Long-term observational data for the size distributions and particulate chemical components have been summarized to understand the past and current particulate conditions in Osaka City. The positive matrix factorization (PMF) method was also applied to estimate the source changes. The observational data obtained using Andersen cascade impactors reveals that for the 40 years from fiscal year (FY) 1976 to 2015, there was a 70% reduction in PM fine (less than 2.1 μm of the aerodynamic diameter) and 76% reduction in PM coarse (over 2.1 μm). These correspond to a 71% and 74% reduction in PM 2.5 (particulate matter less than 2.5 μm in diameter) and PM 10, respectively. From the continuous chemical measurements made in this study, we observed a more than 50% reduction in coarse particulate elemental carbon (EC), SO 4 2−, NH 4 +, Zn, Pb, and Cd, commonly in residential and roadside areas, over the last 20 years. Similarly, the level of the fine particulate EC, Ca 2+, Cl−, Zn, Mg 2+, Pb, and Cd was reduced by more than 50%. Notably, the results of the particulate component analysis of EC fine show a typical reduction of 73%–79% for 20 years, and this is the main component contributing to the reduction of atmospheric particulate concentration. However, there seems to have been no apparent reduction of V fine concentrations, SO 4 2− fine showed a relatively low reduction of 19% to 26%, and NH 4 + fine levels fell by 14% to 21% in 20 years. Since fine sulfate and ammonium have similar behaviors, ammonium sulfate is considered to be a secondary particle aerosol because of long-range transportation. The PMF analysis still estimates a high contribution rate of secondary particles, which is one of the current problems. In contrast, although vanadium is a minor element, it is likely to be generated from harbor areas with ships because they are susceptible to the prevailing sea breeze in summer. Therefore, in the future, it will be necessary to scrutinize and take countermeasures not only for long-range transportation but also for domestic sources.

**KEY WORDS** Elemental Carbon (EC), Long-term observation, Positive Matrix Factorization (PMF), Sulfate, Vanadium

**1. INTRODUCTION**

The behavior of atmospheric particulate matter (PM) is complicated because it is heterogeneous and undergoes spatiotemporal changes (Kelly and Fussell, 2012). PM has wide-ranging effects on health but it impacts the respiratory and cardiovas-
cular systems most strongly (World Health Organization, 2005). A recent study suggested that worldwide, 3.45 million PM$_{2.5}$-related premature deaths occurred in 2007, 12% of which were related to transboundary effects (Zhang et al., 2017).

The size of PM varies from a few nanometers to tens of micrometers, and the mass size distribution, generally in the atmosphere, is divided into bimodal fine (less than around 2 μm) mode and coarse mode (more than around 2 μm). The fine PM contains primary combustion particles, including diesel exhaust particles (DEPs) and secondary particles that have grown by coagulation and condensation. The coarse PM is mainly from mechanically generated or natural airborne particles, such as soil resuspensions (including yellow sand dust), road dust (including brake and tire wear), volcanic ash, sea salts, and powder cement.

For fine particles, the Japanese Ministry of the Environment set a new regulation for PM$_{2.5}$ in 2009 (annual 15 μg/m$^3$; daily 35 μg/m$^3$). The average concentration of PM$_{2.5}$ in the fiscal year (FY, from April to March in next year in Japan) 2017 was 11.6 and 12.5 μg/m$^3$ for 814 general atmospheric monitoring stations and 224 vehicle exhaust monitoring stations, respectively (Japanese Ministry of the Environment, 2019). Overall, 89.9% and 86.2% of general and vehicle exhaust monitoring stations meet the environmental standard rate, respectively. The chemical analysis of PM$_{2.5}$ has also been introduced to estimate the emission sources and promote pollution control, and the number of monitoring sites nationwide was 189 in FY2017.

In contrast, coarse particles have less direct effects on human health than fine particles, although it is reported that coarse particles may trigger adverse responses in the lungs, leading to hospital admissions (Brunekreef and Forsberg, 2005). In addition, coarse particles have a significant indirect influence on the living environment. As such, visibility, soil pollution, farm products, and the influence on specific industrial products are factors of concern. There is a more recent concern regarding resuspended biological PM inhalation by infants (Wu et al., 2018). Many findings, however, do not report on both the chemical components of and long-term changes to atmospheric coarse particles.

The measurement period is important when investigating atmospheric particles, and depends on the purpose of the study. For example, short-term observation will be effective for the concentration of PM$_{2.5}$ that rises with a generation of secondary particles when it is humid (60%–80% relative humidity [RH]) (Wang et al., 2018). Conversely, long-term observation is important when considering the effect of various pollution measures. Regulations on the entry of diesel vehicles into the Tokyo metropolitan area, which began in 2002, and the mandatory installation of diesel particulate filters (DPFs) have greatly contributed to the reduction of DEP, which has long been a problem in Japan (Yamamoto et al., 2007). Even in the Osaka area, the atmospheric particle concentration decreased remarkably both in the roadside and residential areas. The effects of such administrative and technical measures have gradually emerged and should be seen from a long-term perspective.

The objective of this paper is to show the long-term changes in the size distribution of atmospheric particles in Osaka City, with a special focus on the trends of the chemical constituents of coarse and fine particles. Furthermore, the factors of particulate components that decreased during the long term and those that did not decrease were clarified through PMF analysis and meteorological correlations. On public health perspectives, the final aim of this project is to monitor the aerosol levels of Osaka City in the past and future to understand the effects of policies, relationships with industrial structures, and changes in the transportation environment, and to establish the basis for further measures.

