Chemical characteristics and sources of PM$_{2.5}$ in the urban environment of Seoul, Korea

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A B S T R A C T

In Seoul, Korea, episodes of high concentrations of PM$_{2.5}$ (particulate matter $<2.5 \, \mu m$) continue to occur despite the enforcement of air quality standards. Seoul has several sources of pollution owing to its high population density. Therefore, this study evaluated the chemical characteristics of PM$_{2.5}$, including inorganic ions and various gases, focusing on those with concentrations exceeding the standard limit. The study was conducted from June 1 to August 22, 2018, in Seongbuk, and from March 29 to May 31, 2019, in Jungnang. Water-soluble inorganic ions of PM$_{2.5}$ were measured every 30 min using a particle-into-liquid sampler (PILS) combined with two ion chromatographs. In Seongbuk, ammonium sulfate was mainly caused by ammonium-poor conditions. In Jungnang, ammonium nitrate production occurred mainly due to ammonium-rich conditions. In both regions, during the occurrence of concentrations of PM$_{2.5}$ exceeding the standard limit, the proportion of nitrate among inorganic ions was the highest. In Jungnang, two emission sources located in the west and southwest were identified using a conditional probability function. Contaminants from the southwest had high concentrations of nitrates, presumably due to atmospheric stagnation and nitrate mixing in lower planetary boundary layer height due to an increase in surface temperatures at dawn. Pollutants from the west had high concentrations of sulfates. These are generated through photochemical reactions from industrial complexes. Cluster analysis confirmed that 27.2% of the air was stagnant and flowed from the south. In most cases, air pollutants originated from western Korea and coastal China.

1. Introduction

Particulate matter $<2.5 \, \mu m$ in aerodynamic diameter (PM$_{2.5}$) causes asthma and cardiovascular diseases when inhaled and has been reported to be associated with death from kidney and bladder cancers (McConnell et al., 2003; Pope III et al., 2006; He et al., 2017; Turner et al., 2017). It also decreases the Earth’s surface temperature by reflecting solar radiation and absorbing particle moisture, thus producing fog, and reducing visibility (Charlson et al., 1992; Intergovernmental Panel on Climate Change, 2007; Wang et al., 2020). Because of these adverse effects, many countries have implemented policies to reduce PM$_{2.5}$. In addition, much research has been conducted on the formation of PM$_{2.5}$ and its
sources of pollution (Lang et al., 2017; Kang et al., 2020). For Korea, the average PM$_{2.5}$ standard was established in 2015 as 50 and 25 $\mu$g m$^{-3}$ for the 24 h and annual periods, respectively. The standards were strengthened in March 2018 to 35 and 15 $\mu$g m$^{-3}$ for the 24 h and annual averages, respectively, for the protection and regulation of PM$_{2.5}$ (Park et al., 2020a). However, despite these revised standards in Korea, PM$_{2.5}$ still occurs at high concentrations over 150 $\mu$g m$^{-3}$, and intense PM$_{2.5}$ episodes still occur in Seoul (Lee et al., 2022).

PM$_{2.5}$ is classified into two categories: primary PM$_{2.5}$, which is emitted directly from pollution sources, and secondary PM$_{2.5}$, which is generated through various chemical reactions of water-soluble inorganic ions (WSIs) in the air (Liu et al., 2022; Zhang et al., 2022). PM$_{2.5}$ is composed of complex chemical components, such as organic and inorganic ions, black carbon, and crustal elements (i.e., Si, Al, Ca, and Fe). Among these species of components, WSIs, especially sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), and ammonium (NH$_4^+$), which are collectively referred to as SNA, comprise the largest chemical components for 20–70% or even more than 70% of PM$_{2.5}$ (Tian et al., 2017; Guo et al., 2020; Jo et al., 2020; Do et al., 2021). SNA has been detected in ammonium nitrate (NH$_4$NO$_3$), ammonium sulfate ((NH$_4$)$_2$SO$_4$), and ammonium chloride (NH$_4$Cl), which are formed by the neutralization of acidic gases such as ammonia (NH$_3$), nitric acid (HNO$_3$), and sulfuric acid (H$_2$SO$_4$) (Jo et al., 2020; Do et al., 2021). WSIs have been found to play an important role in the formation of haze caused by the intense scattering effect of PM$_{2.5}$ and can affect the size, composition, number density, hygroscopicity, and acidity of PM$_{2.5}$ (Chen et al., 2021; Cheng et al., 2021; Ting et al., 2022). Additionally, WSIs can degrade visibility and accelerate the formation of PM$_{2.5}$ (Begam et al., 2017; Tian et al., 2017; Guo et al., 2020; Cheng et al., 2021).

