Source apportionment of hazardous elements of SPM aerosol in Yokohama, Japan

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INTRODUCTION

Suspended particulate matter (SPM) is increasingly received attention and broadly accepted as a potent air pollutant in urban locations. It is formed from wide ranges of sources and compost of numerous toxic elements. Airborne particulate matter in the urban atmosphere triggers respiratory related diseases and severely impact on human health. It has been proven by several researchers of the profound linkage of the levels of PM and the prevalence of mortality and morbidity [1, 2]. In addition, SPM causes visibility reduction [3] in urban atmosphere. Thus, it was reported as a most significant pollutant to be routinely monitored in ambient air. Source identification and quantification of airborne particulate matter has now become an increasingly important and widespread issue in context of current air pollution perspective. However, inadequate studies have been investigated in apportionment of SPM in Japan [4, 5]. Moreover, it was noted that sources of many elements in ambient particulate matter have not yet been identified. Therefore, bearing the above fact in mind, particular emphasis was given to conduct a comprehensive source analysis of hazardous elements in SPM contemplating substantial number of compositions and several locations in Yokohama, Japan.

MATERIAL AND METHODS

The SPM samples were collected in 1999 to 2005 at two locations (urban site A and suburban site B) of Yokohama, Japan as shown in Figure 1. An extensive chemical analysis of SPM mass was conducted to measure metals (Mg, Al, Ca, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Cs, Ba, Pb and Bi), water soluble ions (Na^+, NH_4^+, K^+, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) and carbonaceous mass (EC and OC) using ICPMS, ion chromatograph and CHN CORDER, respectively. Briefs outline of the experimental procedures are given in Figure 2.

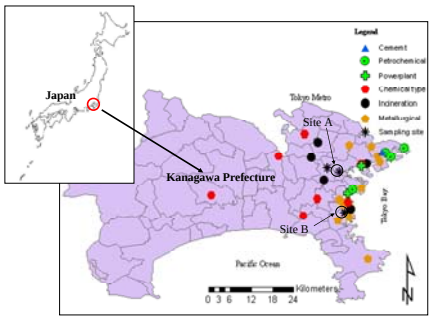

Figure 1 Map of study area: sampling locations and major emission sources around

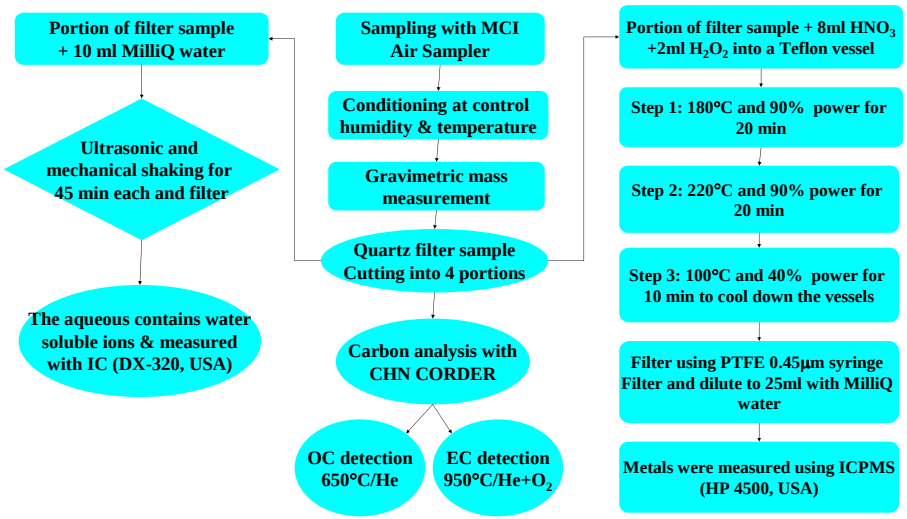

Fig.ure 2 Analytical procedures

Source apportionment procedures: PCA-APCS

Multivariate receptor methods were subjected to perform the source apportionment of SPM in this study. For this purpose, Principal Components Analysis, Absolute Principle Component Score (PCA-APCS) and Multiple Linear Regression (MLR) were employed in illustration of the sources as follows:

$$Z_{ij} = \sum_{k=1}^{p} B_{ik} G_{kj} \quad (1)$$

$$C_i = (b_0)_i + \sum APCS_p * b_{pi} \quad (2)$$

$$C_k = a_0 + \sum_{j=1}^{p} a_j S_{jk} \quad (3)$$

Where,

p: the number of principal components; Z: the n x m matrix of standardized concentrations; B: the n x p principal component loadings matrix; G: the p x m matrix of principal component scores, $(b_0)_i$ is the constant term of multiple regression for pollutants i, b_{pi} is the coefficient of multiple regression of the source p for pollutant i, and $APCS_p$ is the scaled value of the rotated factor p for the samples, C_k is the concentration of an element i during observation k; S_{jk} is the mass concentration of source j

◆ Sensitivity of PCA was tested considering all species of SPM at both sampling sites. The species which are not sensitive to PCA and the concentrations were not changed in comparison with SPM mass were dropped out from the data set.

