

Long-term observation of PM_{2.5} and water-soluble inorganic ions at central Tokyo, Japan

by

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Abstract

Long-term exposure to fine particulate matter, PM_{2.5} has been inviting considerable attentions in relation to adverse health effects. In this study, PM_{2.5} samples were collected at Shibuya, Tokyo, Japan from July 2013 to Nov 2019 and atmospheric concentrations were determined for PM_{2.5} and its water-soluble inorganic ions. This paper aimed to characterize seasonal and yearly variations of atmospheric concentrations of PM_{2.5} and water-soluble inorganic ions using the seven-year result. The analytical results showed the concentration of PM_{2.5} ranged from 2.4 to 39 $\mu\text{g}/\text{m}^3$, with an arithmetic mean of $12 \pm 5.9 \mu\text{g}/\text{m}^3$ ($n = 132$) and higher in spring and winter. No apparent increasing or decreasing tendency was found for the annual variation of PM_{2.5} level. The variation of PM_{2.5} was mostly determined by the content of ammonium sulfate because of significant correlation with concentrations of NH_4^+ and SO_4^{2-} . However, slight decreasing tendency was found in SO_4^{2-} concentration for 7 years. Meanwhile, Na^+ concentration showed significant increase with time. These findings suggest potential changes in the quality of PM_{2.5} at the sampling site.

Keywords: PM_{2.5}, water-soluble inorganic ions, sea-salt, Tokyo

1 Introduction

Air pollution owing to particulate matter is known to cause adverse health effects, visibility im-

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 pairment, and global climate change [1]. Of particular interest is fine particulate matter ($\text{PM}_{2.5}$) with a size of $2.5\text{ }\mu\text{m}$ or less, because increased mortality by pulmonary and/or cardiovascular diseases due to long-term exposure to $\text{PM}_{2.5}$ has been documented in a number of previous epidemiological studies [2, 3]. Additionally, the evidence was provided by recent studies [4] on linear and non-threshold relationship between long-term exposure to $\text{PM}_{2.5}$ and all-cause/cause-specific mortality. $\text{PM}_{2.5}$ is a mixture of various particles emitted and/or generated from natural and anthropogenic sources, and hence appearance of adverse health effects may depend on the chemical composition of $\text{PM}_{2.5}$ at a site of interest. Therefore, understanding chemical composition of $\text{PM}_{2.5}$ is necessary for preventing from health outcomes caused by exposure to $\text{PM}_{2.5}$ and pollution control.

Meanwhile, environmental education plays an important role in developing a common understanding of the fundamental value of the environment [5], and awareness is one of the first steps toward improving air quality [6]. Authors of this study have initiated joint observation of $\text{PM}_{2.5}$ at Shibuya, Tokyo, Japan since July 2013 aiming to cultivate environmental awareness of high-school students and grasp the status of $\text{PM}_{2.5}$ in Tokyo metropolitan area by means of science. Among the chemical components in $\text{PM}_{2.5}$, we have focused on water-soluble inorganic ions. They are known to account for majority of the mass of $\text{PM}_{2.5}$ [7, 8] and the major ions such as sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium ion (NH_4^+) have effects on the hygroscopic nature and acidity of aerosol [7]. Besides, they can be analyzed by ion chromatography (IC) after extraction with water. The IC is suitable for educating high school students in science course because the chromatography is a principle technology in analytical chemistry.

The first two-year result of this study was previously published [9], suggesting the long-range transport of urban aerosols and soil-derived particles when air masses came from Asian continent. However, the air pollution mechanism of the city was not fully evaluated due to a limitation in the number of $\text{PM}_{2.5}$ samples. In this paper, we aimed to characterize seasonal and yearly variations of $\text{PM}_{2.5}$ in relation to those of water-soluble inorganic ions collected at Shibuya using the seven-year result from July 2013 to Nov 2019, in order to better understand the air pollution mechanisms of the city.

2 Methods

2.1 Sampling site

Figure 1 shows the geographical location of Shibuya, Tokyo, Japan. Routine sampling of $\text{PM}_{2.5}$ was conducted at the open-air space in the campus of Tokai University Bosei Senior High School located in Shibuya ward. Shibuya is one of the biggest cities in central Tokyo, having a population density of 15,656 people per km^2 , and is known as a major commercial and business center of Japan. The sampling site of this study is located in cultural and residential area of the city.

