Regional and seasonal characteristics of emission sources of fine airborne particulate matter collected in the center and suburbs of Tokyo, Japan as determined by multielement analysis and source receptor models†

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Received 16th April 2008, Accepted 21st June 2008
First published as an Advance Article on the web 29th July 2008
DOI: 10.1039/b806483k

Airborne particulate matter, suspected to induce adverse effects on human health, have been one of the most important concerns regarding recent air pollution issues in Japan. To characterize regional and seasonal variations in emission sources of fine airborne particulate matter ($d < 2$ μm), monthly samples ($n = 36$ for each site) were collected at urban (Tokyo), suburban (Maebashi), and mountainous (Akagi) sites in Japan from April 2003 to March 2006. Multielement analysis of chemical species (Na, Al, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sb, and Pb) was performed by inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry. The combined source receptor model, which consists of positive matrix factorization and chemical mass balance, determined the contributions of nine emission sources (local and continental soils, road dust, coal and oil combustion, waste incineration, steel industry, brake wear, and diesel exhaust) to the observed elemental concentrations. Large regional differences were identified in the source contributions among the observational sites. Diesel exhaust was identified as the most significant source (70% of identified contributions) at the urban site. Local and continental soils, coal combustion, and diesel exhaust were intricately assigned (20–30% each) to the suburban site. Continental soil was the predominant source (65%) at the mountainous site. Respective significant source contributions dominated the seasonal variations of total elemental concentrations at each site. These results suggest that a better understanding of the regional and seasonal characteristics of impacting emission sources will be important for improving regional environments.

1. Introduction

Airborne particulate matter (APM) contains various kinds of chemicals originating from wide varieties of natural and anthropogenic sources.[1] Since fine APM contains harmful substances such as heavy metallic elements and polycyclic aromatic hydrocarbons, it is expected to induce adverse effects on human health. Moreover, since fine APM has a long residence time, its adverse effects can be widely spread by atmospheric circulation. Recently, anthropogenic emissions from Asian countries have increased with a rapid economic growth, and it is expected to continue increasing over the next several decades.[2] For these reasons, the effect of air pollutants transported by westerlies from Asian countries has been highlighted in Japan.[3,4] Therefore, identification of pollutant sources including not only local but also cross-boundary origins is essential for improving air quality in Japan.

Metallic elements contained in environmental samples are considered to be an excellent fingerprint indicating their origins.[5] Source receptor model, one of the most powerful tools for identifying pollutant sources of APM, can determine source contributions by focusing on the elemental fingerprint.[6] In general, elements originating from the same sources are expected to reveal a similar seasonal trend. Therefore, emission sources could be identified on the basis of seasonal variation of the elemental concentration. A receptor model, positive matrix factorization (PMF), can extract several factors from observational data set according to the difference in seasonal trend.[7] In other words, the advantage of PMF is well-defined source extraction. Extracted factors consist of the contributions to an observational data and chemical profiles. From the relationship of seasonal variation between the extracted factor contribution and wind direction, the most probable location of the emission source can be identified.[8] Moreover, by focusing on the chemical profiles of the extracted factor, emission sources can be assigned to each factor.[9,10] However, since specific sources are often subjectively assigned, the combined sources in one profile may be missed. A conventional source receptor model, chemical mass balance (CMB), can objectively assign several specific sources according to the mass balance of the chemical composition between the source chemical profile database and observed atmospheric concentration.[11] The advantage of CMB is a more

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† Presented at the 2008 Winter Conference on Plasma Spectrochemistry, Temecula, CA, USA, January 7–12, 2008.

clear source assignment. However, since the seasonal trends of observational data cannot be considered in CMB, it is difficult to identify the location of the emission source in most cases.

Consequently, by combining the respective advantages of PMF (source extraction) and CMB (source assignment), we determined the source contribution of metallic elements in fine APM ($d < 2$ μm) collected at three sites (urban, suburban, and mountainous). PMF extracted several significant factors from the observational data set, and the chemical profiles of the extracted factors were subsequently analyzed by CMB which enables assignment of several specific sources. To identify the locations of emission sources, the frequencies of backward air mass trajectories were also estimated. From these combined results, we investigated the regional and seasonal characteristics of the source contributions among three different locations around the Tokyo Metropolitan Area in Japan.

2. Experimental

2.1. Observation sites

Field monitoring of APM was performed monthly at an urban site (Tokyo; 35.7°N, 139.7°E, approximately 70 m above the sea level, asl), suburban site (Maebashi: MA; 36.4°N, 139.1°E, approximately 130 m asl), and mountainous site (Akagi: AK; 36.5°N, 139.2°E, approximately 1500 m asl) (Fig. 1) in the Kanto Area, Japan. The Tokyo Metropolitan Area (TMA), corresponding to the 70 km radius area from the center of Tokyo, has a large population (more than 34 million people corresponding to 30% of the national population)[12] and heavy traffic (18 million vehicles corresponding to 20% of the national number).[13] Massive industrial complexes are distributed around Tokyo Bay. The monitoring site in Tokyo is located in the center of the TMA. The MA site is located in a small city (population, 0.3 million) situated in a northwestern suburban area 100 km away from the center of Tokyo, and residential areas and agricultural fields are spread around this monitoring site. The AK site is located in a mountainous area (16 km north-east of MA) and has no significant anthropogenic sources.

