources of nanoparticulate matter.

Sampling sites and measurement methods

Roadside in Tatebayashi

Roadside in Tokyo

Ambient in Tokyo

> 12 μm
8.5 - 12 μm
5.7 - 8.5 μm
3.9 - 5.7 μm
2.5 - 3.9 μm
1.25 - 2.5 μm
0.76 - 1.25 μm
0.52 - 0.76 μm
0.33 - 0.52 μm
0.22 - 0.33 μm
0.13 - 0.22 μm
0.06 - 0.13 μm
< 0.06 μm

Low pressure impactor
Total 13 stages
(LP-20, Tokyo Dylec inc., Japan)

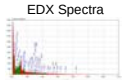
Bulk analysis
Agilent 7500cx
Agilent Technologies Inc.

→ Elemental composition of size classified APM

Single particle measurement
JSM-5600LVB-JED2200
JEOL Ltd.

SEM Image

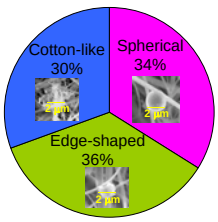
EDX Spectra



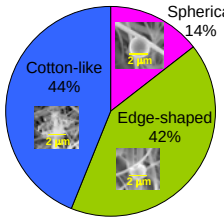
2. Single particle measurement of fine APM (PM2.5) collected at roadside and ambient sites in Tokyo

Shape distributions of fine APM obtained by ambient and roadside sampling in December 2006

Ambient (n = 219)



Roadside (n = 466)



〔Ambient〕
- Respective shape APM were equally distributed.
  - ➢ Spherical
    Originated from waste incineration.

〔Roadside〕
- Cotton-like and edge-shaped APM accounted for a large portion of fine particle.
  - ➢ Edge-shaped
    Mainly originated from mechanical abrasion dusts such as road dusts and brake abrasion dusts.
  - ➢ Cotton-like
    Mainly originated from nano-sized particles (secondary particles) from automobiles.
  - ➢ Spherical
    Hard to be transported to roadside because of shielding by overpass.

Average elemental concentrations (n = 20) in shape classified fine APM collected in December 2006

Ambient	Na	Mg	Al	S	Ti	Cr	Fe	Cu	Zn	Sb	Ba
Spherical	1460	1880	14500	680	770	200	2580	2480	400	1970 (8)	8720
Edge shaped	7480	1540	6060	4590	460	1210	47900	44400	7610	2770 (10)	44400
Cotton like	1140	910	4400	640	110	160	2920	1300	210	270 (4)	11500
Roadside	**Na**	**Mg**	**Al**	**S**	**Ti**	**Cr**	**Fe**	**Cu**	**Zn**	**Sb**	**Ba**
Spherical	1370	6530	8960	1930	1700	230	24700	4090	420	850 (4)	58200
Edge shped	2760	1300	6440	850	800	360	18300	1790	260	1660 (13)	17400
Cotton like	760	800	300	450	420	240	1500	1020	200	770 (10)	5260

Values in parentheses indicate the numbers of APM with [Sb] > 100 μg / g out of 20 particles

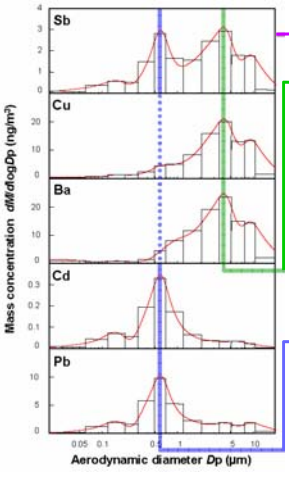
(References)
[a] A. Iijima et al., *Atmos. Environ.*, **41**, 4908-4919 (2007).
[b] Japan Oil, Gas and Metals National Corporation, *2006 Material flow of mineral resource* (2007).
[c] M. Kentner et al., *Int. Arch. Occup. Environ. Health*, **67**, 119-123 (1995).

〔Ambient〕
- High concentration of Sb was found in spherical and edge-shaped fine APM.
  - ➢ Edge-shaped
    Brake pads contain few % of Sb. ref. [a]
    Many of them were originated from mechanical abrasion of brake pads.
  - ➢ Spherical
    Plastic materials are major use of Sb in Japan. ref. [b]
    Some of them were originated from combustion of plastic materials.