2.2 Collection of $\text{PM}_{2.5}$ samples

As shown in Figure 2, $\text{PM}_{2.5}$ was collected on a quartz fiber filter (QMA 47 mm ϕ , Whatman) at a flow rate of 16.7 L/min for 7 days by $\text{PM}_{2.5}$ sampler (Thermo Fisher Scientific, Partisol® - FRM Model 2000). Both before and after sampling, the quartz fiber filters were conditioned more



Fig. 1 Location of sampling site, Shibuya, Tokyo, Japan.

than 24 hours under constant temperature (20°C) and relative humidity ($50 \pm 5\%$), then the weight of filter was quantified by using a microbalance. The concentration of PM_{2.5} was determined by the weight difference and total sampling volume of air. Note that routine collection of PM_{2.5} and measurement of PM_{2.5} concentration were carried out by high school students, and subsequent chemical analysis was conducted by students of Shonan Campus, Tokai University.



Fig. 2 Sampling of PM_{2.5} on the quartz fiber filter at Shibuya, Tokyo, Japan.

2.3 Analysis of water-soluble inorganic ion

Though the analytical procedure was described in previous paper [9], a minor update in the analytical instruments has been made. So, in brief. After measurement of PM_{2.5} concentration, the filters were cut into 14 mmφ pieces by a pierce punch. The two pieces were transferred into

a 50 mL-test tube together and water-soluble inorganic ions in $\text{PM}_{2.5}$ were extracted in 10 mL ultrapure water (Milli-Q) using As-One Shaker SR-1 at 170 rpm for 60 min. After filtration by a disposable cellulose acetate membrane filter having 0.20 μm of pore size (Advantec, DISMIC-25CS), the filtrate was served for ion analysis. Concentrations of the water-soluble inorganic ions such as Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} were determined by IC systems.

The IC system used for cation analysis consisted of Shimadzu LC-20AD pump, SIL-10Ai auto-sampler and COD-10A_{VP} conductivity detector. The following conditions were used: column, $\phi 4.6 \times 150$ mm, 7 μm , ShodexTM IC YS-50 (Showa Denko); eluent, 5.0 mM oxalic acid solution at 1.0 ml/min (isocratic); oven temperature, 40°C; injection volume, 20 μL . Dilution series of $(\text{NH}_4)_2\text{SO}_4$ used for calibration and determination.

Meanwhile, the IC system used for anion analysis consisted of Thermo Fisher Scientific, DionexTM AquionTM with a chemical suppressor AMMS 3000 and DionexTM AS-AP auto-sampler. The following conditions were used: separation column, 4.0×250 mm, IonPac AS9-HC (Thermo Fisher Scientific) with a guard column IonPacAG4 (Thermo Fisher Scientific); eluent, 5 mM sodium carbonate at 1.0 ml/min (isocratic); scavenger for the chemical suppressor, 15 mM sulfuric acid, oven temperature, 40°C; injection volume, 25 μL . Dilution series of reagent grade NaCl, NH_4Cl , KCl, MgCl_2 , CaCl_2 , NaCl, NaNO_3 and Na_2SO_4 in ultrapure water were used for calibration and determination. All the reagents were obtained from Kanto Chemical, Japan.

Significant contamination by field handling and during storage was slightly found in storage blanks for anions, limit of detection (LOD) was defined as three-fold the standard deviation of the blank for anions and of 1.0 $\mu\text{L ml}^{-1}$ of standard solutions for cations (3σ). The LODs resulted in 0.0053 $\mu\text{g/m}^3$ for Na^+ , 0.0030 $\mu\text{g/m}^3$ for NH_4^+ , 0.0023 $\mu\text{g/m}^3$ for K^+ , 0.0032 $\mu\text{g/m}^3$ for Mg^{2+} , 0.013 $\mu\text{g/m}^3$ for Ca^{2+} , 0.0010 $\mu\text{g/m}^3$ for Cl^- , 0.0029 $\mu\text{g/m}^3$ for NO_3^- and 0.0036 $\mu\text{g/m}^3$ for SO_4^{2-} .

