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# Assessment of the sources of suspended particulate matter aerosol using US EPA PMF 3.0

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**Abstract** The main purpose of this paper was to carry out a source apportionment of suspended particulate matter (SPM) samples using positive matrix factorization procedure. The central and local Government of Japan introduced strict emission regulations in 2002/10 and 2003/10, respectively, in curbing SPM pollution from major metropolitans. This paper also highlighted the impact of the measures taken by the central and local Government of Japan on the reduction of SPM and the contributions of sources. SPM samples were collected for 6 years starting from 1999 to 2005 at two sites, i.e., site A (urban) and site B (suburban) of Yokohama, Japan. Microwave digestion and inductively coupled plasma-mass spectroscopy (ICP-MS) were employed to measure Mg, Al, Ca, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Cs, Ba, Pb and Bi, while water soluble ions ($Na^+$, $NH_4{}^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $NO_3{}^-$ and $SO_4{}^{2-}$) as well as carbonaceous mass (EC and OC) were analyzed using ion chromatograph and CHN analyzer, respectively. The sources identified at two sites were automobile, soil dust, marine aerosol, mixed sources, and secondarily formed aerosol. Also, source quantification was performed. Automobile and soil dust were striking contributors at site A. Automobile and soil dust 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 due to the outflows of East Asian emission. In contrast, secondary aerosol in the form of sulfate and ammonium as well as mixed sources (coal, long-transported Cs, and other unknown sources) were remarkable at site B. Stationary/industrial combustion has apparently more impact on the release of SPM components at site B than A. Automobile regulations in 2002 and 2003, respectively, resulted in reduction of SPM by 28% for site A and 16% for site B. There was also net reduction of automobile contribution at both sites due to the above measures being implemented.

**Keywords** Suspended particulate matter · Carbonaceous aerosol · Source apportionment

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## Introduction

Airborne suspended particulate matter with a 100% cut off aerodynamic diameter of 10 μm 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 (Schwartz 1993; Pope et al. 1995a, b; Schwartz 2004). It has also been well-documented in various investigations that SPM has detrimental impacts on human health in Japan (Omori et al. 2003; Yorifuji et al. 2005; Murakami and Ono 2006; Yamazaki et al. 2007). Suspended particulate matter (SPM; 100% cut-off aerodynamic diameter of 10 μm) has been considered in this study.

It is also responsible for changing global climate. For instance, elemental carbon or black carbon has been recognized as the second largest contributor to global warming after $CO_2$ (Ramanathan et al. 2007; Ramanathan and Carmichael 2008). Moreover, solar heating within black carbon (BC)-containing cloud condensation nuclei (CCN) slows or prevents the activation of the CCN into cloud drops. Solar-heated BC-containing droplets are elevated in temperature by fractions of a degree above the ambient, thus raising the droplet vapor pressure and inhibiting activation of the most absorptive CCN (Conant et al. 2002). 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 from sources. Although various source apportionment studies were carried out in Japan (Adachi et al. 1995; Karasawa et al. 1994; Matsuo et al. 2000; Mukai et al. 1994; Wang et al. 2005; Wang et al. 2006; Okamoto et al. 1990; Yoshizumi 1990/91; Fujimura et al. 1993; Kawashima et al. 2005; Sayaka et al. 2002), sources of many elements in ambient particulate matter have not yet been identified (Oura et al. 2007). Vehicular emission regulations, especially for diesel cars have been introduced recently in metropolitan areas in Japan in curbing SPM pollution from major cities (Japan Environmental Council 2003). 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. The present study also aims to make a comparison of the source apportionment results using PMF and principal component analysis followed by absolute principal component score (PCA–APCS) which have been gaining interest in the said field. PMF has been significantly applied in a series of comprehensive source apportionment investigations (Anttila et al. 1995; Polissar et al. 1998b; Lee et al. 1999; Paterson et al. 1999; Xie et al. 1999; Chueinta et al. 2000; Ramadan et al. 2000; Huang et al. 2001; Polissar et al. 2001; Song et al. 2001; Kim et al. 2003; Maykut et al. 2003; Qin and Oduyemi 2003; Begum et al. 2004; Hien et al. 2004; Larson et al. 2004; Li et al. 2004; Liu et al. 2005; Lee and Hopke 2006; Morishita et al. 2006; Ogulei et al. 2006; Qin et al. 2006; Marmur et al. 2007). However, PMF 3.0 developed by US EPA (Norris et al. 2008) has been employed in this study to apportion the sources of particulate matter. PMF 3.0 has also been utilized recently by several investigations in considering a reliable tool to locate and estimate sources (Chan et al. 2011; Morishita et al. 2011; Kertész et al. 2010). PCA is a very old and widely used method in source identification study without any prior knowledge of the origin of particulate matter (Hopke et al. 1976; Henry and Hidy 1979; Henry and Hidy 1982; Roscoe et al. 1982; Thurston and Spengler 1985; Henry 1987; Malm et al. 1990; Gao et al. 1994; Guo et al. 2004; Kim and Masunaga 2005; Park and Kim 2005; Vallius et al. 2005; Ho et al. 2006; Song et al. 2006; Viana et al. 2007). The advantages of PCA and PMF are that they are capable of identifying sources without any prior knowledge of the sources. These two techniques can also provide indistinguishable results (Huang et al. 1999; Viana et al. 2008). However, the biggest advantage of PMF over PCA is non-negativity constraints and each data point individually weighed (Paatero and Tapper 1994; Paatero 1997). Thus, the major objectives of this paper are to (a) perform a comprehensive source apportionment of SPM aerosol in Yokohama, Japan using US EPA PMF 3.0 and

(b) make a comparison of the results to see the strength, consistency as well as discrepancy in applying US EPA PMF 3.0 and PCA–APCS procedures and interpret source results in the light of automobile emission regulations adopted by the central and local Government of Japan.

## Material and methods

### Description of the locations

SPM sampling campaign 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. It has the second largest population (3.6 million) in Japan and is the most densely populated urban area after Tokyo. Yokohama city can be categorized as a residential area as well as a commercial hub with a high density of road traffic. This city hosts five incinerating and three power plants among other industrial and commercial activities. However, two power plants are identified in Fig. 1. Site A is closer to the down town of Yokohama. Industrial and commercial activities at site B were substantially lower than site A. However, various