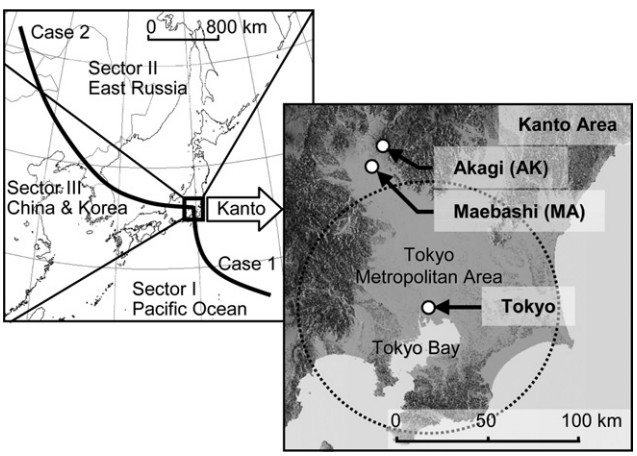

Fig. 1 Observation sites of fine APM and sector classification for backward trajectory analysis; (I) Pacific Ocean, (II) East Russia, and (III) China and Korea. Bold curves indicate typical trajectories (Cases 1 and 2). Backward trajectories had a 5 day duration and arrived at each site at 0300 UT (1200 JST). The calculation altitudes were fixed at 500, 500, and 1500 m for Tokyo, MA, and AK, respectively.

2.2. Elemental analysis

Size-classified APM (with $d < 2$, 2–11, and > 11 μm) was collected monthly from April 2003 to March 2006 on a quartz fiber filter (2500 QAT-UP, Pallflex Products Co., Putnam, USA) using an Andersen low-volume air sampler (AN-200 Tokyo Dylec Co., Tokyo, Japan). In this study, we focused on fine APM ($d < 2$ μm) to highlight the contribution of cross-boundary transport. Most of the analytical data at Tokyo are cited from our previous reports.[1,14] Fine APM samples at MA and AK were digested in a mixture of 2 mL of hydrofluoric acid (50% AAS grade, Kanto Chemical Co., Inc., Tokyo, Japan), 3 mL of nitric acid (60% ultrapure chemicals), and 1 mL of hydrogen peroxide (30% AAS grade) in a microwave digestion system (Multiwave, Anton Paar GmbH, Graz, Austria) under the condition of 700 W for 10 min and 1000 W for a further 10 min. Hydrofluoric acid was evaporated by heating the sample solution at 200 °C on a hot plate, and 0.1 mol L^{-1} nitric acid (prepared from 60% nitric acid) was then added to obtain a 50 mL sample. The concentrations of Na, Al, K, Ca, and Fe were determined by inductively coupled plasma-atomic emission spectrometry (Ciros CCD, Rigaku, Tokyo, Japan), and those of V, Cr, Mn, Ni, Cu, Zn, As, Sb, and Pb were determined by inductively coupled plasma-mass spectrometry (SPQ9000, Seiko Instrument, Inc., Chiba, Japan). All analytical procedures were validated by the certified reference material CRM 1648 (urban particulate matter) prepared by the US National Institute of Standard and Technology. The analytical results showed good agreement with the certified and reference values.

2.3. Air mass trajectory analysis

To clarify the origins of air masses arrived at the sites, the backward air mass trajectories for each monitoring site were calculated for every sampling day. The trajectories had a 5 day duration and arrived at each site at 0300 UT (1200 JST). The Center for Global Environmental Research-Meteorological Data Explorer (CGER-METEX)[15] was used for the calculation of trajectories (approximately 25 trajectories were calculated per month for each site). The air mass origins were classified into three sectors (see Fig. 1, I; Pacific Ocean, II; East Russia, III; China and Korea) according to their atmospheric transport pathways, and the number of sector-classified trajectories was counted by month according to the following criteria: for a trajectory passing through only one sector, 1 count was added to that sector (*e.g.*, Case 1 in Fig. 1; sector I received 1 count); for a trajectory passing through two or three sectors, an equally divided count was added to each sector (*e.g.*, Case 2 in Fig. 1; sectors II and III received 0.5 count each).