2. METHODS

2.1 Sampling Sites and Data Handling

Atmospheric particulate concentrations and size distributions were measured at a general monitoring site in Osaka City for more than 40 years from April 1976 (Fig. 1). Four different sampling sites in a suburban residential area were used during the monitoring period. In 1995, a roadside sampling area was added near Route 43 (R43) and the Hanshin Expressway on the west side of Osaka City. Simultaneous observations of the particulate constituents at the residential and roadside areas commenced in April 1995 and continued for 20 years to March 2015. The sites of the obtained meteorological data are listed in Fig. 1.

In this paper, the long-term data were basically evaluated by the average value every five years. The trend of data over multiple years is important for long-term evaluation since the year-to-year changes in particulate con-
Concentrations are greatly affected by the construction works around the measurement point. In addition, such short-term concentration changes in the particles are also dependent on the weather of a specific year. In Japan, the national census (Ministry of Internal Affairs and Communications), road traffic census, and national urban traffic characteristics survey (Ministry of Land, Infrastructure, Transport and Tourism) are conducted every five years. Therefore, in this paper, the data are organized every five years so that the relationship with these survey results can be considered in the future.

2.2 Meteorological Data Analysis
Monthly average data for temperature, relative humidity, wind direction, and wind velocity were calculated based on an hourly database provided by the National Institute for Environmental Studies (NIES).

2.3 Sampling Methods
The Andersen cascade impactor (Tokyo Dylec. Co. Ltd., AN-200) was used to collect particles separately on nine filter sheets (ADVANTEC TOYO, QR-100, quartz fiber, 80 mm). The size ranges of the particles corresponded to less than 0.43 (back up), 0.43–0.65 (stage 7), 0.65–1.1 (stage 6), 1.1–2.1 (stage 5), 2.1–3.3 (stage 4), 3.3–4.7 (stage 3), 4.7–7.0 (stage 2), 7.0–11 (stage 1), and more than 11 μm (stage 0) in aerodynamic diameter. The sampler was operated at 28.3 L/min for 10–15 days and the filters were changed at both the residential and roadside monitoring sites. As a rule, the monthly average was obtained from the data from the filter replacement day of the first week of the month to the first week of the next month. In exceptional cases, the filters were replaced at the end of the month and sampling was performed once a month.

2.4 Filter Preparation
Before sampling, the filters were preheated in an electric furnace at 800°C for 2 h, kept in a room at 20°C and 50% RH for more than 48 h, and weighed prior to use. After sampling, the filters were re-weighed under the same conditions and were then sealed and stored at −20°C until analysis.
2.5 Mass Concentration Analysis

In this study, PM<sub>fine</sub> is defined as particles with diameters less than or equal to 2.1 μm (stage 5–7 and back up), and PM<sub>coarse</sub> (stage 0–4) as particles with diameters greater than 2.1 μm. A low-volume air sampler (Shintaku Machine Co., Model S-2), which can collect suspended PM (SPM, less than 10 μm of particle diameter) on a filter (ADVANTEC TOYO, QR-100, quartz fiber, 110 mm), was complementarily driven.

It is noted that because the sampler classifies particles with a 50% cut off point, the data obtained are theoretically able to convert to PM<sub>1.5</sub> and PM<sub>10-1.5</sub> mass concentrations from cumulative curves as shown in Supporting Fig. 1. Mass median diameter (MMD), which corresponds to 50% of the cumulative curves was also obtained.

We challenged the parallel comparative measurements using a reference PM<sub>1.5</sub> sampler equipped with a well impactor ninety-six (WINS) impactor (Thermo Fisher Scientific Co. Ltd., Model 2025). Approximately 1.06 ± 0.18 of the mass concentration ratio was obtained for the calculated PM<sub>1.5</sub> by the Andersen cascade impactor to the US Federal Reference Method (n = 8).

Size distribution curves were obtained by the interpolation with the spline function using R version 3.2.1 on a Mac OS 10.7.5. When R did not provide an appropriate solution for the dataset, another calculation method (Kogure, 2013) was partially applied. The size distribution curves were visualized using RINEARN Graph 3D on Windows Vista.

2.6 Chemical Analysis

Chemical analysis was performed on a monthly basis following the method of Funasaka et al. (2003). Soluble anionic species, such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>, and cationic species, such as NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, were analyzed by ion chromatography. Inorganic metals such as Fe, Zn, Mn, and Cu were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or flame atomic absorption spectroscopy (AAS), and Pb, Cd, and V were analyzed by electro-thermal AAS. Elemental carbon (EC) was measured by thermal oxidation (Hayashi et al., 1985; Tanner et al., 1982) using a CHN-CORDER elemental analyzer (Yanaco Co. Ltd., MT-5), according to a previous study (Funasaka et al., 1998). Briefly, a part of the filter was heated at 600°C for 5 min in a helium flow to burn the volatile organic compounds and then reheated at 900°C in helium containing 4% oxygen for 5 min to obtain the EC. As for the organic carbon (OC), no data were collected; OC was suggested to be lost by volatilization during long periods of sampling (Turpin et al., 1994). Our preliminary studies also confirmed the loss of organic matter by the parallel measurement of the Andersen cascade impactor, which was continuously operated for one week, and the PM<sub>1.5</sub> sampler, which had its filter changed daily (data not shown). The fine EC concentration was estimated by the parallel measurement with a low-volume air sampler and an Andersen cascade impactor from April 1995 to March 2011. Thereafter, the fine EC concentration was measured using an Andersen cascade impactor.