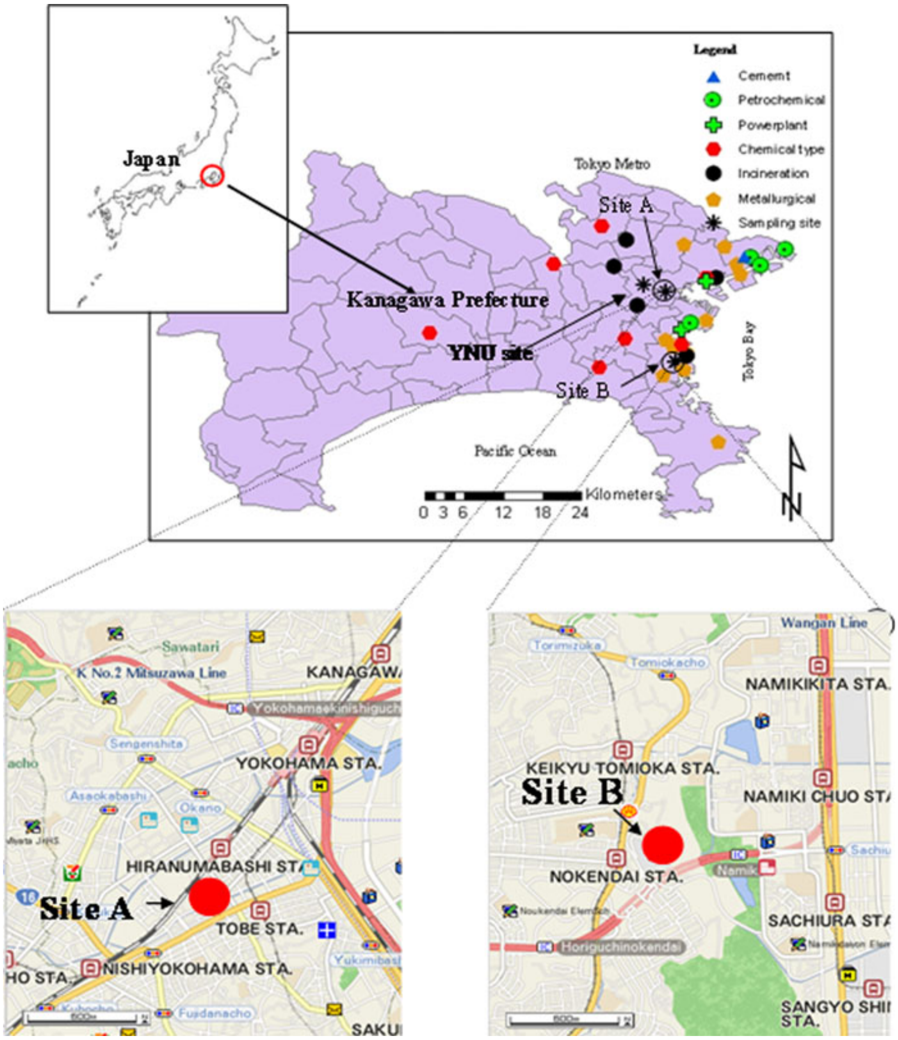


**Fig. 1** Map of the sampling sites and major emission sources

types of industrial activities were intensified at site B. There are various categories of industries located around site B, which are recognized as major emission sources contributing to local air quality. Few of them are indicated in Fig. 1. Most of them at this site are heavy industries such as manufacturer of automobile spare parts, body of vehicles, industrial machineries, etc. Other industries are chemical, pharmaceutical, printing and packaging, electroplating, manufacturer of electronic products, and construction material and equipment. Besides, the average traffic density is considerably high near our sampling sites. The average traffic density per 24 h was about 66,393 for the year 2005 at an expressway (Kanagawa route 1 Yokohane line) of Yokohama. The heavy duty vehicles were reported as half of the total traffic. This expressway route is nearer to site A. However, the Yokohama–Yokosuka road is closer to site B where the average traffic density per 24 h was reported as 26,389 in the same year (Ministry of Land, Infrastructure and Transport 2005). The ratio of light duty vehicles to heavy duty vehicles is shown as 1.5. Heavy duty vehicles are mostly run by diesel engine, while gasoline engines power light duty vehicles. Both sites A and B have been located very close to the highway. The location of the sites is popularly known as the "Keihin industrial area", one of the oldest industrial settings in Japan. Industries around these areas are densely distributed. Moreover, the distance between two sampling sites is short. Thus, sites A and B now appear to be more similar than different. To get better source information using the said receptor models, we need a large set of data. However, the number of samples collected from the above sites is quite small to analyze for individual site with the receptor model. Therefore, we attempted to handle these two sites together.

### Collection of SPM samples and gravimetric mass measurement

SPM samples were collected with Cyclone type 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 on a monthly basis from 1999–2005. However, most ambient monitoring networks and research studies undertake typically 24 h and could extend in the range of 1 h to 1 week. High resolution of filter samples incorporating with wind speed and direction might discriminate little on source apportionment result. The advantage of such long sampling time would allow more of the trace elements to be measured with very low detection limit. The samples for the year of 2003 (i.e., one-sixth of the total samples) were lost as a result of preserving the samples for such a long time. The gravimetric mass was measured at controlled humidity (45 ± 5%) and temperature (20 ± 5°C).

### 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 an 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. Microwave (Berghof Microwave MWS-2, Germany) digestion and ICP-MS (Agilent HP4500, USA) were used to measure various metals. Digestion reagents that were used included 8 ml $HNO_3$ (Kanto Chemial Co., Japan) and 2 ml $H_2O_2$ (Wako Chemical Co, Japan). A similar method has been applied by several researchers (Canepari et al. 2006; Buzica et al. 2006). Details of the analytical procedures were explained in another study (Khan et al. 2010a).

### Multivariate receptor modeling

Multivariate receptor methods were 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 (Norris et al. 2008).

## Positive matrix factorization analysis (PMF 3.0)

PMF is a factor-analysis based receptor model and it has been used most frequently when source profiles are unknown. The PMF model was developed based on the work of Paatero and Tapper (1994) and Paatero (1997). PMF is a multivariate factor analysis tool that decomposes a matrix of sample data into two matrices, i.e., chemical composition profile of each factor, and the contribution of each factor to each sample. It is defined as the following mathematical form in an attempt to identify number of factors $p$, the species profile $f$ of each source, and quantify the sources to each sample:

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \tag{1}$$

Where $X_{ij}$ is the concentration at a receptor for the $j$th species on the $i$th day, $g_{ik}$ is the contribution of the $k$th factor to the receptor on the $i$th day, $f_{kj}$ is the fraction of the $k$th factor that is species $j$, and $e_{ij}$ is the error of the PMF model for the $j$th species measured in the $i$th sample.

An "object function" $Q$, is required to be minimized with the adjusted value of $g$, $f$, and $p$. $Q$ is defined as

$$Q\left(E\right)=\sum_{i=1}^{m}\sum_{j=1}^{n}\left[\frac{e_{ij}}{s_{ij}}\right]^2=\sum_{i=1}^{m}\sum_{j=1}^{n}\left[\frac{x_{ij}-\sum\limits_{k=1}^{p} g_{ik} f_{kj}}{s_{ij}}\right]^2 \tag{2}$$

Where, $s_{ij}$ is an estimate of the "uncertainty" in the $i$th variable measured in the $j$th sample. The US Environmental Protection Agency has upgraded PMF 1.1 into PMF 3.0 with various graphical interface and user friendly options (Norris et al. 2008).

The concentration of compositions data set in SPM samples were carefully evaluated with values of method detection limit (MDL). The species with concentrations below the MDL were replaced with half of the MDL (Baumann et al. 2008; Polissar et al. 1998a, b). The uncertainties of the species concentration were estimated applying the following ad hoc formula (Anttila et al. 1995; Vaccaro et al. 2007):

$$\sigma_{ij} = \sqrt{e_j^2 + \left(d_j X_{ij}\right)^2} \tag{3}$$

Where, $\sigma_{ij}$ is the uncertainty of the species $j$ in sample $i$, $e_j^2$ is the method detection limit of species $j$, $d_j$ is the error percentage of the species measured in SPM samples, $X_{ij}$ is the concentration of species $j$ in sample $i$. The mass of the identified sources was estimated by using the following multiple linear regression analysis (MLR):

$$M_i = s_0 + \sum_{k=1}^{p} s_k g_{ik} \tag{4}$$

Where, $M_i$ is the concentration of particulate matter in the $i$th sample, $s_k$ is regression coefficient, $g_{ik}$ source contribution (average = 1) to be found in the result of PMF modeling.

## Principal component analysis with absolute principal component scores

PCA is a widely used statistical technique in the form of eigenvector analysis. The PCA model extracts a smaller number of uncorrelated components from a large set of variables which explain a maximum of the variance in the data. The new set of variables is simply a linear combination of the measured variables (Thurston and Spengler 1985; Maenhaut and Cafmeyer 1987; Hopke et al. 2006). The APCS was also used to estimate the source components. The factor scores of variables are obtained from PCA by analysis of normalized elemental concentrations. APCS for each component was then estimated by subtracting the factor scores for this artificial sample from the factor scores of each one of the true samples. These APCS were regressed against mass concentration to estimate of the coefficients which were made use to convert the APCS into pollutant source mass contributions from each source for each sample (Thurston and Spengler 1985; Harrison et al. 1996).

