SOURCE APPORTIONMENT OF SUSPENDED PARTICULATE MATTER AEROSOL USING US EPA PMF 3.0

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1. Introduction

Airborne suspended particulate matter (aerodynamic diameter less than 10 μm with 50 % cut off efficiency) is one of the grave air pollutants and cause of concern in an urban site. Several researchers profoundly reported a linear increase of PM_{10} with the rate of mortality[1, 2]. It has also been well documented in various investigations that SPM has detrimental impacts on human health in Japan[3, 4]. Thus, identification of various source characteristics of SPM aerosol is important. Source apportionment of airborne particulate matter has now become an increasingly important and significant tool for current perspectives of air pollution. The findings of this study could help to comprehend the most probable sources and their mechanism of formations. In addition, Positive Matrix Factorization (PMF 3.0) is a robust receptor model in the apportionment of airborne particulate matter. To the best of our knowledge, source apportionment using PMF 3.0 could be new in our study areas. Thus, we have paid attention in this paper to perform a comprehensive source apportionment of SPM aerosol in Yokohama, Japan using US EPA PMF 3.0.

2. Material and methods

2.1 Description of the locations

SPM sampling was conducted at two locations in Yokohama, Japan and shown in **Fig. 1**. Sites A and B are located at Naka and Kanazawa Ward, Yokohama, respectively. The two sites were designated as urban (site A) and suburban (site B) in the early 1970s. Yokohama is a known major commercial hub in the Greater Tokyo area.

2.2 Collection of SPM samples and gravimetric mass measurement

SPM samples were collected with Low Volume Air Sampler (Shintaku Co. Japan). The flow rate of the sampler was maintained at 20 L min^{-1} during the collection of samples in quartz filter paper (110 mm in diameter). The samples were collected for 30 days, i.e., one sample in a month basis during 1999 - 2005. The samples for the year of 2003 were lost. The gravimetric mass was measured at controlled humidity (45 ± 5 %) and temperature (20 ± 5 °C).

2.3 Experimental Analysis:

SPM samples were analyzed for water soluble ions, carbonaceous fractions and various metals. Water soluble ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) ions were measured using ion chromatograph (Dionex, DX-320, USA). Elemental carbon (EC) and organic carbon (OC) were measured from quartz filter samples by using two-step thermal procedure. CHN analyzer (CHN corder MT-3, Yanaco, Japan) was employed to detect EC and OC. A microwave (MWS-2, Berghof, Germany) was used in preparation of the samples to analyze various metals with inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent HP4500, USA).

2.4 Multivariate receptor modeling

Multivariate receptor model was used to perform the source apportionment of SPM in this study. Positive Matrix Factorization method in the form of EPA PMF 3.0 was considered to infer the unknown sources of SPM aerosol.
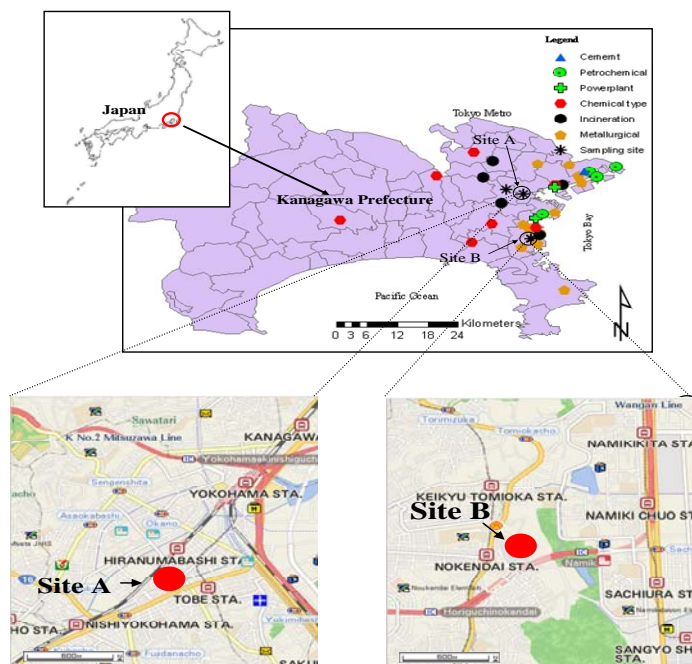
Fig. 1. Map of the sampling sites and major emission sources

3. Results and Discussions

3.1. Concentration of SPM and elemental mass

SPM samples were collected at sites A and B for the period of 1999 to 2005. SPM mass varied from 19.7 to 50.3 μg m^{-3} with an overall mean concentration of 34.2 μg m^{-3} at site A. In contrast, SPM mass ranged from 12.7 to 35.1 μg m^{-3} and overall mean was 22.9 μg m^{-3} at site B. Moreover, water soluble ions i.e. SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} and carbonaceous mass (EC and OC) measured in SPM mass at both sampling sites. However, detailed characterization of SPM and elemental mass were given in another study[5].