3 Results and Discussion

Figure 3 shows variations of atmospheric concentrations of $\text{PM}_{2.5}$ and water-soluble inorganic ions at Shibuya, Tokyo. The date shown in the X-axis is start day of the 7-day samplings. Arithmetic means and standard deviations of each analyte were summarized in Table 1. For the convenience in investigating seasonal differences, the results were classified into four seasons: spring (March to May), summer (June to August), autumn (September to November), and winter (December to February). Pearson's correlation coefficients between paired data on the variation of atmospheric concentrations were calculated using a software, IBM SPSS[®] Statistics ver.23 and shown in Table 2. The correlation analysis has been widely used for source apportionment of particulate matters, because significant mutual correlations between seasonal variations of atmospheric concentrations in PM and its components may show a possibility of sharing the common emission source by the paired variables [10]. Based on the results, seasonal and yearly variations of $\text{PM}_{2.5}$ were characterized in relation to those of water-soluble inorganic ions.

The 7-day average concentration of $\text{PM}_{2.5}$ greatly varied from 2.4 to 39 $\mu\text{g/m}^3$, with an arithmetic mean of 12 ± 5.9 $\mu\text{g/m}^3$ ($n = 132$, Table 1). Since 46% of the data conformed with the World Health Organization's (WHO) guideline value for $\text{PM}_{2.5}$ of 10 $\mu\text{g/m}^3$ as an annual mean,