As we have explained above, the advantage of PMF and PCA is in determining the fingerprints without prior knowledge of the sources by direct measurement or other emission inventories. PMF is more robust over PCA in the results with non-negativity constraints. Moreover, application of different types of receptor models would provide a more robust result based on their strengths (Viana et al. 2008). In considering the above context, this is important to utilize these two models for the same set of data to see the consistency as well as discrepancy. Thus, we appropriately applied these models to evaluate their strength in the identification and estimation of the sources.

Meteorology around the study areas:

The meteorological parameters, i.e., wind speed and wind direction, were recorded at both sites A and B. Wind rose plots were generated by using a WRPLOT View (version 5.9.0, Lakes Environmental, Canada) and presented in Figs. 2 and 3. Each color represents the ranges of wind speed and a value less than 1 knot was recorded as calm wind. The resultant wind dominantly blew from 333° direction at site A. However, three major wind directions were identified at site A namely; N, NNW, and SW. Wind speed was recorded as calm wind for 0.4% of the entire sampling period at site A. On the other hand, 0.2% of the entire sampling time represented calm wind duration at site B. The resultant wind direction at this location was towards 28°. Major wind sector were demonstrated at site B, namely: NW, N, and SSE. The precipitation (mm), temperature (°C), and relative humidity (%) data for the period of January, 1999 to January, 2005 were downloaded from http://www.data.jma.go.jp.

The monthly total rainfall (mm), mean temperature (°C) and relative humidity (%) for the period of 1999 to 2005 have been shown in Fig. 4. The summarized results showed that the monthly total rainfall was recorded as 140.5 ± 11.7 mm. The lowest and highest rainfalls of a month were recorded as 3.0 and 761.5 mm in February, 2000 and October, 2004, respectively. The average temperature and RH (%) of a month were reported as 16.1 ± 0.80°C and 64.5 ± 1.1%, respectively. Temperature was observed as the highest (27.8°C) for August, 1999 and the coldest day (4.6°C) for January, 2001. The largest humidity condition was recorded in June, 1999 (82%) and the driest (44%) in February, 2000.

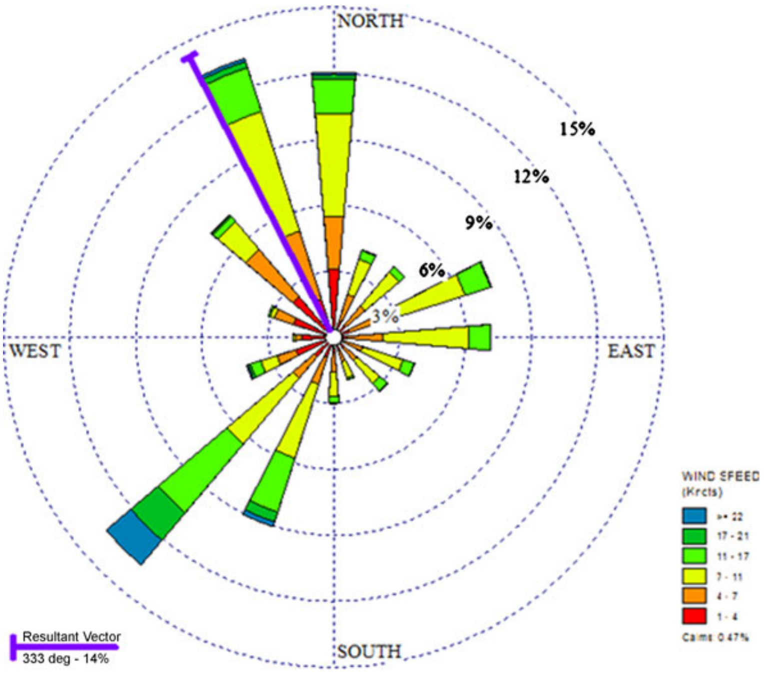


**Fig. 2** Wind rose plot at Site A

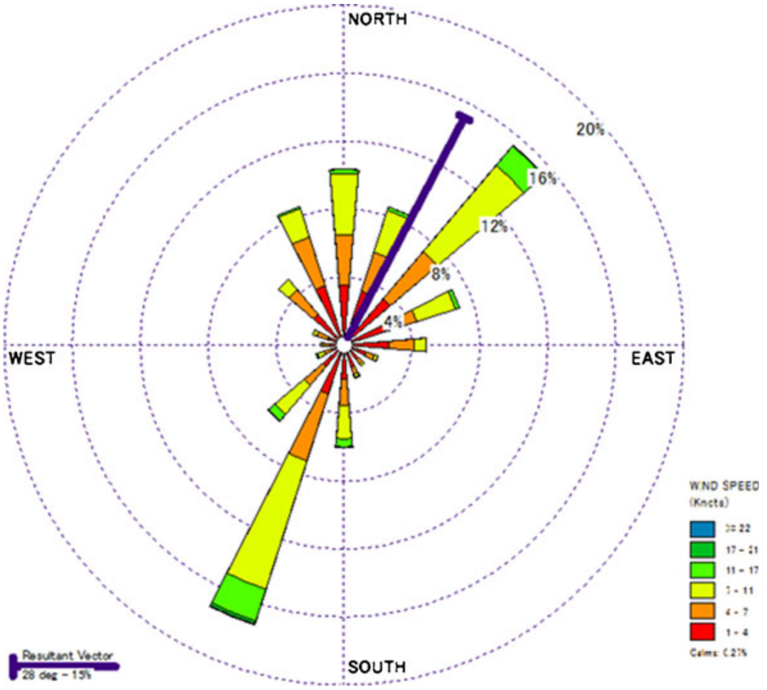


**Fig. 3** Wind rose plot at Site B

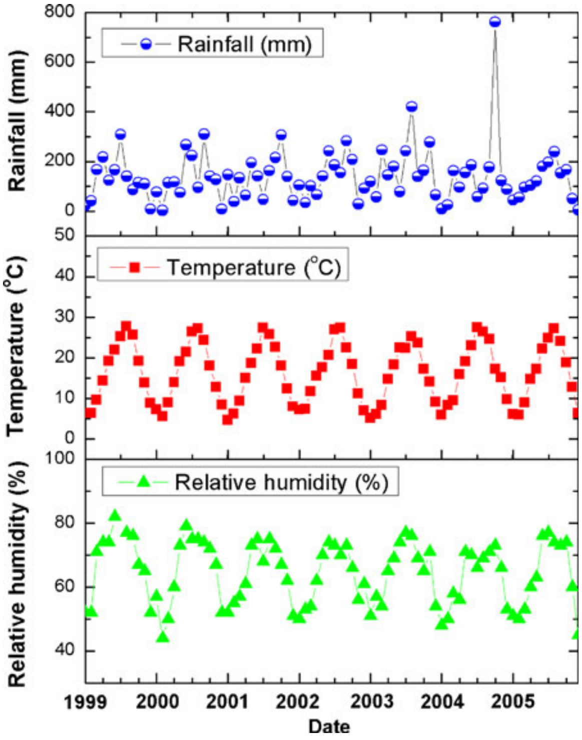


**Fig. 4** Seasonal variation of precipitations, relative humidity and temperature at around sites A and B

## Results and discussions

### Concentration of SPM and elemental mass

SPM samples were collected at sites A and B for the period of 1999 to 2005. The time series of SPM samples are presented in Fig 5. 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. SPM mass demonstrated a substantial decrease in 2005. The SPM mass before 2003 and after 2003 were estimated as 38.3 ± 8.3 μg $m^{-3}$ and 27.5 ± 4.4 μg $m^{-3}$, respectively, at site A and 24.2 ± 5.8 μg $m^{-3}$ and 20.4 ± 3.5 μg $m^{-3}$, respectively, at site B. It seems that the steps taken by the local and central government are effective ways in curbing urban SPM pollution. It is also relevant here to explain a little about the current SPM concentration at the sampling sites A and B. The mean concentrations of SPM were recorded as 27.3 and 24.1 μg $m^{-3}$ at sites A and B in the air quality monitoring network of the Kanagawa Prefectural Government (http://www.city.yokohama.jp/me/kankyou/mamoru/kanshi/hot/ave1004.html) for the period of March, 2009 to March, 2010. Moreover, the