◆ At site A, 25 species were taken into consideration in PCA calculation and 5 species were removed. Meanwhile, 21 species were applied and 9 of them were removed during the data cleaning at site B. However, elimination of few species from the data matrix in some extent weakens the source strength.

◆ PCA-APCS model's performance was also evaluated in the light of correlation coefficient and uncertainty analysis. The correlation coefficients (R^2) among the species at both sites have shown quite high value indicating the model's performance was acceptable. The error (%) of all species was calculated as the subtraction of the mass estimated by model and the analytical methods. The results obtained using the model were very close to the measured value of the respective species in almost all cases.

RESULTS AND DISCUSSIONS

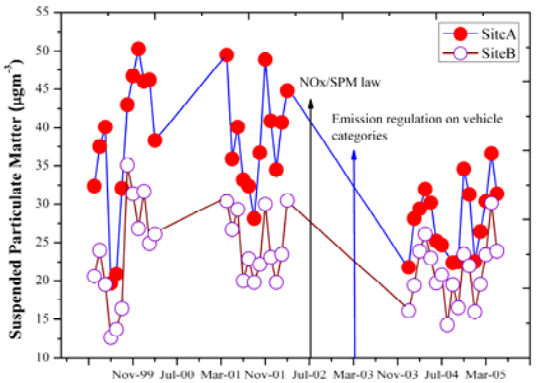

Figure 3 Time series of Suspended Particulate Matter (SPM) during 1999 – 2005 in Yokohama, Japan.

From Figure 3:
The mean concentrations of SPM were estimated as 34.2 and 22.9 μg/m3 at sites A and B. The monthly SPM concentration at site A was significantly higher ($p<0.001$) than site B

Table 1. Summary statistics of SPM mass and its chemical components of the samples collected at Site A and Site B.

	Site A (N=40)				Site B (N=41)			
μg/m³	Mean±SD	Median	Min	Max	Mean±SD	Median	Min	Max
SPM	34.2±8.6	32.8	19.7	50.3	22.9±5.4	23.0	12.7	35.1
EC	5.1±2.2	4.8	1.9	11.1	3.2±1.4	3.0	1.1	7.2
OC	2.4±0.8	2.2	1.2	4.9	1.8±0.6	1.6	1.0	3.6
Na^+	0.68±0.28	0.70	0.16	1.17	0.67±0.26	0.72	0.22	1.24
NH_4	1.1±0.5	1.1	0.40	2.4	1.3±0.5	1.1	0.40	2.8
K^+	0.16±0.08	0.13	0.06	0.40	0.16±0.07	0.16	0.06	0.35
Mg^{2+}	0.12±0.04	0.13	0.03	0.20	0.10±0.04	0.09	0.03	0.17
Ca^{2+}	0.76±0.33	0.73	0.25	1.44	0.24±0.11	0.22	0.08	0.56
Cl^-	0.21±0.39	0.10	<0.01	1.81	0.06±0.12	0.03	<0.01	0.76
NO_3	1.9±1.3	1.8	0.10	5.0	0.94±0.82	0.67	0.03	3.62
SO_4	4.9±2.1	4.5	1.9	12.5	5.0±2.1	4.4	2.3	11.8
ng/m³								
Mg	315.6±130.3	292.7	98.6	759.4	209.9±85.3	191.7	81.5	420.1
Al	693.1±499.1	515.0	119.1	2384.7	143.5±85.2	120.0	38.8	386.8
Ca	423.3±192.0	384.2	160.6	919.7	163.3±67.5	154.3	58.5	360.7
V	8.1±3.1	7.6	2.5	17.5	9.3±2.4	8.6	5.4	15.7
Cr	4.1±2.4	3.0	1.8	9.9	2.8±1.4	2.3	0.96	5.8
Mn	32.5±10.7	33.2	16.0	66.1	16.5±4.9	17.0	5.6	26.5
Ni	5.4±2.2	4.9	1.9	14.2	5.2±1.2	5.1	2.9	7.2
Cu	47.7±19.5	40.8	23.8	96.4	12.9±5.1	12.5	5.9	26.2
Zn	131±70.7	110.0	52.7	343.5	86.9±40.8	79.6	29.4	202.5
Ga	2.1±1.3	1.6	0.91	5.8	2.0±1.3	1.9	0.50	4.4
As	2.6±2.1	1.8	0.75	9.1	3.0±1.5	2.9	0.78	5.6
Se	1.1±0.74	0.95	0.24	4.3	4.3±2.6	3.9	0.31	9.0
Rb	1.2±0.92	0.80	0.25	3.9	1.9±1.3	1.7	0.36	4.4
Sr	6.3±2.8	5.4	2.8	15.6	4.1±1.4	3.7	1.9	6.6
Ag	1.7±1.8	0.76	0.13	5.6	1.6±1.1	2.1	0.21	3.1
Cd	1.2±0.60	1.2	0.26	2.2	2.5±0.89	2.6	0.76	4.2
Cs	0.30±0.36	0.08	0.01	1.1	1.2±1.0	1.8	0.01	2.5
Ba	29.6±15.4	25.0	11.2	75.7	10.4±2.8	10.0	6.0	17.1
Pb	27.2±11.4	24.9	10.6	66.8	21.3±11.4	17.7	6.6	56.4
Bi	0.72±0.49	0.50	0.28	2.3	1.2±1.0	1.8	<0.01	2.5