2.7 Source Apportionment Analysis by PMF

The source contributions of the fine particles at the residential and roadside areas from FY1995–2014 were estimated by PMF 5.0 (The United States Environmental Protection Agency, 2014). The PMF method is a statistical model that extracts several source factors from multicomponent fluctuation elements and estimates the origin of the factors by focusing on the component composition of the extracted factors. The PMF method is different from the chemical mass balance method in that it does not require data on the chemical composition of the source in advance. It should be noted that the results of the PMF method do not always indicate the source, and chemical components that exhibit similar behaviors are included in the same source factor.

In preparing the analytical database, if the concentration of a constituent was lower than the detection limit, the value was rearranged by 1/2 of the detection limit. If the uncertainty data matrix was made by an error fraction as the method detection limit of each constituent. For the source apportionment analysis, the calculation was repeated 20 times, and bootstrap cross-validation was calculated 100 times. For the calculation, 14 constituents (EC, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, V, Mn, Fe, Zn, Pb, and Cd) were used. The results of Na<sup>+</sup> and Cu were excluded because the correlations between the observations and predictions were low ($R^2 < 0.6$). Since the analytical accuracy was comparable to those of the other components, the low reproducibility of these components may be due to the relatively high frequency of outliers in the actual sample, although the reason for this is unknown.

In the PMF model, the solution is calculated so that the Q value, which is the sum of squares of the error in
the factor analysis, is minimized. There are three types of Q value. First, Q\textsubscript{(True)}, which is the value calculated from all the observation data input to the model, and then Q\textsubscript{(Robust)}, which is sampled except for the data with uncertainty-scaled residual values greater than four, were calculated. Finally, Q\textsubscript{(Theory)}, which is theoretically determined, is calculated from the number of samples and the number of factors. In determining the optimum number of factors (p), a statistically optimum p that satisfies Q\textsubscript{(True)} ≈ Q\textsubscript{(Robust)} ≈ Q\textsubscript{(Theory)} is desirable. It is also important to find the physically optimal p that can reasonably explain the actual environment (Iijima, 2011). In this study, nine factors were selected because the average ratio of Q\textsubscript{(True)}/Q\textsubscript{(Theory)} and Q\textsubscript{(Robust)}/Q\textsubscript{(Theory)} was 0.98 at the 15% condition of the model error. We also confirmed the good reproducibility of the bootstrap calculations when determining the number of factors.

3. RESULTS

3.1 Meteorological Observations in Osaka City from April 1995 to March 2015

Prior to the analysis of the behavior of the particulate chemical constituents, the monthly average meteorological data for ambient temperature and relative humidity were obtained (Fig. 2(a)). Typical seasonal changes were observed, with high humidity and temperatures in summer. The monthly average temperature and humidity for the 20 years were 17.1 ± 8.7°C and 66 ± 16% RH, respectively. The maximum and minimum monthly average temperatures recorded were 31.0°C in August 2010 and 4.5°C in January 2011, respectively. The maximum humidity of 77% RH was obtained in June 2011 and the minimum of 55% RH was observed in April 1996 and April 2004.

Fig. 2(b) shows the monthly average wind direction frequencies and wind velocity (downside) in Osaka City. The wind directions from NNE, NE, WSW, W, and N were dominant during the observation period. Fig. 2(c) indicates the monthly changes in wind velocity, with an average velocity during the 20 year period of 2.1 ± 1.4 m/s. A maximum of 2.7 m/s was recorded in December 2005, and a minimum of 1.5 m/s was recorded in November 2004 and 2005 and October and December 2008.

Table 1 summarizes the five-yearly average meteorological data. There were no significant changes in long-term temperature, humidity, and wind velocity; therefore, there were no direct relationships between particu-
late concentration changes and these meteorological parameters with regards to long-term observations although there might have been short-term temperature rises and localized rainfall. In contrast, the NE wind direction frequency gradually reduced from 11% during FY1995–1999 to 7.5% during FY2010–2014; and the WSW and SW frequencies increased slightly. The reason for these long-term changes in wind direction is unknown; however, they are not entirely unrelated to the long-term decrease in particles.

3.2 Forty-year Trend of the Size Distribution of Atmospheric Suspended Particles in the Residential Area during FY1976–2015

The 40-year trend in the size distribution curves of atmospheric particles at the residential area from FY1976-FY2015 is shown in Fig. 3. The results show a typical bimodal mass size distribution of less than or more than approximately 2 μm of the particulate diameter. Furthermore, the MMD was within 1.8 ± 0.7 μm for the 40-year time period.

From FY1976–1980, the fine and coarse particulate concentrations decreased markedly, afterwards, the concentration decrease rate slowed. It is known that PM$_{2.5}$ includes some parts of coarse particles (Fig. 3) and the excess is estimated as an average of 7.4% for the recent five-year data correction period. In contrast, PM$_{10-2.5}$ exclude coarse particles of over 10 μm in diameter. This is equivalent to 41% of the losses.