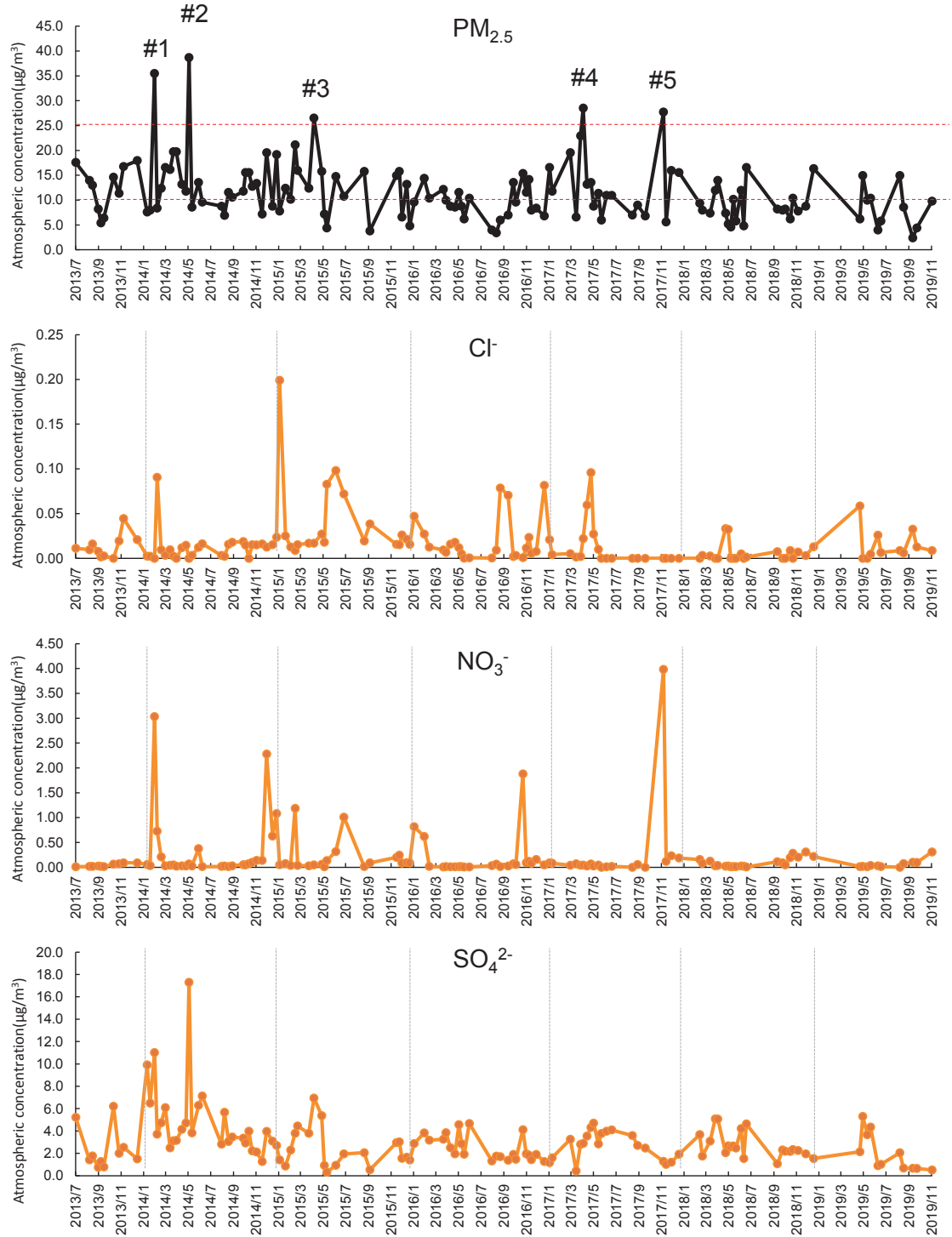


Fig. 3 Variations of atmospheric concentrations of PM_{2.5} and water-soluble inorganic ions collected at Shibuya, Tokyo, Japan from July 2013 to November 2019.

the status of air pollution by PM_{2.5} is suggested not so severe at the sampling site. However, high concentration episodes, #1–#5, were found whose levels greater than WHO guideline value of 25 µg/m³ as a 24-h mean (Figure 3). The PM_{2.5} concentration was found higher in spring and winter due in part to high concentration episodes (#1~#4) caused by the yellow sandstorm,