From Table 1:
The most abundant metals were found to be Mg, Al, Ca, and Zn and Cs was estimated to be the lowest concentration at both sites. The following factors might play striking role for the increased EC and OC observed at site A: (a) it is a densely populated urban area, (b) high frequency of automobile ply every day and (c) coal fired power plant was also located in this area. The carbonaceous matter, SO_4^{2-}, NO_3^-, Ca^{2+} and NH_4^+ were salient contributors to SPM aerosol at both sites.

Table 2. Varimax rotated factor loading at site A sampling location

	Factor 1	Factor 2	Factor 3	Factor 4
EC	0.25	**0.72**	0.50	-0.04
OC	0.04	**0.82**	0.31	0.01
NH_4^+	-0.17	0.47	**0.62**	-0.23
K^+	0.11	0.49	**0.64**	-0.28
Ca^{2+}	0.16	0.10	-0.07	**0.86**
Cl^-	0.18	0.73	0.07	-0.13
NO_3^-	-0.02	**0.84**	0.10	0.29
Mg	0.59	-0.43	0.00	**0.66**
Al	**0.88**	0.02	0.06	0.38
V	**0.73**	-0.48	0.27	0.13
Cr	**0.90**	0.39	0.06	0.01
Mn	**0.70**	0.48	0.11	0.42
Ni	**0.88**	-0.13	0.17	0.09
Cu	0.45	**0.75**	0.07	0.09
Zn	0.61	**0.73**	0.17	0.00
Ga	0.57	**0.75**	0.05	-0.02
As	**0.77**	0.28	0.04	-0.12
Se	0.01	-0.06	**0.89**	0.05
Rb	**0.90**	0.23	0.03	0.15
Sr	**0.92**	0.20	0.03	0.23
Ag	**0.87**	0.39	-0.04	-0.11
Cd	0.38	0.42	**0.70**	0.12
Cs	**0.86**	0.28	-0.02	-0.10
Ba	0.24	**0.83**	-0.04	-0.08
Pb	0.35	**0.79**	0.17	-0.06
Bi	0.75	0.57	0.09	-0.12
Expl.Var	9.43	7.59	2.66	1.78
Eigen Value	12.88	5.13	2.03	1.42
% Total Variance	49.54	19.74	7.81	5.46
Probable sources	Soil dust & Indust.	Road traffic	Incinerator & Power plant	Mineral resus.

Table 3. Varimax rotated factor loading at site B sampling location

	Factor 1	Factor 2	Factor 3	Factor 4
EC	**0.95**	0.07	0.03	0.10
OC	**0.92**	0.02	-0.03	-0.03
NH^4	0.07	-0.08	-0.02	**0.92**
K_+	0.33	-0.10	0.03	**0.83**
Mg_{2+}	-0.52	-0.03	**0.50**	0.15
Ca_{2+}	0.12	0.05	**0.95**	0.08
Cl_-	0.33	0.08	0.04	0.16
NO^3	**0.53**	-0.01	0.35	-0.12
SO^4	-0.36	-0.06	0.08	**0.85**
Al	0.00	0.01	**0.96**	0.01
Ca	0.19	-0.10	**0.95**	-0.04
Mn	0.63	0.27	**0.61**	0.00
Ni	-0.01	**0.84**	-0.12	0.29
Cu	**0.90**	0.26	0.11	-0.10
Zn	**0.95**	0.04	0.13	0.05
As	-0.02	**0.95**	0.13	-0.09
Se	0.05	**0.94**	0.01	-0.06
Ag	0.13	**0.94**	-0.05	-0.07
Cd	0.10	**0.92**	0.09	-0.10
Ba	**0.85**	-0.03	0.14	-0.06
Pb	**0.90**	-0.05	0.14	0.09
Bi	0.07	**0.96**	-0.05	-0.10
Expl.Var	6.37	5.31	3.61	2.48
Eigenvalue	7.67	5.08	3.29	2.42
% Total variance	34.85	23.09	14.98	11.02
Probable sources	Road traffic	Industry & Power plant	Soil dust	Secondary/ Incineration