The five-year average mass concentration of PM$_{fine}$ during FY1976–1980 was 43 μg/m$^3$, which corresponds to 45 μg/m$^3$ of PM$_{2.5}$ calculated from the cumulative curves. Similarly, the PM$_{course}$ concentration during FY1976–1980 was 50 μg/m$^3$, which corresponds to 34 μg/m$^3$ of PM$_{10-2.5}$. In contrast, the average concentrations of PM$_{fine}$ and PM$_{2.5}$ were both 13 μg/m$^3$ during FY2011–2015. The PM$_{course}$ and PM$_{10-2.5}$ were 12 and 9.0 μg/m$^3$, respectively, during FY2011–2015. The fine PM$_{fine}$ and PM$_{2.5}$ were reduced by 70% and 71% of their original values, respectively, over the 40-year period. Similarly, for PM$_{course}$ and PM$_{10-2.5}$ the mass concentration values were reduced by 76% and 74%, respectively.

In Japan, the Atmospheric Pollution Prevention Act
was revised in 1973, and an environmental standard for SPM was established. The remarkable decrease in PM concentrations during the 1970s is attributed to the widespread use of bag filters and electrostatic precipitators in factories and business sites (Japanese Ministry of International Trade and Industry, 1986). A later section addresses the decreasing trend after the 1990s, and it is thought that some administrative regulations for diesel exhaust particulates and dioxins contributed greatly to the observed environmental improvement. Regarding the long-term fluctuations of other gaseous pollutants, the trend shown in Wakamatsu et al. (2013) was also observed in Osaka: SO₂, NOₓ, and hydrocarbons decreased remarkably in the last 40 years, while O₃ did not.

### 3.3 Comparison of the Mass Concentrations between Residential and Roadside Areas during FY1995–2014

The monthly concentrations of coarse and fine particles at the residential and roadside monitoring sites are presented in Fig. 4. It is notable that during FY1995–1997, the PM_{coarse} and PM_{fine} concentrations in the roadside area were higher than those in the residential area. The maximum concentration differences between the two areas were 26 μg/m³ in February 1996 for PM_{coarse} and 16 μg/m³ in March 1996 for PM_{fine}. These concentration gaps correspond to 14 μg/m³ for PM_{10-2.5} and 16 μg/m³ for PM_{2.5}, respectively. Thereafter, the concentration differences gradually decreased, with an average difference of 3.2 and 0.84 μg/m³ for PM_{coarse} and PM_{fine}, respectively, in FY2014. In addition, the gaps corresponded to 1.9 and 0.89 μg/m³ for PM_{10-2.5} and PM_{2.5}, respectively.

Table 2 summarizes the long-term average mass concentration changes in the particles. The MMD is also provided. Notably, the MMD gradually increased in the residential area during the observation period, resulting in the reduction of the fine fraction exceeding that of the coarse fraction. The MMD of 2.5 μm at the roadside area during FY2010–2014 as shown in Table 2 was greater than that obtained from the residential area (2.0 μm). This is attributed to the slightly higher concentration of the PM_{coarse} in the roadside area than in the residential area.
The concentration ratio of PM\textsubscript{fine} to PM\textsubscript{total} ratios during FY2010–2014 were determined to be 0.50 for the residential area and 0.47 for the roadside area.

3.4 Outline of the Trend of Particulate Chemical Constituents during FY1995–2014

The monthly changes in the concentration of atmospheric particulate components for EC, SO\textsubscript{4}\textsuperscript{2-}, NH\textsubscript{4}\textsuperscript{+}, and NO\textsubscript{3}\textsuperscript{-} during the 20-year time period are shown in Fig. 5.

3.4.1 EC Concentration Changes

EC concentration was largely decreased during this 20-year time period in both the residential and roadside areas, as shown in Fig. 5(a). It is also suggested that the concentration difference between the residential and roadside areas was decreased by FY2009. This was due to the fact that the influence of DEP derived from the automobile exhaust gas, which had contributed significantly to the PM concentration, was greatly reduced, and the difference in concentration between the roadside and residential areas was minimized.

3.4.2 Sulfate, Ammonium, and Nitrate Concentration Changes

The concentration changes in coarse and fine sulfate are shown in Fig. 5(b) and (c). The ratio of the coarse and fine mode of sulfate was, on average, 15:85 for the residential area, and 17:83 for the roadside area. The coarse SO\textsubscript{4}\textsuperscript{2-} concentration was relatively reduced, although the concentration differences between the residential and roadside areas were not as significant when compared to the fine EC trend by FY2009 (Fig. 5(a)). The concentration of fine sulfate gradually reduced at the residential and roadside areas, although the reduction rate was smaller than that of the coarse reduction rate. Typically, high concentration tendency of fine SO\textsubscript{4}\textsuperscript{2-} has been seen in July, and this is attributed to the promotion of photochemical reactions in the atmosphere.