2.4. Principal of receptor models

The PMF model basically assumes that the number of factors is p, that is, several sources impacting a receptor, and that the linear combinations of these impacts from the p factors give rise to the observed concentrations of various elements.[7] In PMF, the objective is to estimate the contributions and chemical profiles of

Table 1 Source chemical profile database for CMB

Emission source	Elemental concentration (%)													
	Na	Al	K	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Sb	Pb
Local soil [a]	0.92	8.93	0.83	1.54	0.0221	0.0057	0.114	5.90	0.0043	0.0112	0.0154	0.00100	0.000109	0.0032
Continental soil [b]	1.59	5.4	2.04	2.73	—	—	0.048	2.20	—	—	—	—	—	—
Road dust [c]	1.58	5.1	1.29	5.06	0.00978	0.0649	0.0814	4.74	0.0540	0.0574	0.161	0.000594	0.00315	0.0257
Coal combustion [d]	0.97	2.6	1.0	2.3	0.013	0.040	0.031	1.8	0.018	—	0.30	0.026	0.0081	0.20
Oil combustion [d]	1.0	0.21	0.085	0.085	0.92	0.021	0.012	0.46	0.49	—	0.040	0.0023	0.0069	0.033
Waste incineration [c]	2.62	8.26	2.41	8.35	0.00745	0.0235	0.0689	3.11	0.00496	0.0837	0.291	0.00161	0.00899	0.0349
Steel industry [e]	1.3	1.1	3.0	1.0	0.0089	0.052	4.5	15	0.035	0.26	0.83	0.013	0.037	0.23
Brake wear [c]	0.103	0.27	1.49	1.19	0.0118	0.00429	0.0246	3.01	0.00445	4.20	0.125	—	1.39	0.00228
Diesel exhaust [f]	0.13	0.16	—	0.15	0.00073	0.0036	0.0019	0.10	0.0032	0.011	0.062	0.00037	0.0020	—

[a] Recalculated from ref. 18. Surface soils ($n = 99$) were sampled in the Tokyo Metropolitan Area, Japan. [b] Recalculated from ref. 19. Surface soils ($n = 3$) were sampled in Inner-Mongolia Plateau. [c] Cited from ref. 1. Road dust was sampled from an arterial highway in Tokyo, waste incineration fly ash was sampled from a municipal incinerator in Tokyo, and brake dust was sampled from an automotive brake pad. Fe data in brake wear was cited from ref. 20. [d] Cited from ref. 21. Coal combustion particulates ($n = 5$) and oil combustion particulates ($n = 13$) were sampled from boilers and heavy oil boilers in Japan, respectively. [e] Cited from ref. 22. Dust particulates ($n = 5$) were sampled from coke heating cupola furnaces in Japan. [f] Recalculated from ref. 23.

p factors which are potentially impacting to a receptor. The uncertainty for each elemental concentration was specified as the analytical detection limit, and the percentage uncertainty was assumed as 5%. Mathematical algorithm was processed by the EPA-PMF.[7]

The general CMB model consists of a solution to linear simultaneous equations expressing each observed chemical concentration as the sum of the products of source chemical profiles and source contributions.[16] In this study, sources having high multicollinearity were excluded by the least-square method to eliminate negative contributing sources. Mathematical algorithm was processed using the Visual Basic for Applications CMB8J[17] transcribed from the CMB8 algorithm. The source chemical profile data base[18–23] used in this study is shown in Table 1.

3. Results and discussion

3.1. Results of elemental analysis for fine APM

Results of multielement analysis for fine APM collected at the Tokyo, MA, and AK sites are summarized in Table 2. For most elements, the highest concentrations were observed at Tokyo, whereas the intermediate and lowest values were observed at MA and AK, respectively. This shows that the concentrations of the elements are dependent on the distance of these sites from central Tokyo. Total elemental concentrations at each site tended to increase from December to May (winter to spring). Enrichment factor (EF) is a good indicator to distinguish whether an element originates from natural or anthropogenic sources. Generally, EF was calculated as the ratio of elemental composition between APM and a reference sample such as the Earth's crust.[1] When the EF of an element is close to 1, this element is considered to originate from natural sources. When EF is much larger than 1, it is likely that the element originates from anthropogenic sources. The EFs summarized in Table 2 were calculated by using the elemental composition of the Earth's crust[24] as a reference sample. It should be noted that the EF values depend on the reference sample composition. In fact, Krachler *et al.*[25] demonstrated that the EF varies an order of magnitude among different reference samples. In this study, the EF only aimed to distinguish whether the element originated from natural or anthropogenic sources. As seen the EFs of Na, K, Ca, and Fe are close to 1 at all the monitoring sites, indicating that these elements probably

Table 2 Average elemental concentrations and enrichment factors (EF) in fine APM (April 2003–March 2006)