As of 2019, approximately 20% of the Korean population lived in Seoul, with around 50% of that residing in the Seoul metropolitan area (SMA) (Won et al., 2021). Owing to this high population density, various emission sources are in the SMA, such as construction, gas stations, and automobiles. In addition, many sources of various forms contribute to the highly polluted atmosphere in the SMA (Park et al., 2020b). Some studies have reported that secondary inorganic aerosols (SIA), such as sulfate and nitrate, constitute a large source of PM$_{2.5}$ in the SMA (Ryou et al., 2018; Park et al., 2020a, 2022). The SIA in the SMA were also affected by long-range transport from China and by emissions from around the SMA (Kim et al., 2021b, 2022). Therefore, it is necessary to understand the inflow and characteristics of the SIA in Seoul.

Previous studies have measured the SIA using filter sampling in ambient air (Zhang et al., 2019a, 2019b; Guo et al., 2020; Zhao et al., 2022). This method was used to collect PM$_{2.5}$ on filters using a vacuum pump. The SIA on collected filters were extracted from deionized water or solvents and analyzed by ion chromatography. However, this filter sampling method may be affected by chemical and physical factors during the collection, storage, and extraction of the filters. Furthermore, it has a long processing time in the laboratory (a few hours to a few days) and produces low-resolution data, making it difficult to measure daily patterns or chemical reactions in ambient air (Tutsak and Kočak, 2019; Zhang et al., 2019a). To understand and identify the chemical composition and characteristics of PM$_{2.5}$, a particle-into-liquid sampler (PILS) combined with ion chromatography was used in this study during the summers of 2018 and 2019. In addition, this study identified major air pollution sources that could be targeted in future mitigation measures for PM$_{2.5}$.

2. Methods

2.1. Sampling sites

The physical and chemical properties of secondary PM precursors and PM in Seoul were measured from June 1 to August 22, 2018 (summer) in Seongbuk (37.585949° N and 127.052420° E) and from March 29 to May 31, 2019 (spring) in Jungnang (37.589729° N and 127.079042° E). The sampling sites were located approximately 5 km apart, both approximately 5 km northeast of Myeongdong (downtown) in Jung-gu, Seoul. The Naebu Expressway is located approximately 1 km east of the Seongbuk sampling site, around which residential complexes are distributed. The Jungnangcheon and Dongbu Expressways are located approximately 700 m west of the Jungnang sampling site and are surrounded by nearby residential complexes (Fig. 1). In Table 3, note that PM$_{2.5}$ was not measured in 2018; instead, data from Yongdoo Elementary School (37.575698° N, 127.028709° E), located 1 km south of Seongbuk, were used.