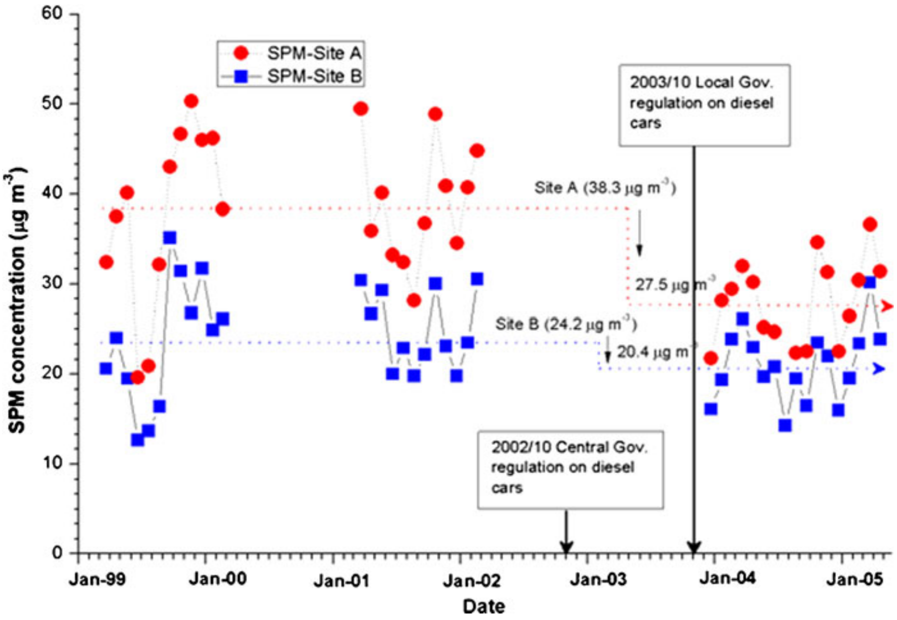


**Fig. 5** Time series of SPM at sites A and B

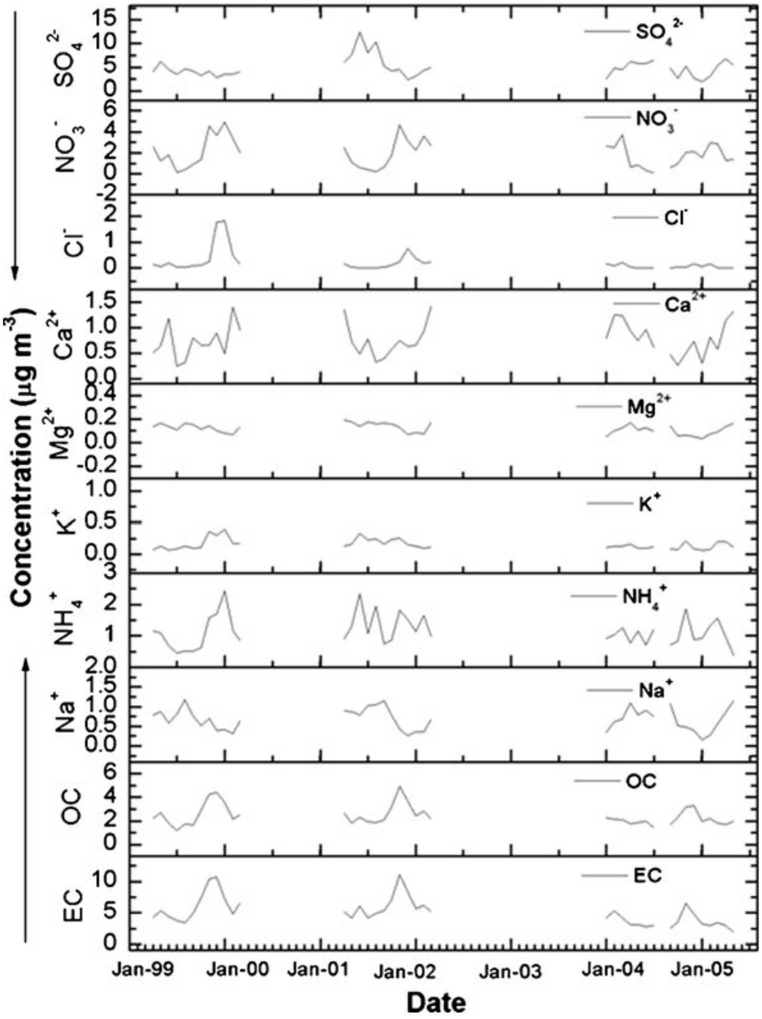
time series of water soluble ions, i.e., $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $NH_4^+$, $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$ and carbonaceous mass (EC and OC) measured in SPM mass at both sampling sites are presented in Figs. 6 and 7. A significant decrease of elemental concentrations was found at site A (Fig. 6) after the introduction of diesel regulation in 2003. EC concentration demonstrated as 6.11 ± 2.17 and 3.62 ± 1.15 μg m$^{-3}$ before and after 2003. In contrast, no significant time trend of chemical species was observed at site B. However, detailed characterization of SPM and elemental mass were discussed in another study (Khan et al. 2010a).

## Discrimination of sources in SPM aerosol

The receptor model, i.e., EPA PMF 3.0 was used to perform source discrimination in 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) the types of the location of sites A and B are similar as they are situated near a highway. It also described above that the areas around the sampling sites are located in the Keihin industrial area which has been recognized as having the highest proximity of industrial distribution. Furthermore, the distance between two sites is shorter. Thus, it was fair enough to label sites A and B as similar in nature. Similar reasons were considered by Jorquera (2009) to apportion the sources of $PM_{10}$ and $PM_{2.5}$ samples collected from three sites applying EPA PMF. 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, (d) to reduce the uncertainty of the apportionment results.

During the application of PMF 3.0, a number of factors was selected after the evaluation of 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 (Paatero and Hopke 2003), (b) the goodness-of-fit parameters, i.e., *Q* (robust) and

**Fig. 6** Time series of ions and carbon at site A



*Q* (true), were optimized changing the number of factors, and compared with *Q* (theoretical). *Q* (robust), the goodness-of-fit parameter calculated excluding outliers, defined as samples for which the scaled residual is greater than 4 and *Q* (true) is calculated including all points (Norris et al. 2008). Accordingly, five factors were decided and the lowest value of *Q* (robust) and *Q* (true) were produced as 2,756 and 2,764, respectively, for 81 samples and 234 computational steps. Theoretical *Q* value was approximately 1,875. It was approximated as $nm - p(n+m)$, where $n$ was the number of species, $m$ was the number of samples in the data set, and $p$ was the number of factors fitted by the model. Based on this definition, theoretical *Q* was estimated as $\{30 \times 81 - 5 \times (30 + 81) = 1875\}$. Residuals ($e_{ij}/s_{ij}$ in Eq. 2) from base run were also checked and most of the species were shown in the range of -3 to +3. Extra modeling uncertainty used was 12%. The source contributions (average = 1) produced by PMF 3.0 at the base run of the lowest *Q* value were used as independent and SPM mass as dependent variables in MLR analysis. As a result, the coefficient of each factor in multiple regression analysis was demonstrated as significant and positive for the calculation of source contribution. To accurately use and interpret the factor profile, the solution of model run must be rotated back to the real solution using the Ppeak function of PMF 3.0. Fpeak run was also performed in our study using the strength of Fpeak rotation from −1 to +1.