The trend of NH\textsubscript{4}\textsuperscript{+} is displayed in Fig. 5(d) and (e). The ratios of the coarse and fine modes of NH\textsubscript{4}\textsuperscript{+} were 4:96 for both the residential and roadside areas. This result indicates that the fine fraction of the particulate ammonium was lower than that of the sulfate because particulate ammonium is mostly derived from secondary gas-to-particle formations, such as condensation. The long-term monthly change in fine sulfate is synonymous with that of ammonium. Furthermore, significant corre-
Fig. 5. Monthly average concentration of particulate EC, sulfate, ammonium and nitrate ion at the residential and roadside areas in Osaka City from FY1995 to 2014. *Calculated from parallel measurements between low-volume and Andersen cascade impactor from April 1995 to May 2011.
lations were obtained for both the residential ($R = 0.75$, $p < 0.001$, $n = 240$) and roadside areas ($R = 0.86$, $p < 0.001$, $n = 240$).

The concentration changes in the coarse and fine particulate NO$_3^-$ are shown in Fig. 5(f) and (g). Particulate NO$_3^-$ has a bimodal size distribution, which is derived from secondary fine particle formation and coarse particles from sea salt and soils. The ratio of the coarse and fine mode of nitrate was, on average, 70:30 for the residential area and 72:28 for the roadside area.

### 3.4.3 Twenty-year Trend of Particulate Compositions

The five-year average particulate composition changes of the fine constituents measured in this research are shown in Fig. 6. During FY1995–1999, the EC ratio was high for both residential and roadside areas, at 25% and 32%, respectively. These ratios were reduced to 12% and 14% in FY2010–2014, respectively. Conversely, the ratios of sulfate and ammonium gradually increased. Sulfate was 24% and 18% in FY1995–1999, increasing to 31% and 30% in FY2010–2014 in the residential and roadside areas, respectively. Similar to sulfate, the ratios for ammonium increased from 6.8% and 5.8% in FY1995–1999 to 10% and 9.5% in FY2010–2014 in the residential and roadside areas, respectively.

Table 3 summarizes the five-year average concentration changes in the particulate constituents measured in this study from FY1995 to 2014. The reduction percentage was calculated by the concentration differences between FY2010–2014 and the FY1995–1999 baseline. The concentration ratios of the residential to roadside areas were also calculated. The coarse EC concentrations were mostly reduced during the 20-year period, with 78% and 80% reductions in the residential and roadside areas, respectively. For the coarse particles, SO$_4^{2-}$ concentrations were reduced by 56% at both sites. The concentrations of coarse Ca$^{2+}$, which were unevenly distributed in the coarse mode, were reduced by 43% and 47%, respectively, in the residential and the roadside areas. For the metals, coarse particulate Pb and Cd concentrations were reduced significantly in both the residential and roadside areas.

For the fine fraction, numerous particulate constituents were largely reduced following the reduction of EC with 73% and 79% reduction in the residential and roadside areas, respectively. In particular, the Ca$^{2+}$, Cl, Zn, Mg$^{2+}$, Pb, and Cd concentrations were often reduced by more than 50% at both sampling sites during the 20-year period; however, the reductions in fine SO$_4^{2-}$ and NH$_4^+$ concentrations were relatively low, at 19%-26% and 14%-
Table 3. Summary of the mass concentrations of the particulate constituents in Osaka city calculated every five years from FY1995 to 2014.

| Constituents     | Residential monitoring site (A) | Roadside monitoring site (B) |
|------------------|---------------------------------|-----------------------------|
|                  | FY1995 | FY2000 | FY2005 | FY2010 | FY2010 | FY1995 | FY2000 | FY2005 | FY2010 | FY2010 |
|                  | Conc. | Conc. | Conc. | Conc. | Conc. | Conc. | Conc. | Conc. | Conc. | Conc. |
|                  | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] | [ng/m3] |
| SO2              | 39.2  | 34.2  | 33.2  | 21.1  | 17.1  | 10.3  | 3.1   | 3.1   | 3.1   | 3.1   |
| NO2              | 49.8  | 47.1  | 43.9  | 27.6  | 23.6  | 17.2  | 8.1   | 8.1   | 8.1   | 8.1   |
| CO               | 26.1  | 23.1  | 21.1  | 13.6  | 11.6  | 8.1   | 4.1   | 4.1   | 4.1   | 4.1   |
| HCO3             | 21.1  | 19.1  | 17.1  | 11.6  | 9.6   | 6.1   | 3.1   | 3.1   | 3.1   | 3.1   |
| Cl               | 149.3 | 145.3 | 135.3 | 87.6  | 73.6  | 57.6  | 29.6  | 29.6  | 29.6  | 29.6  |
| SO4              | 34.2  | 30.1  | 28.1  | 17.6  | 14.6  | 11.6  | 7.1   | 7.1   | 7.1   | 7.1   |
| NO3              | 29.1  | 26.1  | 24.1  | 15.6  | 13.6  | 11.6  | 6.1   | 6.1   | 6.1   | 6.1   |
| Mg2              | 14.9  | 12.9  | 11.9  | 7.6   | 6.6   | 5.6   | 3.1   | 3.1   | 3.1   | 3.1   |
| K                | 3.1   | 2.9   | 2.7   | 1.7   | 1.5   | 1.3   | 0.8   | 0.8   | 0.8   | 0.8   |
| Zn               | 0.8   | 0.7   | 0.6   | 0.4   | 0.4   | 0.3   | 0.2   | 0.2   | 0.2   | 0.2   |
| Fe               | 1.7   | 1.5   | 1.4   | 0.9   | 0.9   | 0.8   | 0.5   | 0.5   | 0.5   | 0.5   |
| Cu               | 0.3   | 0.3   | 0.3   | 0.2   | 0.2   | 0.2   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Ni               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Mn               | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |

Conc.\([\text{FY2010-2014}]\)/Conc.\([\text{FY1995-1999}]\); ††calculated from parallel measurements between low-vol and Andersen cascade impactor from April 1995 to March 2011.