3.2 Discrimination of sources in SPM aerosol

Receptor model, i.e., EPA PMF 3.0 was used to perform source discrimination considering 30 species (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, EC, OC, Mg, Al, Ca, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Cs, Ba, Pb and Bi) and 81 samples collected from two sites of Yokohama, Japan. The samples of the two sites were used together in PMF analysis because (a) number of samples collected at each site was relatively small and (b) distance between the two sites was also small (about 12 km). The purposes of this approach being selected for the apportionment of SPM sources using PMF 3.0 are a) to evaluate the results of the samples collected from nearby proximity of multiple locations, b) to justify and establish the data analysis approach for further use, c) to obtain more consistent source profiles with physical meanings to comprehend the most probable unknown transport and source patterns at the close proximity of two sampling sites, and d) to reduce the uncertainty of the apportionment results. The obtained factors by the PMF model are shown in **Fig. 2**. Number of factors was selected after evaluating the following steps: a) signal to noise of the input variable was carefully examined and values less than 0.2 were recorded as bad, 0.2 to 2 were recorded as weak and above 2 were recognize as strong, b) the goodness-of-fit parameters, i.e., Q (robust) and Q (true) were optimized changing the number of factors and compared with Q (theoretical).

Secondarily formed aerosol and refuse incineration source

Factor profile 1 as shown in **Fig. 2** was enriched with SO_4^{2-}, NH_4^+ and K^+ and might be recognized as a secondarily formed aerosol and incineration source. SO_4^{2-} was the largest contributor to SPM aerosol collected at both sites A and B. SO_4^{2-} and NH_4^+ are formed from the precursor gases of SO_2 and NH_3. Industrial combustion plays key roles for the release of SO_2 into ambient air. Keihin industrial area, one of the largest and oldest

industry sites in Japan, is located in and around Yokohama. Thus, intensified industrial activities around the sampling sites may largely responsible for elevated SO_4^{2-} concentration. Moreover, during the sampling period, volcano at Miyake Jima Island located about 150 km south of the sites was active and erupted severely in August, 2000. This volcano might have influenced the enhanced concentration of sulfate at both sites A and B. K^+ was used as a tracer of meat cooking and refuses burning in an urban setting. It was also used to identify refuse incineration source in Kobe city of Japan. Yokohama city hosts five municipal solid waste incinerating plants. Incinerating plants are important sources which discharge various elements of SPM aerosol.
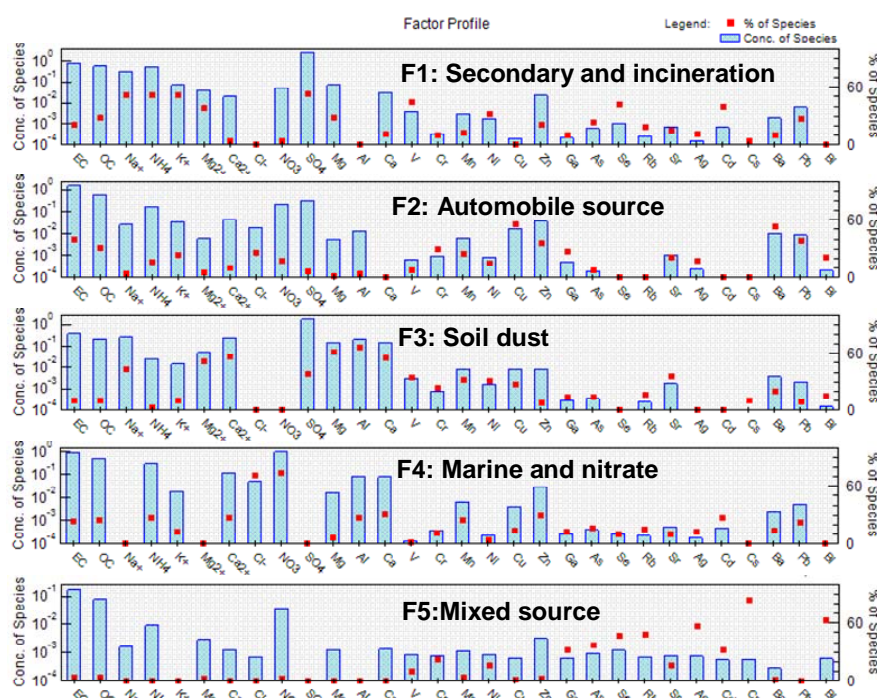