2.2. Measurement equipment

2.2.1. Particulate matter measurement

To observe inorganic ionic components, such as SNA in secondary PM in central Seoul, a PILS (Metrohm, Switzerland) and ion chromatography (IC; 883 Basic IC Plus, Metrohm, Switzerland) were combined (PILS-IC) for sampling and measurement (Table 1). The PILS-IC was installed according to the method described by Kang et al. (2020). The PILS uses high-temperature (150 °C) water vapor to grow particles with a diameter larger than 50 nm and then collects the particles (Venter et al., 2001). The inlet flow rate of the PILS was approximately 16.7 L min$^{-1}$, which was adjusted by installing a pressure regulator at the rear end of the orifice. The particle size of the inserted samples was increased by the water vapor supplied by the steamer inside the PILS. The grown particles collided with the impactor plate and spread along its surface to a metal mesh located on the side of the impactor. The samples were mixed with Lithium bromide (LiBr), which was the internal standard; thus, the concentration was calculated by considering the dilution factor. The solution collected in the vial was automatically injected into the IC every 30 min using a syringe pump. For quality assurance/quality control (QC/QA) of inorganic ionic components, blank and standard solutions were measured periodically (every 10–12 days) to determine the minimum detection limit (MDL) and uncertainty. The MDLs (uncertainties in %) for the IC analysis were 0.06 $\mu$g m$^{-3}$ (5.18%) for Cl$^-$, 0.13 $\mu$g m$^{-3}$ (5.06%) for NO$_3^-$, 0.15 $\mu$g m$^{-3}$ (3.25%) for SO$_4^{2-}$, 0.21 $\mu$g m$^{-3}$ (6.57%) for Na$^+$, 0.05 $\mu$g m$^{-3}$ (4.81%) for NH$_4^+$, 0.08 $\mu$g m$^{-3}$ (17.8%) for K$^+$, 0.10 $\mu$g m$^{-3}$ (12.1%) for Ca$^{2+}$, and 0.04 $\mu$g m$^{-3}$ (22.6%) for Mg$^{2+}$. The average Li$^+$ and Br$^-$ concentrations were 0.029 ± 0.005 and 0.031 ± 0.004 ppb, respectively. These results indicate that the measurement of the WSIs was maintained under stable and reliable conditions during this study (Zhang et al., 2019a).

2.2.2. Measurement of gaseous substances

Large amounts of gaseous HNO$_3$ and NH$_3$ present in the air tend to dissolve in water and are converted to NO$_3^-$ and NH$_4^+$, which must be removed during sampling because they can lead to overestimation of concentrations in the IC analysis. To accurately measure NO$_2^-$ and NH$_4^+$ in the inserted samples, two annular denuders (URG Corporation, Chapel Hill, NC, USA), which can remove gaseous precursors (HNO$_3$ and NH$_3$), were installed at the front of the PILS. The annular denuders were coated with two solutions to collect gaseous precursors on the glass surface. To collect HNO$_3$, a coating solution was prepared by adding 5.05 g of sodium carbonate (Na$_2$CO$_3$), 4 ml of glycerol (C$_3$H$_8$O$_3$), and 250 ml of methanol (CH$_3$OH) in deionized water. To collect NH$_3$, a coating solution was prepared by adding 100 ml of deionized water and 6.26 ml of phosphoric acid (H$_3$PO$_4$) to 900 ml of methanol.

To observe gaseous precursors (HNO$_3$, sulfur dioxide (SO$_2$), NH$_3$, and carbon dioxide (CO)), sampling was performed during the summer 2018 measurement period in Seongbuk and the spring 2019 measurement period in Jungnang, using an ammonia analyzer EAA-30r-EP (Los Gatos Research, USA), a 48i gas filter correlation (GFC) CO analyzer (Model 48i, Thermo Scientific, USA), a UV fluorescence method (MEZUS-110, KENTEK, Korea) for SO$_2$, and the parallel-plate diffusion scrubber ion chromatography (PPDS-IC; Metrohm) technique for HNO$_3$ (Table 1). NH$_3$ measurements were performed such that the inlet tubing
temperature was maintained at 45 °C to reduce the degree of NH₃ adsorption to the tubing (Kim et al., 2021a).

2.3. Conditional probability function (CPF) analysis

A conditional probability function (CPF) analysis was conducted to identify the inflow paths and sources of pollutants at the sampling sites. This technique simultaneously identifies the direction of the main emission sources in a CPF and provides information regarding their dispersion in bivariate polar coordinates (Uria-Tellaetxe and Carslaw, 2014; Kim et al., 2018). A CPF is generally used to identify the sources of local pollution (Jain et al., 2020; Kanchanasuta et al., 2020). Uria-Tellaetxe and Carslaw (2014) identified high-concentration emission sources using CPF results, where the concentrations of pollution sources above the 75th percentile were selected.