〔Roadside〕
- High concentration of Sb was found in edge-shaped and cotton-like fine APM.
  - ➢ Edge-shaped
    Originated from mechanical abrasion of brake pads.
  - ➢ Cotton-like
    May be originated from nucleation of SbH_3 generated from a starter battery. ref. [c]

3. Bulk analysis and single particle measurement of size classified APM collected at a roadside site in Tatebayashi

Elemental distribution of size classified APM (collected in September 2008)



(Reference)
A. Iijima et al., *Environ. Chem.*, **6**, 122-132 (2009).

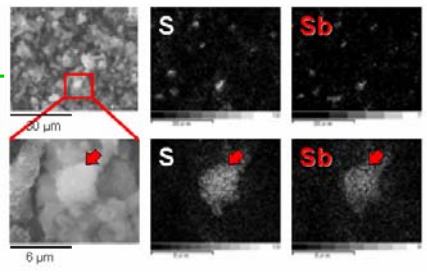
Sb showed bimodal profile. The peaks are found at ca. 4 μm (coarse) and 0.6 μm (fine) fractions.

[Coarse fraction]
- ➢ Elemental distribution
  Sb, Cu and Ba showed the peaks at the same particle size fraction. These elements are considered as a tracer of brake dusts.
  Elemental ratios of Cu/Sb and Ba/Sb of brake dusts were calculated in our previous study (Iijima et al., 2007). These values are similar to the elemental ratios in the coarse fraction.
- ➢ Single particle measurement
  Intensive signal of S and Sb were simultaneously detected in an edge-shaped particle. Also the same results were obtained in the measurement of brake dusts.

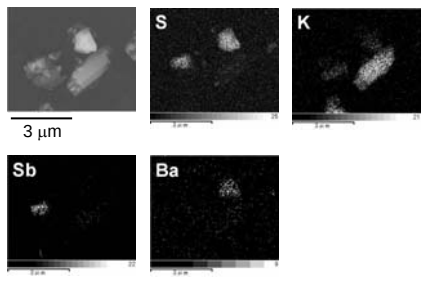
[Fine fraction]
- ➢ Elemental distribution
  Sb, Cd and Pb showed the peaks at the same particle size fraction. These elements are considered as a tracer of fly ash originated from waste incineration.
  Elemental ratios of Cd/Sb and Pb/Sb of fly ash were calculated to be ca. 0.1 to 0.4. (Iijima et al., 2009) These values are similar to the elemental ratios in the coarse fraction.
- ➢ Single particle measurement
  Intensive signal of S and K and weak signal of Sb were simultaneously detected in an edge-shaped particle. Also the same results were obtained in the measurement of fly ash.

Shape and elemental mapping of size classified APM, brake dusts and fly ash originated from incineration

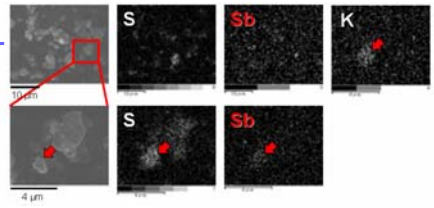
Coarse fraction APM (3.6 μm < Dp < 5.2μm)



Brake dusts collected from indoor experiments

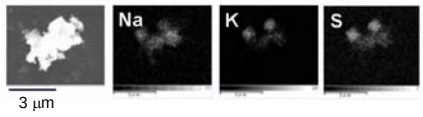


Fine fraction APM (0.5 μm < Dp < 0.7μm)

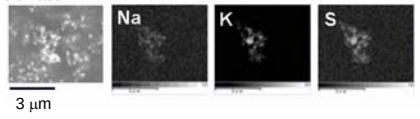


Fly ash collected from incineration plants

waste



biomass



4. Conclusions

- From measurement at roadside and ambient sites in Tokyo, automobile originated particles were dominant at roadside and brake dusts were a prominent source of Sb. Especially, cotton-like particles (submicron size) at roadside contained high amount of Sb. This nanoparticles may be originated from nucleation of SbH_3 generated from a starter battery.
- From bulk analysis and single particle measurement of size classified APM collected at a roadside site in Tatebayashi, the distribution of Sb concentration in size-classified APM showed a characteristic bimodal profile in which peaks were found in coarse (3.6 – 5.2 μm) and fine (0.5 – 0.7 μm) fractions.
- The coarse fraction of APM were presumably associated with brake dust sources, whereas the fine fraction was associated with fly ash originated from incineration.