Element	Elemental abundances in Earth's crust[a] /μg g^{-1}	Tokyo[b]		Maebashi (MA)		Akagi (AK)	
		/ng m^{-3}	EF	/ng m^{-3}	EF	/ng m^{-3}	EF
Na	23 600	151	3.08	79.5	1.63	36.7	2.17
Al	79 600	165	1.00	165	1.00	57.0	1.00
K	21 400	164	3.70	86.4	1.95	35.2	2.29
Ca	38 500	157	1.96	144	1.81	67.4	2.45
V	98	4.19	20.6	2.03	10.0	0.765	10.9
Cr	126	2.04	7.82	2.65	10.2	0.570	6.32
Mn	716	14.1	9.52	10.2	6.86	3.34	6.51
Fe	43 200	219	2.44	147	1.64	48.1	1.55
Ni	56	2.46	21.2	1.87	16.2	1.24	31.0
Cu	25	7.21	139	4.36	84.3	1.87	104
Zn	65	86.1	639	43.6	324	15.8	339
As	1.7	1.29	365	0.994	283	0.619	509
Sb	0.3	2.47	3970	2.17	3500	0.498	2320
Pb	15	19.3	628	12.9	421	6.13	578

[a] Cited from ref. 24. [b] Cited from ref. 1 and 14.

originated from natural sources. The EFs of the other elements, such as Zn, As, Sb, and Pb are found to be quite large, suggesting that these elements probably come from anthropogenic sources. In particular, Sb has a markedly high EF. Several recent studies documented that Sb enrichment may be associated with vehicular traffic.[1,19,26,27] Note that the EFs of most elements at AK were almost equal to those in MA, although there were no significant anthropogenic sources around AK. These observations suggest that long-distance transport of anthropogenic pollutants from the TMA or the Asian continent most likely affects the air quality at mountainous areas.

3.2. Seasonal profiles of backward air mass trajectories

Fig. 2 shows the seasonal profiles of backward air mass trajectories at three monitoring sites. As for the meteorological characteristics in Japan, the southeastern monsoon dominates in summer, whereas the northwestern monsoon dominates in winter. Although the seasonal profiles of air mass origins were consistent with these meteorological characteristics, a regional difference was found for each site. Except in winter, the frequency of sector I (Pacific Ocean) at Tokyo was larger for two other sites, and in particular, this sector was dominant in summer. On the contrary, the frequency of sector III (China and Korea) at AK was larger than for two other sites. Because AK is located at high altitude, the westerlies from the Asian continent might strongly affect mountainous air mass advection during all seasons.

3.3. Factor extraction and source assignment by PMF-CMB

PMF extracted four (TF1–TF4), four (MF1–MF4), and five (AF1–AF5) factors for Tokyo, MA, and AK, respectively. Extracted factor contributions and elemental profiles are depicted in Fig. 3 and 4, respectively. As mentioned above, total elemental concentrations tended to increase from winter to spring. Model calculations using the extracted factors were in good agreement with the observational data ($r^2 = 0.988$ for Tokyo, 0.984 for MA, and 0.986 for AK). First, to identify the location of an emission source, the correlation coefficient was calculated between the sector-classified air mass frequencies (Fig. 2) and the extracted factor contributions (Fig. 3). Table 3(a) shows the correlation coefficient between these two data, both of which were obtained for each month. Next, according to the mass balance between the source chemical profile database (Table 1) and each elemental profile extracted by PMF (Fig. 4), CMB assigned nine specific emission sources (two natural sources; continental and local soils, seven anthropogenic sources;

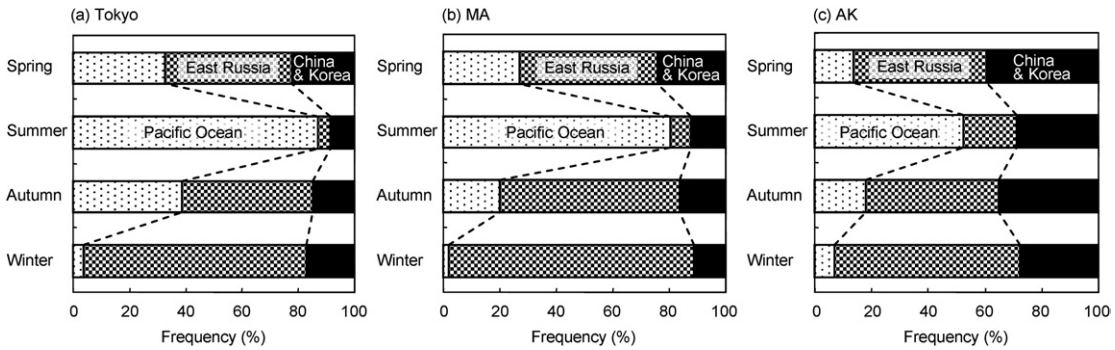

Fig. 2 Frequency distribution of sector-classified air mass trajectories for (a) Tokyo, (b) MA, and (c) AK. According to the advection route, daily backward trajectories were classified into three sectors: ⁝⁝(I) Pacific Ocean, ▩; (II) East Russia, and ■; (III) China and Korea. The frequency of sector-classified daily trajectories was counted by month according to the criteria described in the text. Monthly data were seasonally averaged (Spring: March to May; Summer: June to August; Autumn: September to November; Winter: December to February).