Fig. 2. Source profiles of SPM aerosol for sites A and B, Yokohama

Automobile source
Factor profile 2 is dominated by EC, OC, Cu, Zn, Ba and Pb as shown in **Fig. 2**. It was identified as an automobile source as the species were representative of automobile exhaust. EC and OC are released from vehicle exhaust and diesel engine might be the predominant contributor of EC[6]. The important source of Cu and Ba are automobile break pad and worn off tyre is a major source of Zn. Concentration of Zn and fine-grained particles (i.e. diesel exhaust particles in the form of EC) are also significantly high in the dust collected in the heavy traffic road. Although Pb has been phased out from gasoline fuel in Japan, Pb might be re-suspended with soil and road dust for past use of gasoline[7].

Soil dust source
Ca, Al and Mg dominated in factor profile 3 as presented in **Fig. 2**. Thus, this profile was best suited for soil dust source. The tracer associated with this profile clearly supports the existence of soil and dust re-suspension sources. Al was used as a soil dust source in Kobe city of Japan as well[8]. There might have contributions from local, regionally transported as well as pre-existing elements re-suspended to this source. For instance, arrival of spring dust storm originated from East Asia has a suspected role to exhibit maximum SPM concentrations in Japan. Re-suspended soil dust containing Al, Ca and Mg may also cause high concentration of SPM aerosol at both sampling sites.

Nitrate and sea salt
NO_3^- and Cl^- were significantly enriched in factor profile 4 demonstrated in **Fig. 2** and are recognized as sea salt

and nitrate aerosol source. NO_3^- is secondarily formed aerosol from the precursors of oxides of nitrogen. However, Cl^- was present in considerable extent in this profile which supposed to be predominantly released from sea salt[9]. Cl^- released from marine source primarily attached with coarse particulate matter. Cl^- has a tendency to react with atmospheric acid gases such as HNO_3 and that leads to form coarse NO_3^- particles. The above nature of NO_3^- and Cl^- could be considered as the regions of the combined sources.

Mixed source
Factor profile 5 was classified as mixed sources as shown in **Fig. 2** (i.e. coal combustion, long transported Asian dust and recycle plant) and the tracers were used to explain this sources included As, Se, Rb, Ag, Cs and Bi. As and Se are widely accepted source tracer of coal combustion[10]. For instance, one of coal-fired power plant and steel industry using coal might cause the discharge of As and Se. Cs was reported as an element transported with dust particles from Asian continent.

3.3 Quantification of resolved sources
The estimated contributions of the sources were indentified at sites A and B. The predominant source of SPM mass at site A was soil dust, with an average concentration of 11.5 $\mu g\ m^{-3}$ which accounted for 34 % of total SPM mass. The other major sources followed in decreasing order as automobile (8.2 $\mu g\ m^{-3}$ and 24 %), marine and nitrate (6.9 $\mu g\ m^{-3}$ and 20 %), secondary and incineration (3.1 $\mu g\ m^{-3}$ and 9 %), Mixed source (coal combustion, long transported Asian dust and recycle plant) (0.30 $\mu g\ m^{-3}$ and 1 %) and unaccounted mass (4.2 $\mu g\ m^{-3}$ and 12 %). In contrast, among the identified sources at site B, secondary aerosol source in combination with incineration were dominant with an average of 9.4 $\mu g\ m^{-3}$. These sources accounted for 41 % of SPM mass. The other sources followed by marine and nitrate (4.2 $\mu g\ m^{-3}$ and 18 %), soil dust (2.8 $\mu g\ m^{-3}$ and 12 %), automobile (1.8 $\mu g\ m^{-3}$ and 8 %), mixed source (coal combustion, long transported Asian dust and recycle plant) (1.4 $\mu g\ m^{-3}$ and 6 %) and unaccounted mass (3.2 $\mu g\ m^{-3}$ and 14 %).

Thus, soil dust and automobile were striking contributors at site A. A conclusion was made that soil and automobile sources of SPM aerosol might be produced from local origin at current study areas. Besides, Asian dust had an impact on high concentrations of SPM aerosol in some certain period of the year. In contrast, secondary aerosol in the form of sulfate and ammonium coupled with incineration as well as mixed sources (coal, long transported Cs, and recycle) were remarkable sources at site B. Stationary/industrial combustion had apparently more impact on the release of SPM components at site B than A

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