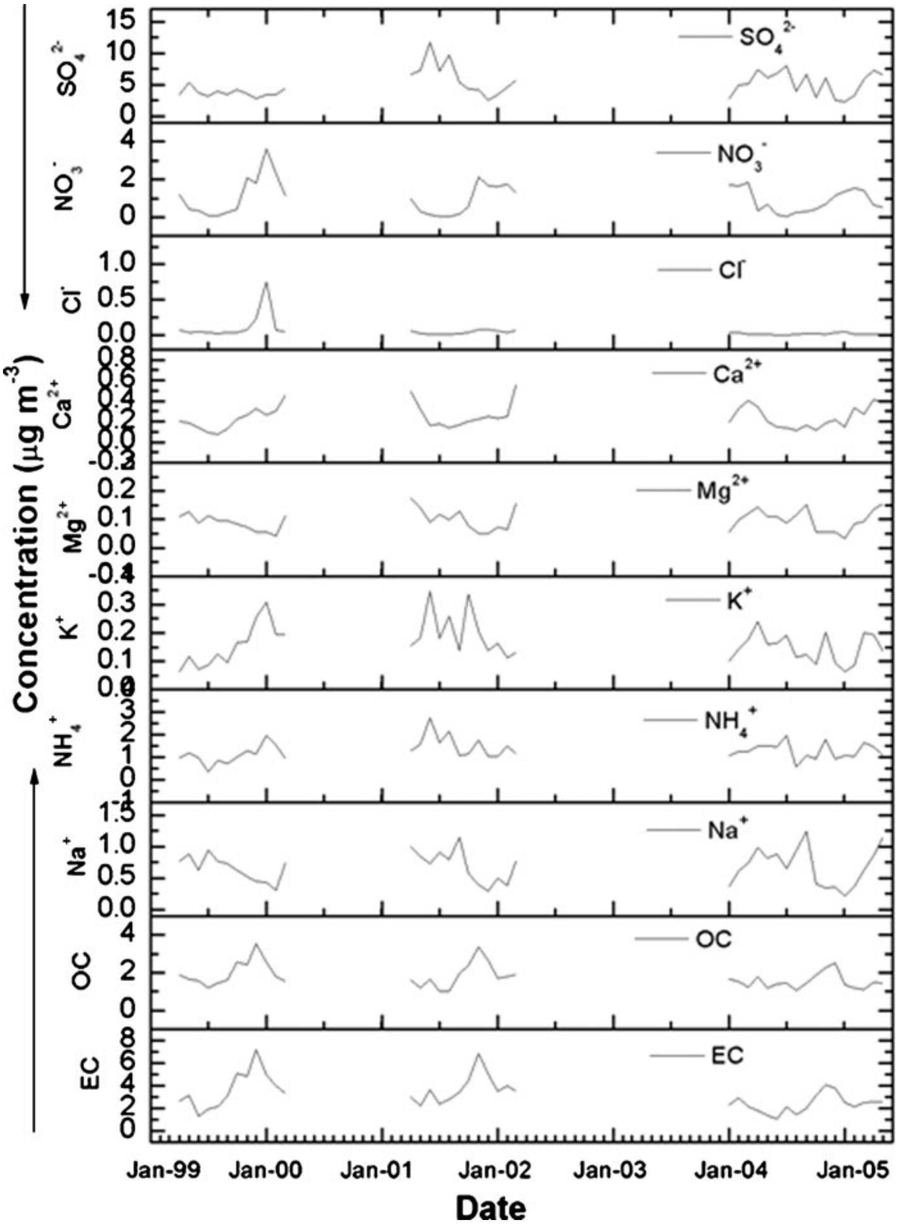


**Fig. 7** Time series of ions and carbon at site B

Moreover, Fpeak without rotation (Fpeak = 0) was also executed. We have considered all Fpeak rotations and physical meaning and PMF result without Fpeak rotation was selected (Fpeak = 0) to explain source profile and source contribution. PMF source profiles of sites A and B are presented in Fig. 8. Source apportionment has also been conducted by using the PCA–APCS methods. Brief comparisons of both methods are discussed in the following section.

### Secondarily formed aerosol source

Factor profile 1, as shown in Fig. 8, was enriched with $SO_4^{2-}$, $NH_4^+$, and $K^+$ and might be recognized as a secondarily formed aerosol 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 $NH_3$, respectively. Industrial combustion plays key roles for the release of $SO_2$ into ambient

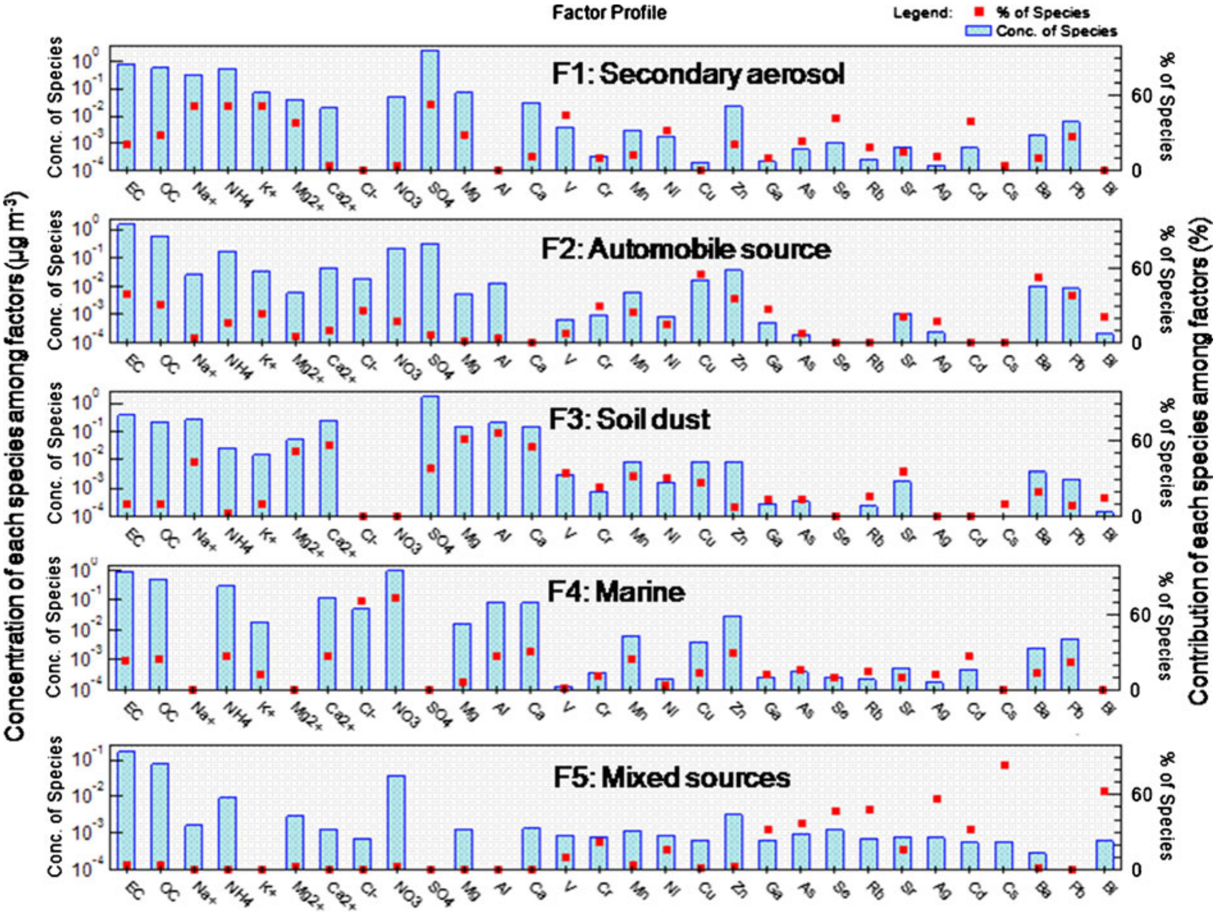


**Fig. 8** Source profiles of SPM aerosol for sites A and B, Yokohama

air. The 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 be responsible for elevated $SO_4^{2-}$ concentration. Moreover, during the sampling period, the 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. On the other hand, $K^+$ was used as a tracer of meat cooking and waste incineration in an urban setting (Wang et al. 2007) as well as biomass and wood burning (Watson and Chow 2001). It was also used to identify refuse incineration source in Kobe City, Japan (Adachi et al. 1995). Yokohama city hosts five municipal solid waste incinerating plants. Incinerating plants are significant sources which discharge various elements of SPM aerosol. EC also contributed significantly in this source factor. It was discussed in several papers that the residence time of EC in the form of BC is 7–8 days in ambient air before it has been removed through wet or dry deposition. BC particles become internally mixed on a time scale of 12 h in urban plumes with non-sea salt sulfate and other organics (Moteki et al. 2007). Thus, EC particles in this source factor might be aged aerosol transported from long distances.