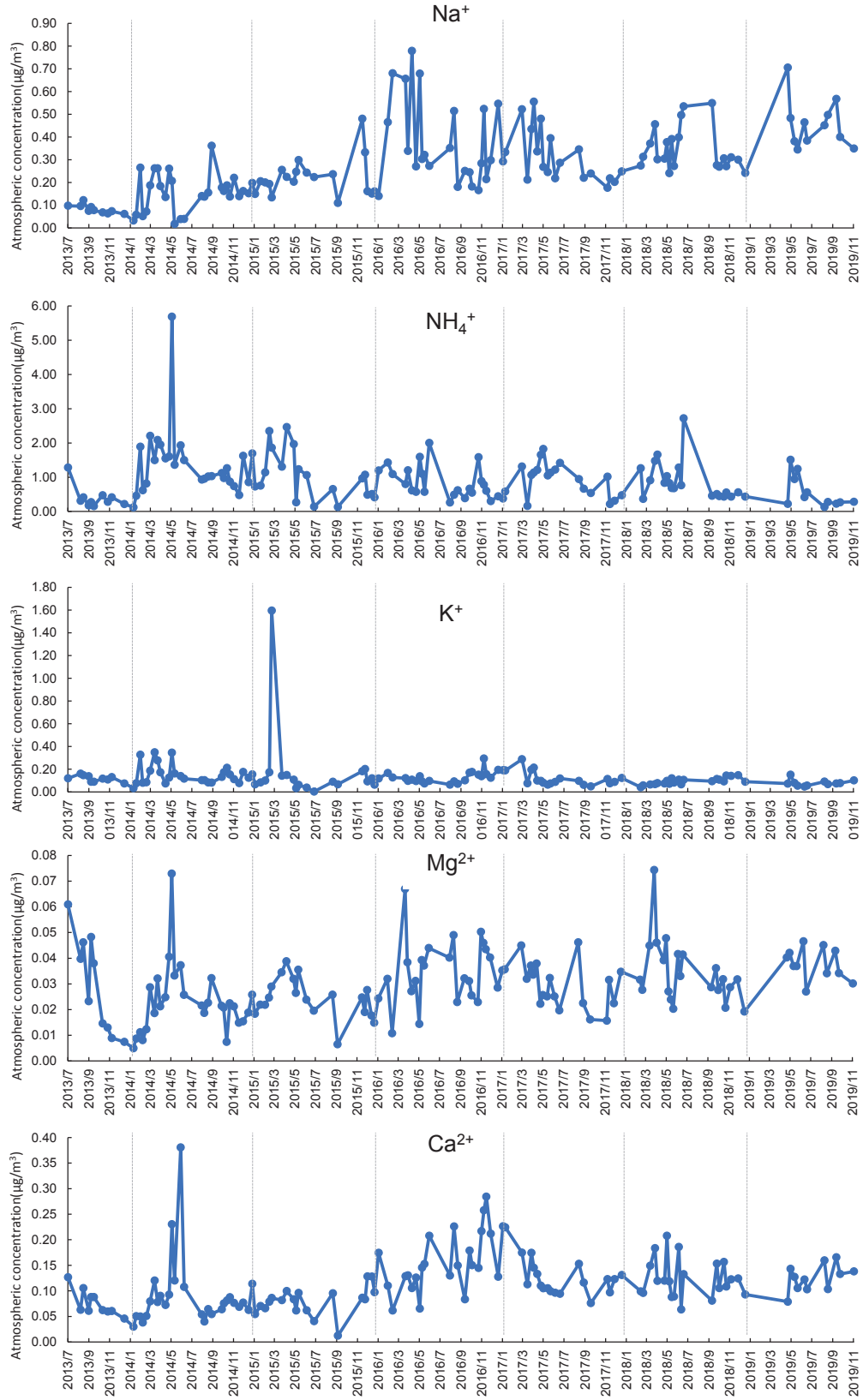


Fig. 3 continued

Table 1 Analytical results on the concentrations of PM_{2.5} and water-soluble inorganic ions collected at Shibuya, Tokyo, Japan from July 2013 to November 2019 in the unit of $\mu\text{g}/\text{m}^3$.

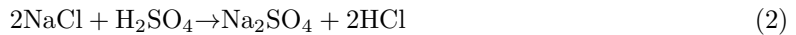
	Spring ($n = 37$)	Summer ($n = 26$)	Autumn ($n = 38$)	Winter ($n = 31$)	All ($n = 132$)
PM _{2.5}	14 ± 7.0	9.2 ± 3.8	9.7 ± 3.8	13.1 ± 6.6	12 ± 5.9
Na ⁺	0.34 ± 0.18	0.28 ± 0.14	0.25 ± 0.14	0.23 ± 0.13	0.28 ± 0.16
NH ₄ ⁺	1.4 ± 0.94	1.09 ± 0.56	0.59 ± 0.34	0.73 ± 0.46	0.95 ± 0.70
K ⁺	0.17 ± 0.25	0.085 ± 0.034	0.11 ± 0.037	0.13 ± 0.065	0.13 ± 0.14
Mg ²⁺	0.034 ± 0.015	0.033 ± 0.010	0.029 ± 0.011	0.023 ± 0.011	0.030 ± 0.013
Ca ²⁺	0.11 ± 0.043	0.12 ± 0.065	0.11 ± 0.048	0.12 ± 0.065	0.11 ± 0.054
Cl ⁻	0.018 ± 0.023	0.014 ± 0.027	0.013 ± 0.017	0.023 ± 0.037	0.017 ± 0.026
NO ₃ ⁻	0.093 ± 0.22	0.085 ± 0.21	0.12 ± 0.30	0.50 ± 0.93	0.19 ± 0.52
SO ₄ ²⁻	4.0 ± 2.6	3.2 ± 1.7	2.2 ± 1.3	2.7 ± 2.4	3.0 ± 2.2

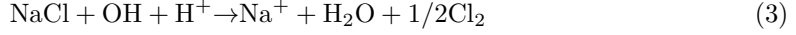
Table 2 Pearson’s correlation coefficients between paired data of PM_{2.5} and each water-soluble ion. Values highlighted in bold are significant at $p < 0.01$.

	PM _{2.5}	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
PM _{2.5}	1								
Na ⁺	-0.08	1							
NH ₄ ⁺	0.63	0.00	1						
K ⁺	0.34	-0.05	0.30	1					
Mg ²⁺	0.02	0.38	0.25	0.03	1				
Ca ²⁺	0.06	0.23	0.17	0.07	0.62	1			
Cl ⁻	-0.12	-0.01	-0.09	-0.08	-0.16	-0.16	1		
NO ₃ ⁻	0.44	-0.14	0.14	0.06	-0.25	-0.06	-0.01	1	
SO ₄ ²⁻	0.54	-0.13	0.75	0.20	0.11	0.04	-0.19	0.13	1

so-called Kosa [9], and relatively low in summer and autumn. No apparent increasing or decreasing tendency was found for the annual variation of PM_{2.5} level within the monitoring duration.