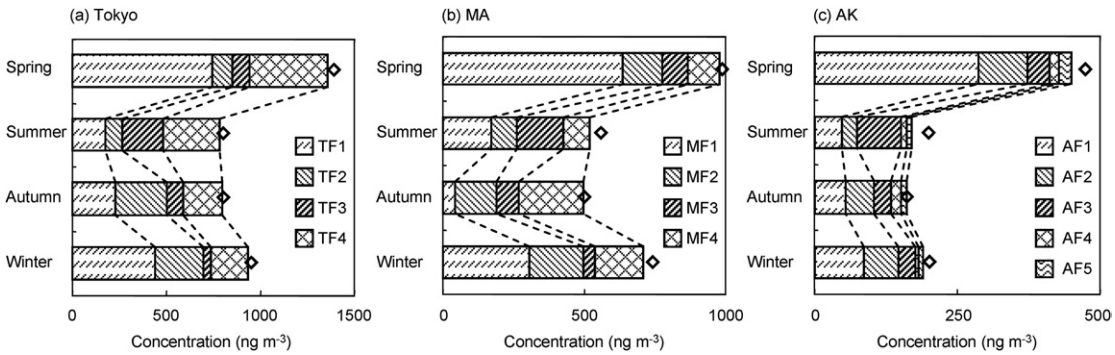

Fig. 3 Seasonal variation of extracted factor contributions to total element concentration observed in (a) Tokyo, (b) MA, and (c) AK. PMF extracted four (TF1–TF4), four (MF1–MF4), and five factors (AF1–AF5) from the observational data set in Tokyo, MA, and AK, respectively. ◇ indicates total elemental concentration analyzed in this study. Monthly data were seasonally averaged (Spring: March to May; Summer: June to August; Autumn: September to November; Winter: December to February).

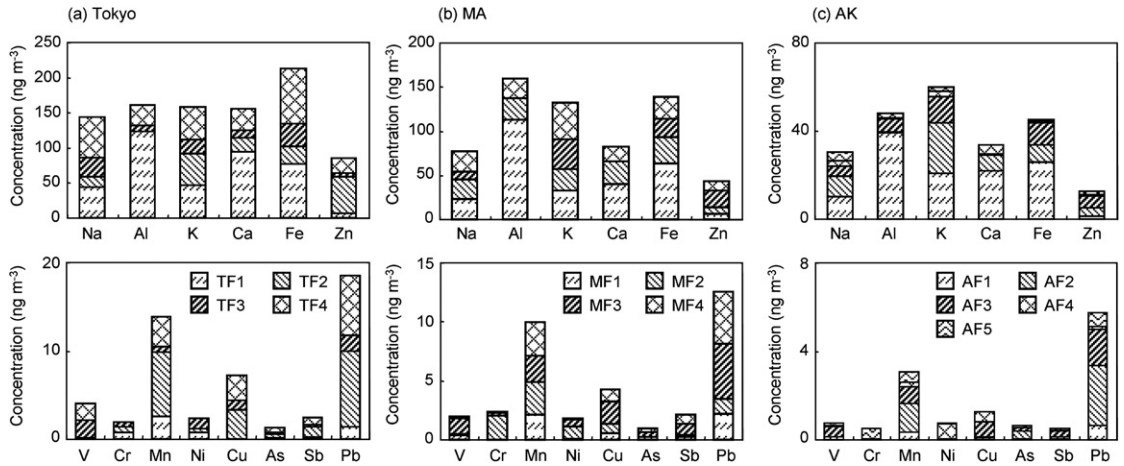

Fig. 4 Elemental profiles of extracted factors for (a) Tokyo, (b) MA, and (c) AK. TF1–TF4, MF1–MF4, and AF1–AF5 indicate PMF extracted factors in Tokyo, MA, and AK, respectively.

Table 3 Summary of potential sources given by the combined PMF and CMB model

(a) Correlation coefficient[a] between the factor contribution and the sector-classified air mass frequency

		Tokyo				MA				AK				
Sector	Region	TF1	TF2	TF3	TF4	MF1	MF2	MF3	MF4	AF1	AF2	AF3	AF4	AF5
I	Pacific Ocean	*−0.57*	*−0.45*	**0.70**	*−0.10*	*−0.22*	*−0.41*	**0.84**	*−0.47*	*−0.03*	*−0.48*	**0.43**	0.31	0.00
II	East Russia	**0.40**	**0.53**	*−0.67*	*−0.05*	**0.11**	**0.49**	*−0.83*	**0.34**	0.02	0.24	*−0.53*	*−0.22*	*−0.15*
III	China and Korea	**0.62**	0.16	*−0.35*	0.30	0.31	0.06	*−0.28*	0.29	**0.36**	**0.73**	0.06	*−0.11*	0.28

(b) Source contribution[b] assigned by the CMB (%)