## Automobile source

Factor profile 2 is dominated by EC, OC, Cu, Zn, Ba, and Pb as shown in Fig. 8. It was identified as an automobile source as the species were representative of automobile exhaust. EC and

OC are released from vehicle exhaust (Rodriguez et al. 2004; Takahashi et al. 2008) and diesel engine might be the predominant contributor of EC (Funasaka et al. 1998). The significant source of Cu and Ba is an automobile brake pad (Garg et al. 2000; Sternbeck et al. 2002) and worn-off tires are a major source of Zn (Sörme et al. 2001). 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 roads (Yagi and Tainosho 2003). 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 (Mar et al. 2000). However, Pb might form from some other sources including smelters, lead batteries, leaded paints (Báez et al. 2007), and incineration of municipal solid waste (Zhang et al. 2002).

### Soil dust source

Ca, Al, and Mg dominated in factor profile 3 as presented in Fig. 8. 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 (Oura et al. 2007; Wang et al. 2006; Okuda et al. 2006). Al was used as a soil dust source in Kobe City, Japan as well (Adachi et al. 1995). There might have contributions from local, regionally transported as well as pre-existing elements re-suspended to this source. For instance, the arrival of a spring dust storm originating from East Asia has a suspected role in exhibiting maximum SPM concentrations in Japan (Funasaka et al. 2003; Kanai et al. 2005). Re-suspended soil dust containing Al, Ca, and Mg may also cause high concentration of SPM aerosol at both sampling sites (Srivastava et al. 2008; Wang et al. 2006). Moreover, this source did not containe any $Cl^-$ and $NO_3^-$ due to an unknown reason.

### Marine aerosol

$Cl^-$ and $NO_3{}^-$ were significantly enriched in factor profile 4 demonstrated in Fig. 8 and are recognized as marine aerosol source. $Cl^-$ was present in a considerable extent in this profile which was supposed to be predominantly released from sea salt (Kaneyasu et al. 1995). $Cl^-$ released from marine source primarily attached with coarse particulate matter. However, $NO_3{}^-$ is a secondarily formed aerosol from the precursors of oxides of nitrogen. $Cl^-$ has a tendency to react with atmospheric acid gases such as $HNO_3$ and that leads to form coarse $NO_3{}^-$ particles (Hong et al. 1999; Wang and Shooter 2001). The abundance of $NO_3{}^-$ in this profile could be the result of the reactions explained above. Although the profile is classified as marine, the influence of anthropogenic sources cannot be ruled out as we observed significant amounts of EC and OC which are signatures of an anthropogenic source.

### Mixed source

Factor profile 5 was classified as mixed sources as shown in Fig. 8 (i.e., coal combustion, long-transported Asian dust, and other unknown sources) and the tracers were used to explain this sources included As, Se, Rb, Ag, Cs, and Bi. As and Se are widely accepted source tracers of coal combustion (Ministry of the Environment 1997; Okuda et al. 2006; Harrison et al. 1996; Xie et al. 2006). For instance, one 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 the Asian continent (Fukuyama and Fujiwara 2008; Khan et al. 2010a). However, it is difficult to predict the sources of Rb, Ag, and Bi in this profile.

### Quantification of resolved sources

The estimated contributions of the identified sources at sites A and B are shown in Figs. 9 and 10, respectively. 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 aerosol source (6.9 $\mu g\ m^{-3}$ and 20%), secondary aerosol source (3.1 $\mu g\ m^{-3}$ and 9%), mixed source (coal combustion, long transported Asian dust and other unknown sources; 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,

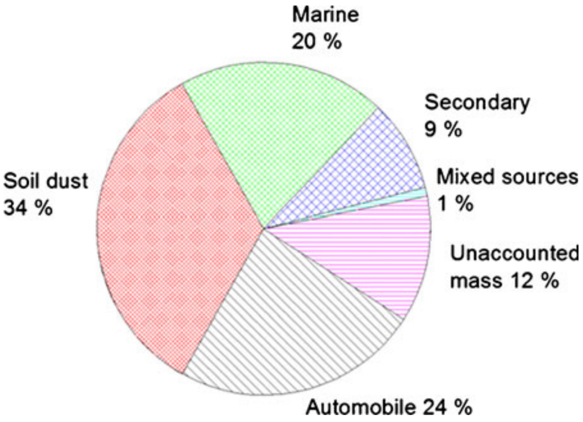


**Fig. 9** Source contribution at site A, Yokohama

secondary aerosol source was dominant with an average of 9.4 μg $m^{-3}$. This source accounted for 41% of SPM mass. The other sources followed by marine aerosol (4.2 μg $m^{-3}$ and 18%), soil dust (2.8 μg $m^{-3}$ and 12%), automobile (1.8 μg $m^{-3}$ and 8%), mixed source (coal combustion, long transported Asian dust and other unknown sources; 1.4 μg $m^{-3}$ and 6%), and unaccounted mass (3.2 μg $m^{-3}$ and 14%). The contribution of automobile at site A was more than double at site B. The following reasons might be responsible for the high contribution of traffic at site A: (a) it is an urban site and (b) the high frequency of automobiles that ply the route every day. Additionally, heavy duty vehicles were commonly found in more than half of the total vehicles at site A. These kinds of vehicles are mostly run with diesel engines which have been suspected to be the gross polluters in major Japanese cities. However, the Government of Japan has taken various measures namely: motor vehicle emission regulations on new vehicles, regulations on vehicles in use in specific areas, and measures to promote the use of low-pollution vehicles aiming to attain environmental quality standards of SPM by FY 2010 (Japan Environmental Council 2003). Soil dust was the predominant contributor at site A compared to site B. Soil dust largely contributed to SPM mass at site A. The reasons underlying the high contribution of soil dust might be (a) high population density and (b) high frequency of different mode of traffic. In addition, sampling site A is located at a junior high school. Various kinds of activities and games performed at the playground might be one of the reasons that cause high emission of soil dust. Marine aerosol and nitrate posed almost similar contribution at both sites A and B as both sites are located quite close to the seashore. Moreover, gas phase $NO_3^-$ has a tendency to react with particulate phase $Na^+$. Thus, the above mechanism probably led to the formation of $NO_3^-$ particles in coarse particulate matter (Hong et al. 1999). As expected, the contributions of secondary aerosol combining with incineration source dominated at site B. The precursors of the secondary aerosol were $SO_2$ and $NH_3$. Industrial production might have played key roles for the release of $SO_2$ at site B. Consequently, the increasing numbers of industrial activities were recognized at this site as major emission sources contributing to local air quality. The industrial activities at site B include various heavy industries, i.e., manufacturer of automobile spare parts, body of vehicles, industrial machineries, etc. Other industries are chemical, pharmaceutical, printing and packaging, electroplating, manufacturer of electronic products, and construction material and equipment. However, another precursor, i.e., $NH_3$, might possibly be released from a nearby agriculture field. Coal combustion source coupled with long transported Cs and other unknown sources made minor contribution at both sites. Contributions of As and Se to SPM were also shown to be of somewhat lower concentrations in comparison with the results observed as 42.1 and 19.5 ng $m^{-3}$ and 6.7