3. Results and discussion

3.1. Characteristics of PM₂.₅ in Seoul’s atmosphere

3.1.1. Chemical composition of PM₂.₅

Water-soluble inorganic ionic components were observed during the summer measurement period in Seongbuk from June 1 to August 22, 2018, and the spring measurement period in Jungnang from March 29 to May 31, 2019 (Table 2). All results are shown for the WSIs of PM₂.₅, except for the organics. The composition of WSIs in the PM₂.₅, for the known species (nitrate, sulfate, ammonium, and crustal elements) from the IC measurement is shown in Fig. 2. Both sampling sites had relatively low concentrations compared to those recorded in previous studies at different sites (Table 2). For example, a sampling site in Jongno (Park et al., 2020a), found in the center of Seoul (37.58 °N, 127.00 °E), is enclosed by various sources of pollutant emissions. Another site in Eunpyeong, located on the rooftop of a building in Northwest Seoul (Park et al., 2018), is situated 67 m above the ground and represented an urban monitoring site in Bulkwang, Seoul (37.610646 °N, 126.933707 °E). Gwangjin, as listed in Table 2, is located on the north side of the Han River in Seoul in the large water purification system of Gwangjin, which is enclosed by commercial and residential buildings (37.547080 °N, 127.092492 °E) (Shon et al., 2012; Son et al., 2012). Kim et al. (2007) collected samples from the rooftop of the Graduate School of Public Health of Seoul National University in Jongno, Seoul (approximately 17 m above the ground, 37.464871 °N, 126.954736 °E). Overall, the results of all studies listed in Table 2 showed that higher concentration of PM₂.₅ and nitrate, and a lower concentration of sulfate, were found in spring, in comparison to summer. It was considered that the lower nitrate in summer was affected by thermal decomposition at high temperatures, and the higher sulfate in summer was attributed to sulfate oxidation from SO₂ under the meteorological conditions of higher temperature and humidity (Khoder, 2002; Chan et al., 2018).

During the 2018 measurement period in Seongbuk, the PM₂.₅ concentration was 18.45 μg m⁻³, and among the WSIs components, the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The instruments used for the measurement of gas and particle phases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Instrument</td>
</tr>
<tr>
<td>Gas</td>
<td>EAA-30r-EP</td>
</tr>
<tr>
<td></td>
<td>MEZUS 110</td>
</tr>
<tr>
<td></td>
<td>T500U</td>
</tr>
<tr>
<td></td>
<td>PPDS-IC</td>
</tr>
<tr>
<td></td>
<td>48i</td>
</tr>
<tr>
<td>Particle</td>
<td>T640</td>
</tr>
<tr>
<td></td>
<td>PILS-IC</td>
</tr>
</tbody>
</table>

Fig. 1. Locations of the sampling sites; operated in Seongbuk (Korea University, 37.585949 °N, 127.025420 °E) during the summer of 2018 (from June 1 to August 22, 2018) and Jungnang (KT plaza branch, 37.589729 °N, 127.079042 °E) during the spring of 2019 (from March 29 to May 31, 2019).
μg m⁻³ increased to 5.70 μg m⁻³ during the eight days (April 23 and May 2, 2018). These results indicate that the quality standard daily average in Korea for eight days (April 23 and May 2, 2018). During this period, PM\(^{2.5}\) was characterized by a high concentration of ammonium-rich conditions, the concentration of PM\(^{2.5}\) exceeded the air quality standard daily average in Korea (35 μg m⁻³) for three days (June 24, June 25, and July 23). Among the WSII components, the concentration of SO\(_4^{2-}\) increased to 5.70 μg m⁻³, indicating a decreased composition of 34.8% during the three days. The concentration of NO\(_3^-\) was the highest at 5.97 μg m⁻³, with an increased composition of 36.5%. In 2019, in Jungnang, the PM\(^{2.5}\) concentration was 22.58 μg m⁻³, and among the WSII components, NO\(_3^-\) had the highest concentration of 4.50 μg m⁻³ (43.4% of the WSII composition). During this period, PM\(^{2.5}\) exceeded the air quality standard daily average in Korea for eight days (April 23 and May 4, 5, 12, 13, 23, 24, and 25). The concentration of NO\(_3^-\) increased to 9.50 μg m⁻³, indicating a decreased composition of 50.4% during the eight days. Finally, the SO\(_4^{2-}\) concentration increased to 4.54 μg m⁻³, indicating a decreased composition of 24.0%. These results indicate that the measurement periods were characterized by a high concentration of PM\(^{2.5}\), from the formation of nitrate compared to sulfate.