Reduction was calculated in 100\%\((\text{Conc.\([\text{FY1995-2014}]\)/Conc.\([\text{FY1995-1999}]\)]\).
Fig. 7. Correlation of monthly concentration of coarse and fine SO$_4^{2-}$ between residential and roadside areas in Osaka City from FY1995 to 2014.
Regarding the fine particulate SO$_4^{2-}$, long-term changes in the relationship of the coarse and fine particulate sulfate concentrations between the roadside and residential areas were compared (Fig. 7). Five-yearly monthly concentrations were plotted with correlation coefficients. Although all the relationships were statistically significant ($p < 0.001$), the concentration changes differed between the coarse and fine fractions. As described above, the concentration of the coarse mode sulfate was significantly reduced compared to that of the fine mode during the 20-year study period. It is, therefore, suggested that primary particles exhausted by the fixed outbreak source were decreased by countermeasures; however, the amounts of secondary particulates remain a current problem.

3. 5 Relationship between the Wind Direction Tendency and Vanadium Behavior

As shown in Table 3, the long-term decrease tendency of the particulate concentration significantly depending on the chemical constituent. Among them, a clear decrease in the concentration of vanadium has not been observed in the last 20 years. To investigate the behavior of vanadium concentrations, an aerial factor is discussed in this section. Fig. 8 shows the change in the five-year monthly average concentration of fine vanadium at the roadside and residential areas. Here, the reason for comparing the roadside and residential areas is not because vanadium is caused by automobile exhaust gas, but for the purpose of comparing Dekijima ES, located geographically near the port area, to other measurement points in the inland area (Fig. 1). The characteristic of vanadium is summarized by the following three points: (1) first, the tendency to rise in the long term from April to August did not change, (2) the concentration was always high in the roadside area from April to September, and (3) the tendency to decrease was not observed during the past 20 years, and the increase in concentration from June to August was shown in the roadside area after FY2005.

In this section, the possibility of the aerosol constituents being carried by the westerly wind was investigated. According to Fig. 2, the wind directions in summer in Osaka were mainly SSW, SW, and WSW, whereas the winter season had more wind from the NE. Fig. 9 shows the Pearson correlation coefficient (R) between the concentrations of fine PM and representable particulate constituents (V, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, K$^+$, Cd, EC), and each wind direction frequency. Here, when R was significantly high ($**p < 0.001, n = 240$), we thought that the pollutants would indicate the direction in which they were carried by the wind. Therefore, it was found that the characteristic Osaka summer wind from S to W significantly affected the rise in vanadium concentrations. A similar

![Fig. 8. Five-year monthly average concentration of fine vanadium in the residential and roadside areas.](image-url)
trend was shown for sulfate and ammonium; however, the correlation coefficients were slightly lower. In contrast, nitrate exhibited a significant correlation with wind from the WNW, NW, and NNW, which were dominant wind directions in the winter season.

Osada et al. (2019) suggested that the optical black carbon, nickel, and vanadium concentrations commonly increased during summer daytime with sea breezes in Nagoya, Japan. Heavy oil combustion, including from ships along the coastline, is considered to be the original source. Our result, indicating a significant relationship between fine vanadium concentrations and sea breeze frequencies is consistent with their conclusion. Therefore, the effects from the Osaka Bay area have continuously persisted for the 20-year period of this report. This finding is supported by the higher concentration of fine vanadium (Fig. 8) and higher R value (Fig. 9) in the roadside area located near the Osaka Bay area compared to the residential areas (Fig. 1).

3.6 PMF Source Apportionment of the Fine Particles

The source concentration profiles using the PMF model are presented in Fig. 10. The fine mass concentration is also shown in the left side of the figure.

Factor I shows a high concentration of EC. In addition, Zn and Ca are commonly evident. EC is known to be an index of DEPs (Shareef and Bravo, 1988). Zn and Ca are derived from the combustion of motor oil (Zieba, 1998). Therefore, this factor was determined to be a direct traffic-related factor.

Factor II was considered to be a secondary sulfate owing to its commonly high concentration of sulfate and ammonium.

Factor III shows the highest concentration of Fe, Mn, and Zn. It is also reported that the concentrations of particulate Fe, Mn, and Zn around the steel industry zone were significantly higher than those at the background site in the Yangtze River Delta region in China (Dai et al., 2015). In Japan, however, the effluent gas in the large-scale ironworks was treated in a closed system, and these elements were thought to be derived from the scattering of minor dust emission sources and boilers (Japanese Ministry of the Environment, 1997). We, therefore, determined this factor to be derived from industrial activity.

For factor IV, vanadium was solely detected among the predicted nine factors. Vanadium and nickel are contained in crude oil (Moreno et al., 2010), and thus were regarded as indices of heavy oil combustion, including in the harbor area.

Factor V had a greater nitrate concentration, and the secondary nitrate was assigned to this factor.