Emission source		TF1	TF2	TF3	TF4	MF1	MF2	MF3	MF4	AF1	AF2	AF3	AF4	AF5
Natural	Local soil	—	—	—	—	35.2	—	—	—	—	—	10.5	—	—
	Continental soil	21.7	—	—	—	22.1	—	—	29.6	80.8	—	—	—	—
Anthropogenic	Road dust	3.7	—	—	—	—	7.8	—	—	—	—	—	—	—
	Coal combustion	4.5	9.9	14.2	—	39.4	2.1	—	32.7	10.5	0.7	—	0.7	—
	Oil combustion	—	—	5.2	—	—	—	18.0	0.2	1.1	1.3	18.0	0.1	8.5
	Waste incineration	—	—	—	—	3.1	—	—	—	—	—	—	—	—
	Steel industry	0.3	1.8	0.2	1.6	0.9	1.5	7.7	4.8	—	22.9	5.7	—	10.7
	Brake wear	—	0.9	0.4	3.6	0.5	0.1	4.8	2.8	0.2	0.7	4.3	0.2	6.3
	Diesel exhaust	70.0	46.7	51.6	—	—	—	67.1	—	—	—	—	23.3	—
Assigned		100.2	59.3	71.5	5.2	101.2	78.6	30.6	70.3	92.6	25.6	38.4	24.3	25.5
Unassigned		—	40.7	28.5	94.8	—	21.4	69.4	29.7	7.4	74.4	61.6	75.7	74.5

[a] Bold, significant ($p < 0.005$) positive correlation, italic, negative correlation. [b] Values which exceed 100% were caused by the uncertainty of calculation process in CMB analysis.

road dust, coal and oil combustion, waste incineration, steel industry, brake wear, and diesel exhaust) to each extracted factor. Table 3(b) shows the assigned source contributions. The notable features of the respective factors are described as follows.

(1) Factors: TF1, MF1, and AF1. These were significant factors at all sites from winter to spring (Fig. 3). Elements having low EFs were largely apportioned to these factors (Fig. 4), indicating that natural sources most likely affected to them. Note that a significant local soil contribution was found only at MA, whereas continental soil contribution was commonly found at all three sites (see Table 3(b)).

Generally, soil samples have various particle sizes depending on their origins. The particle sizes of the local soil in the Kanto area range from 1.6 to 31 μm.[28] Hence, few fractions of local soil may be collected as fine APM ($d < 2$ μm). At MA, however, the monitoring site is surrounded by agricultural fields, so that the contribution of local soil emission to fine APM fraction cannot be neglected. On the other hand, the geographical features of Tokyo (surrounded by concrete and asphalt paved road) and AK (covered with snow from December to April when wind blows strongly in Japan) may decrease local soil emission. On the contrary, the particle size of the continental soil (yellow sand) revealed a tri-modal structure ($d \approx 0.1$, 1.3–1.7, and 4.5–5 μm).[29]

Therefore, considerable amounts of continental soil could be transported by westeries toward Japan and collected as fine APM at three sites. In particular, continental soil dominated in AF1.

Coal combustion was also found in these three factors. Since major energy sources are quite different between China (coal) and Japan (oil),[30] the contribution of coal combustion can be considered as one of the key sources of anthropogenic emission from China. The magnitude of coal combustion was found to be much lower than those of continental soil in TF1 and AF1, whereas that of coal combustion in MF1 is almost twice larger than that of continental soil. However, there was no significant source related to coal combustion around all sites. This inconsistent outcome probably resulted from the uncertainties of calculation process in CMB. The elemental profile of MF1 had a relatively large Pb fraction compared with those of TF1 and AF1 (Fig. 4). In this study, Pb was treated as a fingerprint of coal combustion source in the chemical profile database (see Table 1). CMB assigned more than 75% of the Pb fraction in MF1 to this source. As a result, coal combustion revealed a considerably large contribution to MF1, suggesting that other Pb emission sources around MA should be investigated. On the other hand, diesel exhaust had a large contribution to TF1. In most cases of air masses transported from continental sectors, trajectories finally passed through the northern part of the TMA having a highly dense traffic zone.

(2) Factors: TF2, MF2, and AF2. Elements having high EFs were largely apportioned to these three factors (*e.g.*, Mn, Zn, Cu, Sb, and Pb for TF2; Cr, Mn, and Ni for MF2; Mn, As, and Pb for AF2) as shown in Fig. 4, indicating that anthropogenic sources most likely affected them. In fact, CMB assigned several anthropogenic sources such as diesel exhaust, coal combustion, and steel industry to these factors (see Table 3(b)). Coal combustion was commonly assigned to these factors, and statistically significant correlations were found between these factor contributions and air mass frequency from the continental sectors (see Table 3(a)). Therefore, these three factors may be combined anthropogenic sources that include cross-boundary origins.