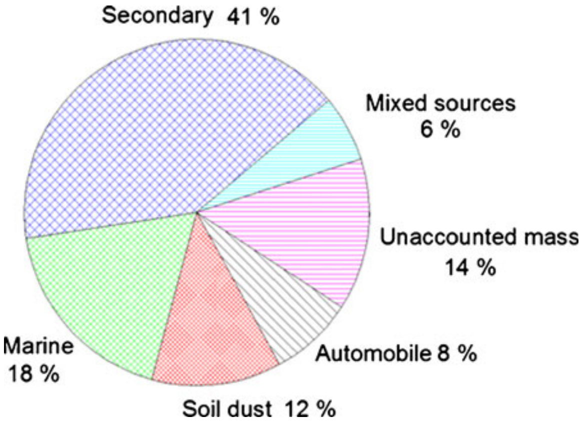


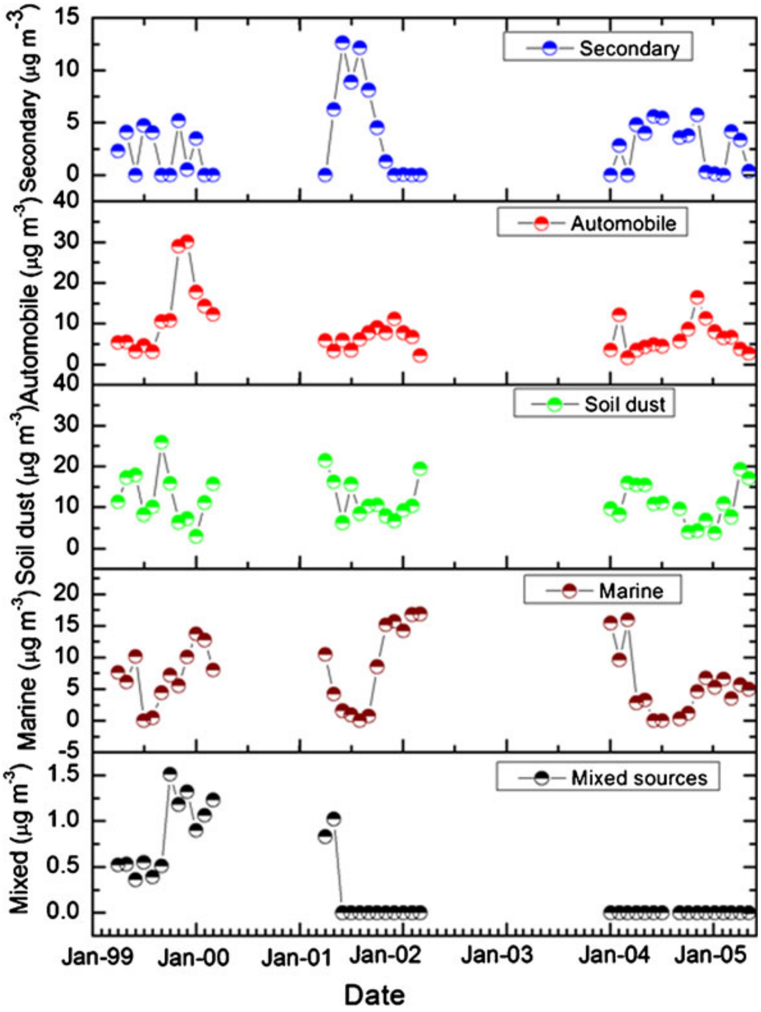
**Fig. 10** Source contribution at site B, Yokohama

and 4.9 ng m$^{-3}$ at Shanghai, China (Zheng et al. 2004) and Birmingham, UK (Harrison et al. 1996), respectively.

### Time series of the sources contribution

Time series of estimated source contributions at sites A and B are shown in Figs. 11 and 12. Automobile contributions predicted by PMF 3.0 for sites A and B were presented in Figs. 11 and 12 and found a large variation over the span of samples collection period. Secondary aerosol coupled with incineration source showed an elevated contribution during summer months at both sites A and B. Sulfate is the most dominating tracer to the above source profile and the increased photochemical activity is one of the important reasons for the enhanced sulfate concentration during the summer months (Husain and Dutkiewicz 1990; Khan et al. 2010b). Contribution of soil appeared as a robust source for both sites A and B during the spring months (Figs. 11 and 12) at both sites. A similar phenomenon was described by Funasaka et al. (2003); Kanai et al. (2005); and Khan et al. (2010a, b) that arrival of spring dust storm originating from East Asia has a suspected role to in exhibiting maximum SPM concentrations in Japan. Marine source showed considerably high contribution during the winter months at both sites (Figs. 11 and 12). Nitrate also contributed considerably to this source factor. Nitrate aerosol might be responsible for the extended contribution made by this source since lower temperature favors the formation of nitrate aerosol (Seinfeld

**Fig. 11** Time series of sources contribution estimated at site A



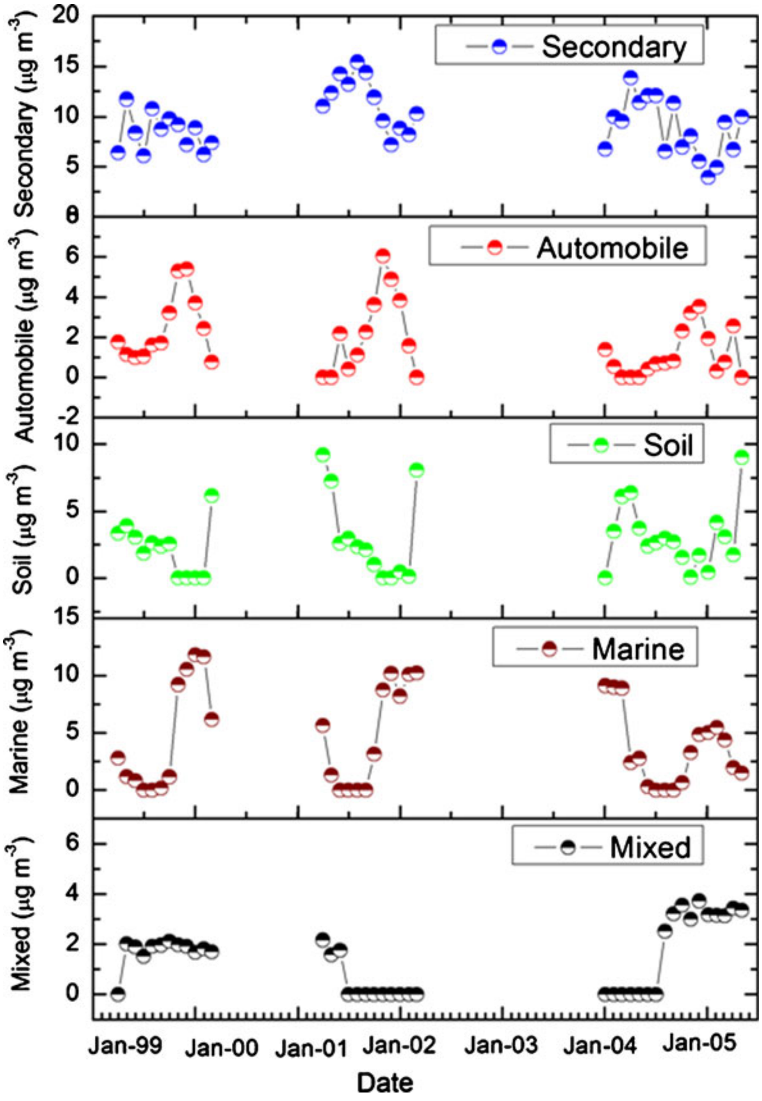


**Fig. 12** Time series of sources contribution estimated at site B

and Pandis 2006; Khan et al. 2010c). Mixed sources largely contributed by coal combustion, long-transported Cs, and other unknown sources did not exhibit any time-dependent response in the whole sampling period starting from April 1999 to May 2005. However, a considerable variation of mixed sources was shown in 2005 at site B.