### 3.1.2. Interactions between PM and gaseous precursors

The reaction of ammonia with nitric acid (HNO\(_3\)) and sulfuric acid (H\(_2\)SO\(_4\)) contributes to the formation of ammonium nitrate (NH\(_4\)NO\(_3\)) and ammonium sulfate ((NH\(_4\))\(_2\)SO\(_4\)). Therefore, it is necessary to identify the atmospheric conditions of ammonia in ambient air. Seinfeld and Pandis (2006) reported that the atmospheric conditions of ammonia are restrictive factors for secondary aerosol formation. Under ammonium-rich conditions, the concentration of PM\(^{2.5}\) can increase because SO\(_2\) or NO\(_x\) are continuously generated in the SIA. In this study, ammonium-poor conditions did not cause an immediate increase in the concentration of PM\(^{2.5}\), likely owing to its limited reaction with acidic precursors (HNO\(_3\) and H\(_2\)SO\(_4\)) to generate SIA. However, SIA may also be formed if insufficient ammonia is supplied from other sources or by long-range transport.

#### Table 2

Comparison of PM\(^{2.5}\) average concentrations with those of previous studies.

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>Season</th>
<th>PM(^{2.5}) μg m⁻³</th>
<th>NO(_3^-) μg m⁻³</th>
<th>SO(_4^{2-}) μg m⁻³</th>
<th>NH(_4^+) μg m⁻³</th>
<th>Temp °C</th>
<th>RH %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seongbuk</td>
<td>2018</td>
<td>Summer</td>
<td>18.5 ± 11.3(^a)</td>
<td>1.9 ± 2.9</td>
<td>4.1 ± 3.2</td>
<td>2.33 ± 1.8</td>
<td>27.8 ± 4.6</td>
<td>54.3 ± 14.7</td>
<td>This study</td>
</tr>
<tr>
<td>Jungnang</td>
<td>2015</td>
<td>Summer</td>
<td>34.1 ± 19.9</td>
<td>4.5 ± 5.1</td>
<td>10.9 ± 2.0</td>
<td>2.5 ± 1.8</td>
<td>17.5 ± 5.0</td>
<td>46.8 ± 19.9</td>
<td>Park et al. (2020a)</td>
</tr>
<tr>
<td>Eunpyeong</td>
<td>2011</td>
<td>Summer</td>
<td>69.3 ± 11.4</td>
<td>11.2 ± 2.5</td>
<td>9.6 ± 1.46</td>
<td>6.9 ± 1.2</td>
<td>12.9 ± 1.4</td>
<td>54.8 ± 4.7</td>
<td>Park et al. (2018)</td>
</tr>
<tr>
<td>Gwangjin</td>
<td>2010</td>
<td>Summer</td>
<td>25.4 ± 15.7</td>
<td>13.6 ± 7.2</td>
<td>7.0 ± 4.4</td>
<td>3.7 ± 3.6</td>
<td>25.8 ± 3.3</td>
<td>74.8 ± 15.9</td>
<td>Shon et al. (2012)</td>
</tr>
<tr>
<td>Jungnang</td>
<td>2003–2004</td>
<td>Summer</td>
<td>36.2 ± 11.1</td>
<td>6.6 ± 5.9</td>
<td>8.7 ± 7.1</td>
<td>6.5 ± 5.3</td>
<td>11.0 ± 6.6</td>
<td>61.0 ± 19.9</td>
<td>Kim et al. (2007)</td>
</tr>
</tbody>
</table>

\(^a\) Average ± Standard deviation.