(3) Factors: TF3, MF3, and AF3. Large portions of V and/or Ni were mainly assigned to these three factors (Fig. 4). Both V and Ni have been shown to be good indicators of heavy oil combustion.[21] In fact, CMB commonly assigned oil combustion to these factors (see Table 3(b)). Additionally, these factor contributions typically increased in summer, and had statistically significant correlations with the air mass frequency from the Pacific Ocean (see Table 3(a)). In most cases of air masses originally transported from the maritime sector, trajectories finally passed through the Tokyo Bay containing massive industrial complexes. Therefore, we assumed that these factors probably reveal local anthropogenic sources.

(4) Factor: TF4. The obvious seasonal trend of this factor is not seen (Fig 3). Note that little (5.2%) source contribution was assigned to this factor (Table 3(b)). Even though it had relatively large fractions of Zn and Pb, CMB could not assign any sources to a large portion of these elements. This might suggest that not yet known anthropogenic sources regarding Zn and Pb emission had large contributions to this factor.

(5) Factor: MF4. Although the elemental profile of MF4 was similar to MF1, the seasonal trend of this factor contribution was quite different (Fig. 3 and 4). Continental soil and coal combustion were largely assigned to MF4. Statistically significant fair positive correlation was found with the air mass frequency from East Russia as shown in both Tables 3(a) and (b). Therefore, this factor may be combined natural and anthropogenic sources that originate from the Asian continent.

(6) Factors: AF4 and AF5. Small fractions of each element were apportioned to these two factors (Fig. 4). Statistically significant correlations were not found between any sectors and these factors (see Table 3(a)). Hence, these two factors probably reveal local emissions sources. As shown in Table 3(b), assigned source contribution was low (approximately 25% in total), indicating that not yet known sources may contribute to AK.

3.4. Regional difference and seasonal characteristics of source contributions

To characterize the regional differences of the impacting sources, we attempted to partition local/cross-boundary and natural/anthropogenic contributions to the obtained results. First, from the results shown in Table 3(a) and (b), factors having a statistically significant positive correlation with the continental sectors (II or III) and/or including the source contribution of continental soil were interpreted as the combined origin of local and cross-boundary emission sources (L + C). Second, other factors were interpreted as only of local origin (L). Next, we distinguished the combined origins of both natural and anthropogenic (N + A) and only anthropogenic (A) sources. Table 4 shows a summary of interpretation for each factor. From this interpretation, local and cross-boundary contributions were partitioned and are shown in Fig. 5(a). In this estimation, continental soil and coal combustion, which were contained in the L + C factors, were interpreted as cross-boundary origin, and the other sources were interpreted as local origin. The local origins accounted for 80, 50,

Table 4 Interpretation of emission sources[a] for each extracted factor by PMF

	Tokyo				MA				AK				
Emission source	TF1	TF2	TF3	TF4	MF1	MF2	MF3	MF4	AF1	AF2	AF3	AF4	AF5
Local/cross-boundary	L + C	L + C	L	L	L + C	L + C	L	L + C	L + C	L + C	L	L	L
Natural/anthropogenic	N + A	A	A	A	N + A	A	A	N + A	N + A	A	N + A	A	A

[a] L: local source; C: cross-boundary source; N: natural source; A: anthropogenic source.

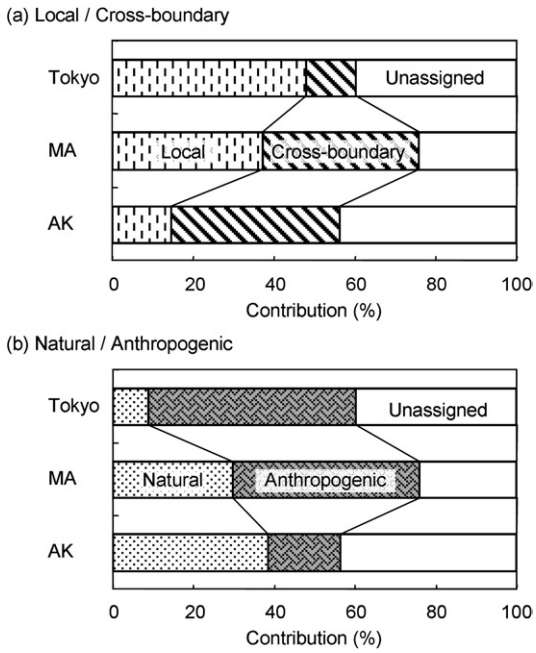

Fig. 5 Partitioning of emission sources for (a) local/cross-boundary and (b) natural/anthropogenic origins. From Table 3(a) (correlation between the extracted factor contributions and the sector-classified air mass frequencies) and Table 3(b) (source assignment to each extracted factor), local/cross-boundary and natural/anthropogenic contributions were separately determined.

and 25% of the identified contributions (correspond to 50, 35, and 15% of total contributions) for Tokyo, MA, and AK, respectively. Fig. 5(b) shows the partitioning between the natural and anthropogenic origins. The anthropogenic origins accounted for 85, 60, and 30% of the identified contributions (correspond to 50, 45, and 20% of total contributions) for Tokyo, MA, and AK, respectively. Therefore, local anthropogenic sources considerably affected air quality at urban Tokyo. On the contrary, cross-boundary natural sources have remarkable effects on air quality at the mountainous AK. Suburban MA had been affected by both local anthropogenic and cross-boundary natural origins.