## Impact of emission regulations

Automobile emission regulations enacted and executed in 2002 and 2003 might have a substantial impact to lower the concentrations of SPM aerosol. It was estimated that the average contributions of automobile source before and after 2003 were, respectively, 9.3 ± 7.3 and 6.5 ± 4.0 µg m$^{-3}$ for site A and 2.3 ± 1.8 and 1.1 ± 1.2 µg m$^{-3}$ for site B. Khan et al. (2010a) also reported that a substantial amount of SPM level was reduced at sites A and B. Net reduction of SPM automobile contribution due to emission control regulation was estimated. It has shown that there was 30% reduction in automobile source contribution at site A. However, there was a large variation in the contribution of automobile source. Seasonal contributions of automobile source were estimated for prior to and after the introduction of the automobile regulations. A paired *t* test was performed using the seasonal sources contributions of the pre- and post-introduction of automobile regulations. We used seasonal data prior to the law, i.e., spring 1999, summer 1999, autumn 1999, winter 2000, and spring 2000. These results were compared with seasonal data after the introduction of the law, i.e., spring 2004, summer 2004, autumn 2004, winter 2005, and spring 2005. During these paired *t* tests, the sources contribution of spring 2001, summer 2001, autumn 2001, winter 2002, spring 2002, and winter 2004 were not used as there were no matching pair of data. A net reduction of the automobile contribution was found (prior, 11.8 μg m$^{-3}$ and after the regulation, 6.2 μg m$^{-3}$) at site A. However, reduction of this source at site A was not significant (*t* stat, 2.44, $p < 0.07$). Similarly, a net reduction of the automobile source was found (prior, 2.1 μg m$^{-3}$ and after the regulation, 1.2 μg m$^{-3}$) at site B and the reduction was also not significant (*t* stat, 2.49, $p < 0.07$) at site B. Marine and mixed sources were significantly (*t* stat, 3.07, $p < 0.04$ and *t* stat, 5.36, $p < 0.01$) reduced at site A. Other sources at sites A and B were not significantly impacted by automobile regulations. The reasons underlying the above observations should possibly be because of the limited number of data used in this study. The span of the filter samples were collected for quite longer and that also could have impacted on some signatures of sources.

## Comparison of the results of PMF 3.0 and PCA–APCS

Comparison of the source apportionment results by PMF 3.0 and PCA–APCS was made and presented in Table 1. Samples collected from two sites (sites A and B) were used together in PMF source apportionment procedures. Consequently, PCA–APCS approach accounted for a similar dataset as used for the PMF analysis. Thus, we noticed that major source fingerprints were commonly resolved by the PMF 3.0 and PCA–APCS models. As explained above, PMF 3.0 identified five sources of SPM aerosol at sites A and B. However, PCA–APCS extracted four sources and interpretations were made with physical meanings. The sources of SPM aerosol predicted by PCA–APCS were automobile, soil dust, secondarily formed aerosol, and combustion of heavy-fuel oil as demonstrated in Table 1. It could be summarized from Table 1, that the most vibrant sources, i.e., automobile, soil dust, secondarily formed aerosol, were derived in both PMF 3.0 and PCA–APCS procedures. The standard errors of the mean between similar sources of sites A and B by both procedures were also estimated and presented in Table 1. The results showed that the SEM (%) of the most striking sources was much lower compared to subsequent sources. And the sources with lower contribution exhibited comparatively flat results with higher SEM (%). However, the contribution of automobile source showed somewhat higher SEM (%) at site A. Moreover, there was an unknown reason for a large variation of automobile sources quantified by the two models. A similar explanation was unanimously exerted by several research groups participating at a source apportionment workshop (Hopke et al. 2006).

Additionally, PCA–APCS extracted combustion of heavy-fuel oil. This source could well explain the chemical nature of SPM aerosol at the present study areas. For instance, oil-fired power generating plant and a large density of ship movement in Yokohama port could discharge the

**Table 1** Comparison of the source apportionment result using PMF 3.0 and PCA–APCS

| Contributing sources | PMF 3.0 | | PCA–APCS | | SEM (%) | |
|---|---|---|---|---|---|---|
| (μg m$^{-3}$) | Site A | Site B | Site A | Site B | Site A | Site B |
| Soil dust | 11.5 ± 5.3 | 2.8 ± 2.5 | 11.9 ± 3.7 | 8.5 ± 2.9 | 0.18 (18) | 2.8 (280) |
| Automobile source | 8.2 ± 6.3 | 1.8 ± 1.7 | 14.2 ± 7.3 | 5.8 ± 3.8 | 3.0 (300) | 2.0 (200) |
| Secondary | 3.1 ± 3.4 | 9.4 ± 2.8 | 6.1 ± 2.7 | 6.9 ± 2.3 | 1.5 (150) | 1.3 (130) |
| Fuel oil combustion | – | – | 0.22 ± 0.16 | 0.19 ± 0.09 | – | – |
| Marine | 6.9 ± 5.2 | 4.2 ± 4.0 | – | – | – | – |
| Mixed sources | 0.30 ± 0.38 | 1.4 ± 0.73 | – | – | – | – |
| Undefined | 4.2 ± 5.4 | 3.2 ± 3.1 | 1.90 ± 4.8 | 1.60 ± 2.1 | – | – |

Contribution (μg m$^{-3}$) = mean ± standard deviation. *SEM%* standard error of the mean respective tracers (V and Ni) to SPM aerosol. However, combustion of fuel oil did not appear in PMF source profiles. PMF procedures also separated marine aerosol as well as mixed sources with significant amount of SPM mass contribution at sites A and B. PCA–APCS and PMF 3.0 procedures left unaccounted 1.9 and 1.6 μg $m^{-3}$ as well as 4.2 and 3.2 μg $m^{-3}$ of SPM mass at sites A and B, respectively.

## Conclusions

A source apportionment study of SPM samples was carried out using US EPA PMF 3.0. SPM samples collected over 6 years (1999 to 2005) at urban (site A) and suburban (site B) areas of Yokohama, Japan. The sources identified at two sites were automobiles as inferred from the tracers of EC, OC, Cu, Zn, Ba and Pb; soil dust as explained by Ca, Mg, and Al; marine aerosol source as inferred from the tracers of $Cl^-$; mixed sources associated with the tracers of Se, Rb, Ag, and Bi; secondary aerosol as inferred from the tracers $SO_4^{2-}$, and $NH_4^+$. Also, source quantification was performed. Soil dust and automobile sources were striking contributors at site A. However, these sources made less than half of contributions to site B compared to site A. Thus, it could be reasonable to conclude that soil and automobile sources of SPM aerosol might be produced from local origin at the current study areas. Besides, Asian dust has an impact on the intensified SPM concentration in some certain period of the year. Since automobiles are still robust contributors to SPM at urban site like A, this paper recommends continuing the current effective measures to reduce emission from this source. However, there was about 30% of reduction in the contribution of automobile to SPM pollution at site A after the introduction of strict automobile emission regulation. In contrast, secondary aerosols in the form of sulfate and ammonium as well as mixed sources (coal, long-transported Cs, and other unknown sources) were remarkable at site B. We presume that stationary/industrial combustion has more impact on the release of SPM components at site B than A. A comparison was made with the results of PMF 3.0 and PCA–APCS. SPM aerosol samples collected from two sites were treated together in PMF apportionment procedure. Consequently, PCA–APCS accomplished source apportionment using the similar set of samples. The most vibrant sources commonly resolved by both PMF 3.0 and PCA–APCS procedures showed consistent results. However, the uncertainty was somewhat larger for the sources with small contribution. Thus, the procedures of data selection being tested in this investigation could be a reasonable way of handling data produced from multiple sites at close proximity within the study area.

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