Factor VI was determined to be a soil resuspension factor. Although the chemical indexes for soil-derived particles are usually Al and Si, there are no data regarding this in this study. Alternatively, we selected Ca and Mg as soil indices according to a previous report that analyzed the metallic and soluble ionic constituents of soil samples collected in Osaka City (Miyazaki et al., 1995). In the study, the average concentrations of Ca and Mg in the surface soil were 1.55 and 0.124 mg/g (n = 18), respectively.

Factor VII had a particularly high Pb concentration, and Zn, Ca, K, and Fe were also detected. Pb and Zn were rich in the road dust samples in Osaka City (Miyazaki et al., 1995). It was also reported that Ca and Fe are commonly included in paved and unpaved road dust (Japanese Environmental Agency, 1997). This factor was therefore determined to be road dust resuspension.

Factor VIII was specified to be refuse incinerators. Our results showed relatively high K and Zn, which are the representative chemical indices of refuse incinerator emissions (Japanese Environmental Agency, 1997; Mamuro et al., 1979).

Factor IX included high concentrations of Cl, which is derived from the secondary formation of particulate chloride. Although the particles derived from sea salt and soils are mainly composed of Na and Cl, Na was excluded from the PMF analysis in this study. Significant correlations between the observed Na and Cl were obtained for the coarse particles in both the roadside (R = 0.69, p < 0.001, n = 58) and residential (R = 0.63, p < 0.001, n = 60) areas from FY2010 to 2014. Conversely, correlations were weak for the fine particles in the roadside (R = 0.28, p < 0.05, n = 58) and residential (R = 0.27, p < 0.05, n = 60) areas during the same period. It is therefore assumed that the characteristic Cl in this factor is associated with anthropogenic sources, such as secondary particulate formations, rather than natural airborne particles, such as those derived from sea salt.

3.7 Long-term Changes in the Predicted Source Contributions for Fine Particles

3.7.1 Predicted Mass Concentration Changes

The long-term changes in the observed and predicted
mass concentrations are compared in Fig. 11. The relationship between the observed and predicted mass concentrations during all time periods is also shown on the left in Fig. 11. Significant correlations were obtained both in the roadside ($R = 0.94, p < 0.001, n = 192$) and residential areas ($R = 0.90, p < 0.001, n = 201$). Therefore, the PMF calculation adopted in this study (factor number = 9, extra modeling unit 15%, 14 chemical con-
substituents) may suggest that most of the fine particulate mass concentrations observed are explained by the predicted values.

3.7.2 Source Contribution Changes
The predicted source contribution changes in the nine evaluated factors for fine particles between the roadside and residential areas are summarized in Fig. 12, where average source concentrations were calculated every five years from FY1995–1999, FY2000–2004, FY2005–2009, and FY2010–2014. The fractional concentrations were also separately predicted by season: spring was from April to June, summer was from July to September, autumn was from October to December, and winter was from January to March. All five-yearly average contributions are displayed on the right side of each figure as “ALL”.

3.7.3 Factor I: Traffic Exhaust
A large decrease in the predicted fine mass concentration was obtained during the 20-year period both in the roadside and residential areas, reflecting a decrease in the actual particulate concentration (Fig. 6). In particular, the source contribution from Factor I (40%), which was deemed primary traffic exhaust represented as DEPs in the roadside area during FY1995–1999, was reduced slightly to 38% in FY2000–2004 and was then reduced markedly to 17% in FY2005–2009 and further to 8.7% in FY2010–2014. Similarly, the source contribution from factor I (28%) at the residential area during FY1995–1999 was reduced to 24% in FY2000–2004, 12% in FY2005–2009, and 7.7% in FY2010–2014. With regard to DEP reduction, the enforcement of diesel exhaust restrictions occurred in the Tokyo area from 2002, and the concentration of EC consequently decreased (Yamamoto et al., 2007). Hence, some countermeasures such as the introduction of DPFs, and regulation of large cars in the downtown area have also been effective in the Osaka area. This factor is relatively high in autumn and winter because aerosols remain in the low-rise troposphere due to the occurrence of an inversion layer, particularly before 2009.

3.7.4 Factor II: Secondary Sulfate
In contrast, the source contribution from factor II associated with secondary sulfate commonly increased at both the roadside and residential areas. This is because the decrease in fine sulfate during the 20-year period was not as high as that in EC (Table 3). The predicted five-yearly PMF calculation increase was 15%, 25%, 37%, and 39% in the roadside area. The increasing tendency of the source contributions from factor II over the five-year period was relatively high in the residential area, at 27%, 37%, 41%, and 47%.

There was a relatively high contribution of factor II in the spring and summer seasons; however, the contribution in winter was high in the recent data from FY2010–2014. Ikeda et al. (2015) reported that the effect of PM$_{2.5}$...
Fig. 11. Comparison of observed and predicted mass concentration changes for fine particles.
from China was apparent in the Kyusyu and Kinki (which includes Osaka) areas during January 2010 through emissions-sensitive weather research and forecasting community multiscale air quality (WRF/CMAQ) chemical transport model. A high contribution of factor II shown in this study may, therefore, be affected by long-distance transport from East Asia.