The seasonal characteristics of the four major source contributions (local and continental soils, coal combustion and diesel exhaust) for each site are summarized in Fig. 6.

(1) Tokyo. At this urban site the diesel exhaust was the most significant source (70% of total assigned contributions). In particular, this contribution tended to increase from winter to spring, when air masses passed through a highly dense traffic zone located in the northern part of the TMA. Hence, regulating emission from diesel vehicles may be effective in improving air quality in the city. Since October 2003 the enforcement of the regulation of high-emission diesel vehicles was enacted around Tokyo, and so, it is necessary to monitor the contribution of diesel vehicles in the next decade to evaluate the effect of such regulation.

(2) Maebashi. At this suburban site the source contributions are very complex. Local and continental soils, coal combustion, and diesel exhaust were complicatedly assigned. Seasonal variation of total elemental concentration was dependent on these four contributions, suggesting that the consideration of both local and cross-boundary emission sources may be indispensable to APM. Coal combustion had a considerably large contribution (30% of total assigned contribution). However, CMB probably overestimated this contribution from the unknown Pb sources as mentioned above. Hence, when significant Pb sources will be identified, a large fraction of the overestimated contribution may be accurately reassigned.

(3) Akagi. At this mountainous site the continental soil was the dominant source. The seasonal variation of total elemental concentration was strongly dominated by this source. Although significant anthropogenic contributions were not found, the contribution of coal combustion revealed an obvious increase as well as that of continental soil. This suggests that the further worsening of air quality in Asian continental countries can also affect air quality at mountainous areas in Japan.

4. Conclusion

Multielement analysis and the combined positive matrix factorization and chemical mass balance model clarified regional and seasonal characteristics regarding the emission sources of metallic elements in fine airborne particulate matter. Different elemental fingerprints reflected unique sources at urban, suburban, and mountainous sites around Tokyo Metropolitan Area, Japan. At the urban site (Tokyo), local anthropogenic

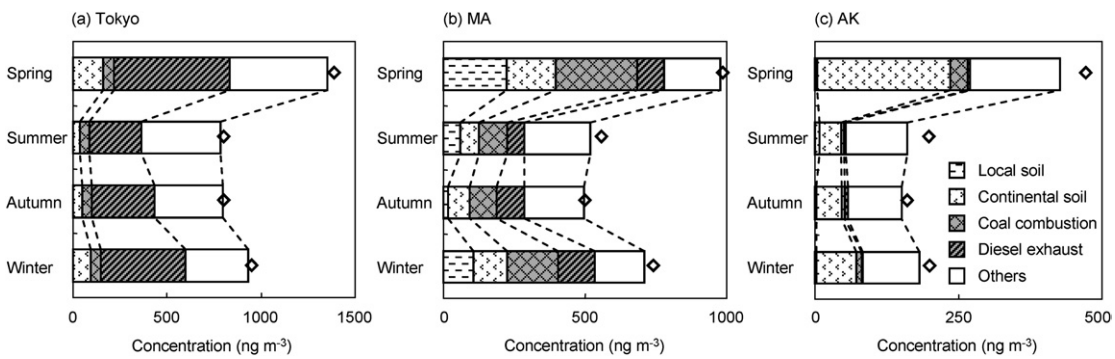

Fig. 6 Regional and seasonal characteristics of four major source contributions (local soil, continental soil, coal combustion, and diesel exhaust) for (a) Tokyo, (b) MA, and (c) AK. ◇ indicates total elemental concentration analyzed in this study.

sources were dominant. On the other hand, cross-boundary natural sources were significant at mountainous site (Akagi). The suburban site (Maebashi) revealed an intermediate feature between urban and mountainous sites. This study demonstrated the combined source receptor model was a powerful tool for the quantitative determination of the regional and seasonal differences of the source contributions. A better understanding of regional and seasonal characteristics of emission sources will greatly contribute to policy and decision making for improving regional environments.

Acknowledgements

This research was supported in part by a Grant-in-Aid for Young Scientists (B), 19710022, 2007 from the Ministry of Education, Science, Sports and Culture, Japan, and a grant from the Gunma Prefectural Institute of Public Health and Environmental Sciences. We would like to thank the efforts of Ms Akiko Kambe, Mr Kazuhiro Sakai, Mr Takaaki Tamura, and Ms Miyuki Kinoshita (Chuo University) for providing the monitoring data for Tokyo. We wish to thank Dr Hirokazu Kimura (Infectious Diseases Surveillance Center, National Institute of Infectious Diseases) for providing advice and technical assistance.

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