Total mass of the eight kinds of water-soluble inorganic ions accounted for 44% of the mass of PM_{2.5} in spring, 52% in summer, 35% in autumn, 34% in winter and 41% for all samples. As shown in Table 1, Atmospheric concentrations of the ions followed the order of $\text{SO}_4^{2-} \gg \text{NH}_4^+ > \text{Na}^+ > \text{NO}_3^- > \text{K}^+ > \text{Ca}^{2+} \gg \text{Mg}^{2+} > \text{Cl}^-$ in all PM_{2.5} samples ($n = 132$). However, this order slightly changed with seasons. While SO_4^{2-} was most abundant in every season, concentration of NO_3^- was relatively high in winter and low in spring to autumn, and that of NH_4^+ was higher in spring and summer. In general, Na^+ and Cl^- are major components of sea-salt particles whose molar ratio of Cl^-/Na^+ is 1.13 in sea water. Since the sampling site is located about 5 km apart from the seashore of Tokyo bay, contribution of sea-salt particles is plausible. However, Cl^- level was much lower than that of Na^+ with 0.063 ± 0.14 of molar ratio of Cl^-/Na^+ in all samples ($n = 132$), probably because of “chlorine loss”. This is a phenomenon that volatile hydrogen chloride (HCl) and chlorine (Cl_2) are released by a heterogeneous reaction of sea salt particles with acidic pollutants such as HNO_3 , H_2SO_4 and/or OH radical in air [11, 12].





As was shown in Table 2, $\text{PM}_{2.5}$ concentration significantly correlated with those of NH_4^+ ($r = 0.63$, $p < 0.01$) and SO_4^{2-} ($r = 0.54$, $p < 0.01$). As well, NH_4^+ concentration significantly correlated with that of SO_4^{2-} ($r = 0.75$, $p < 0.01$). This means variation of $\text{PM}_{2.5}$ was mostly determined by the content of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, typically produced by a reaction between ammonia and sulfate in air.



However, the yearly change in SO_4^{2-} concentration seems to be different with that in $\text{PM}_{2.5}$. The most abundant anion contributed to high concentration episode of #1–#3, whilst no apparent contribution was found in #4 and #5. Furthermore, slight decreasing tendency was found in the annual variation for SO_4^{2-} concentration within seven years. One possible reason is that the contribution of long-range transport of SO_4^{2-} from Asian continent is gradually decreased with an effort in improving air pollution in Chinese big cities, for example, use of natural gas as an alternative to coal and petroleum which are major emission source of sulfur dioxide, a precursor of SO_4^{2-} [13].

A pair of Mg^{2+} and Ca^{2+} showed a significant correlation with $r = 0.62$ ($p < 0.01$). Both mineral ions are well known to enrich in a desert sand by soil salinity, and hence they are good indicators of the long-range transport of soil dust from Chinese desert area. Even though higher levels of both ions were found at the high concentration episodes of #1 and #2, they did not apparently contribute to other episodes (#3–#5). Since no significant difference was in seasonal variation, usual emission source of Mg^{2+} and Ca^{2+} at Shibuya may be a local road dust which often contains cement particles.

Among the water-soluble inorganic ions, only the concentration of Na^+ , $[\text{Na}^+]$ showed significant and exponential increase with time, t ($r^2 = 0.45$, $p < 0.001$). Note t is the elapsed time (day) after the first sampling of July 26, 2013.

$$[\text{Na}^+] = 0.11\text{e}^{0.007t} \quad (5)$$

As mentioned above, Na^+ is a typical component originated from sea-salt particles. This may suggest influence of sea-salt particles from Tokyo bay or others is increasing, whilst the reasoning of this significant increase should be carefully done considering the meteorological conditions and other possible emission sources which should be explored.

4 Conclusion

This study aimed to characterize seasonal and yearly variations of $\text{PM}_{2.5}$ in reaction to those of water-soluble inorganic ions collected at Shibuya, Tokyo, Japan using the seven-year result from July 2013 to Nov 2019. Analytical results showed the concentration of $\text{PM}_{2.5}$ ranged from 2.4 to 39 $\mu\text{g}/\text{m}^3$, with an arithmetic mean of 12 ± 5.9 $\mu\text{g}/\text{m}^3$ ($n = 132$) and higher in spring and winter. No apparent increasing or decreasing tendency was found for the annual variation of $\text{PM}_{2.5}$ level in this study. The $\text{PM}_{2.5}$ concentration significantly correlated with those of NH_4^+ ($r = 0.63$,

$p < 0.01$) and SO_4^{2-} ($r = 0.54$, $p < 0.01$). This means the variation of PM_{2.5} was mostly determined by the content of ammonium sulfate. However, slight decreasing tendency was found in SO_4^{2-} concentration for 7 years. Meanwhile, Na^+ concentration showed significant increase with time. These findings suggest potential changes in the quality of PM_{2.5} at the sampling site, so we have to keep watching.

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