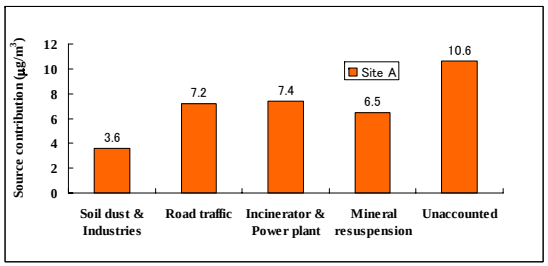

Figure 4 Contribution of various sources to SPM aerosol calculated at site A

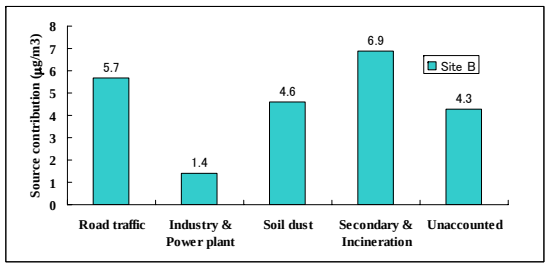

Figure 5 Contribution of various sources to SPM aerosol calculated at site B

From Figures 4 and 5
- The most significant sources at site A were road traffic as well as incineration and power plant accounting for 7.2 and 7.4 μg/m³, respectively.
- The leading contributors to traffic source were reported as EC, OC, NO_3^-, Cu, Zn, Ba and Pb representing 2434.0, 1059.3, 1737.2, 23.3, 79.0, 19.7 and 13.9 ng/m³ of SPM mass in comparison with the contributions to other sources of the respective elements.
- The incineration and power plant are distinguished sources at site A compared to site B. The metallic elements appeared in these sources i.e Se and Cd are most considered as a signature of these sources as well as poses profound toxic effect.
- At site B, the secondary aerosol combining of incineration as well as road traffic are associated with 6.9 and 5.7 μg/m³ of mass and recognized as most striking contributors. NH_4^+, K^+ and SO_4^{2-} were major tracers of this source and presented as 1018.8, 142.4 and 4407.2 ng/m3 of mass. The tracers of road traffic at site B were EC, OC, NO_3^-, Mn, Cu, Zn, Ba and Pb and accounted for 2744.8, 1168.4, 915.8, 6.6, 9.6, 81.7, 5.1 and 21.7 ng/m³, respectively.
- The tracers and nature of the traffic source at both sites were similar. The distances of the sites as well as local dispersion of SPM aerosol were considerable in this regards.

From Table 2:
- Factor 1 represents soil and fugitive dust source and also some industrial setup actively causes metals emissions.
- The elements are appeared in factor 2 might have linkage to automobile source.
- The tracers of the factor 3 evidently support the contribution of incinerators and power plant to SPM mass in this site.
- Factor 4 was represented mineral resuspension as the huge application of cement and other construction material are common in use around this sampling site.

From Table 3:
- The composition of factor 1 is almost resembled as the traffic source was produced at site A.
- Factor 2 represents a mixture of industrial and power plant source.
- The picture of the tracers associated with factor 3 clearly supports the existence of soil and dust resuspension sources in referring numerous evidences.
- Factor 4 represents secondary aerosol as well as incineration source.

CONCLUSION

The standout conclusions of this study include:
- The main results of this study elucidated the in-depth chemical compositions and the sources of SPM mass collected from 1999 to 2005 at sites A and B. The mean concentrations of SPM were measured as 34.2 and 22.9 μg/m³ at sites A and B.
- PCA-APCS technique was employed to comprehend the sources. During the apportionment study, model performance was also evaluated. Similar number of sources having different nature was extracted at both sites.
- The sources were identified at site A included a) soil dust & industries, b) road traffic, c) incinerator & power plant, d) mineral resuspension.
- At site B, the sources were predicted as a) road traffic, b) industry & power plant, c) soil dust, d) secondarily formed aerosol & incineration.
- Road traffic and incineration & power plant were the most significant sources at site A. However, road traffic and secondarily formed aerosol combining incineration are found to be predominant source at site B.
- From findings of the above discussions, the tracers and nature of the traffic source at both sites were similar. The remarkable contributions of the sources were noticeable at site A leaving a large amount of mass unaccounted. Moreover, many hazardous elements existed into the sources may bolster the exposure of human health in current locations.

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