### 3.7.5 Factor III: Industrial

Factor III, which is apportioned as an industrial contribution, showed a slight reduction in concentration during the 20-year period. For the roadside and residential areas, the average concentrations of 3.2 μg/m³ and 2.8 μg/m³ in FY1995–1999 were reduced to 2.6 μg/m³ and 1.8 μg/m³, respectively, in FY2010–2014. In Osaka, the blast furnace of a large-scale ironworks was closed down in recent years, which may explain the reductions in concentration. The emission contributions of factor III, however, relatively increased from 12% in FY1995–1999 to 20% in FY2010–2014 in the roadside area. This is attributed to the fact that the reduction in DEP concentration of factor I was significantly higher than that of factor III.

### 3.7.6 Factor IV: Heavy Oil Emission

As demonstrated in Fig. 8, factor IV, heavy oil emission, showed a high contribution from spring to summer (Fig. 12). This tendency is commonly seen in both the roadside and residential areas. The predicted average contributions of factor IV increased from 6.9% and 5.9% in FY1995–1999 to 15% and 12% in FY2010–2014 in the roadside and residential areas, respectively. Source countermeasures in the Osaka Bay area, including ships, is one of the issues in recent years.

### 3.7.7 Factor V: Secondary Nitrate

The seasonal behavior of factor V (secondary nitrate) is typical, and the contributions were high from autumn to winter (Fig. 12). The average contribution of factor V showed no significant difference during the 20-year period. In the most recent data from FY2010–2014, the average contributions of factor V were 8.1% and 9.1% in the roadside and residential areas, respectively.

### 3.7.8 Factors VI and VII: Soil and Road Dust

Factors VI and VII are the natural airborne particles derived and aerially resuspended by soil and road dust, respectively. The average contributions of factor VI gradually reduced from 7.7% and 7.7% in FY1995–1999 to 5.4% and 5.0% in FY2010–2014 in the roadside and residential areas, respectively. Similarly, the average contribu-
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3. 7. 9 Factor VIII: Municipal Incineration Facilities

Factor VIII, which is related to emissions from municipal incineration facilities, is considered to be the most significant. Although the predicted contribution is low, the percentage reduced significantly during the 20-year period. At the roadside and residential areas, the contributions of 1.8% and 2.4% in FY1995–1999, respectively, reduced to 0.53% and 0.69% in FY2009–2014, respectively. Laws concerning special measures against dioxins were introduced by the Environment Agency of Japan in 1999, whereby regulations for gas and effluent emissions relating to dioxins have been established. Hence, controlling dust emissions is largely effective for reducing contributions (Shiota et al., 2011).

3. 7. 10 Factor IX: Secondary Chloride

Factor IX, which is concerned with secondary chloride, showed a minor contribution of 0.67% in both the roadside and residential areas in FY2010–2014, although relatively high contributions were indicated in the autumn and winter seasons before FY2009. It is reported that NH₄Cl is a major chemical form of fine particles, which is transformed by HCl (Chang and Allen, 2006). Our results indicate that although a certain amount of gas-to-particle formation may occur, the chloride concentration in fine particles is lower than that in coarse particles (Table 3), and therefore, the contribution ratio to fine particles is relatively low.

3. 7. 11 Additional Remarks

The source assignment calculation solely quantified the results for the measured chemicals. Components that could not be measured analytically, such as OC, need to be considered in future research. The results of inverse calculations that incorporate them as unknown factors are preliminary and are shown in Supporting Fig. 2.

4. CONCLUSIONS

1) Long-term observations by the Andersen cascade impactor in Osaka City quantitatively demonstrate a decreasing trend of fine particles and coarse particles over 40 years. Our results find that PM_{2.5}fine and PM_{2.5} were reduced by 70% and 71%, respectively, over the 40-year period. Similarly, for PM_{10-2.5} and PM_{10-2.5} the mass concentrations were reduced by 76% and 74%, respectively.

2) According to the results of the particle component analysis, EC_{fine} showed a typical reduction of 73%–79% over 20 years, with many other particle components also decreasing; however, the degree of decrease varied depending on the component. In contrast, SO_{4}^{2−}_{fine} remained at a 19%–26% reduction, whereas SO_{4}^{2−}_{coarse} was reduced by 56%, implying that the amounts of secondary particles are only current problems.

3) Vanadium has not decreased over the last 20 years; it is suggested to originate from Osaka Bay, which contains ships and other heavy oil users, owing to its strong and statistically significant correlation with wind direction.

4) The PMF analysis results of fine particles extracted nine factors to investigate long-term fluctuations. Sulfate is naturally derived or transported from overseas, and its contribution rate is high because the reduction rates of other constituents were higher. In addition, industry and secondary nitrate also have relatively high contribution rates, and the effects of domestic emissions are also highlighted.

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SUPPLEMENTARY MATERIALS

**Fig. S1.** Particle size conversion. First, the particle collection diameters set for each stage of the Andersen cascade impactor and the cumulative frequency of the mass concentration are plotted on a semi-logarithmic graph. Then, a complementary curve is drawn. Finally, the cumulative frequencies at 2.5 μm and 10 μm are estimated based on the graph; these are then multiplied by the mass concentration and converted into the concentration. The mass median diameter is interpolated from the point at which cumulative frequency is 50% point.

**Fig. S2.** Average source apportionment of atmospheric fine particles at roadside and residential locations in Osaka City over a 20 year period (FY1995 to 2014), as predicted by PMF model. Unknown factors have been added and the data was recalculated.