\(^b\) The data from a sampling site located 1 km south of Seongbuk was used instead because PM\(^{2.5}\) was not measured in 2018.

\(^c\) Located in the center of Seoul, Korea (37.581° N, 127.001° E).

\(^d\) Located in the northwest part of Seoul (37.61° N, 126.93° E).

\(^e\) Located on the roof of the Graduate School of Public Health of Seoul National University (37.514° N, 126.9° E).

\(^f\) Located in the center of Seoul, Korea (37.581° N, 127.05° E).

\(^g\) Located on the roof of the Graduate School of Public Health of Seoul National University (37.514° N, 127.001° E).

#### Table 3

The mass concentrations of PM\(^{2.5}\), NO\(_3^-\), SO\(_4^{2-}\), NH\(_4^+\) and crustal elements in measurement periods and episodes exceeding the Korean air quality standard (35 μg m⁻³).

<table>
<thead>
<tr>
<th>Site</th>
<th>Case</th>
<th>PM(^{2.5}) μg m⁻³</th>
<th>NO(_3^-) μg m⁻³</th>
<th>SO(_4^{2-}) μg m⁻³</th>
<th>NH(_4^+) μg m⁻³</th>
<th>Crustal elements(^h) μg m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seongbuk</td>
<td>Summer</td>
<td>18.45</td>
<td>1.91</td>
<td>4.13</td>
<td>2.33</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>PM(^{2.5}) over 35 μg m⁻³ (^a)</td>
<td>36.39</td>
<td>5.97</td>
<td>5.70</td>
<td>4.46</td>
<td>0.23</td>
</tr>
<tr>
<td>Jungnang</td>
<td>Spring</td>
<td>22.60</td>
<td>4.50</td>
<td>2.92</td>
<td>2.54</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>PM(^{2.5}) over 35 μg m⁻³ (^b)</td>
<td>42.31</td>
<td>9.50</td>
<td>4.54</td>
<td>4.12</td>
<td>0.72</td>
</tr>
</tbody>
</table>

\(^h\) Crustal = Cl\(^-\) + K\(^+\) + Ca\(^2+\) + Na\(^+\) + Mg\(^2+\)

\(^a\) April 23 and May 4, 5, 12, 13, 23, and 25, 2019.

\(^b\) Located on the roof of the Graduate School of Public Health of Seoul National University (37.514° N, 127.001° E).

\(^c\) Seongbuk for the measurement period exceeding the Korean air quality standard.

\(^d\) Eunpyeong for the measurement period exceeding the Korean air quality standard.

\(^e\) Jungnang for the measurement period exceeding the Korean air quality standard.

\(^f\) Seongbuk for 8 days (April 23 and May 2, 2018).

\(^g\) Gwangjin for the entire measurement period (from March 29 to May 31, 2019).

\(^h\) Park et al. (2018)
Pathak et al. (2009) reported a change in the molecular ratio of NO$_3^-$ and SO$_4^{2-}$ according to the change in the molecular ratio of NH$_4^+$ and SO$_4^{2-}$. When the molecular ratio of NH$_4^+$ to SO$_4^{2-}$ was 1.5, the production of NH$_4$NO$_3$ was apparent through the reaction of the two gaseous substances, NH$_3$ and HNO$_3$. Therefore, it was indicated that the main reaction of [NH$_4^+$/[SO$_4^{2-}$] with a ratio below 1.5 is heterogeneous and with a ratio above 1.5 is a homogeneous reaction. The heterogeneous reaction results indicate the preferential reaction of (NH$_4$)$_2$SO$_4$ in the aqueous phase, followed by the production of NH$_4$NO$_3$. However, the homogeneous reaction results indicate that NH$_4$NO$_3$ increased as its concentrations of NH$_3$ and NO$_x$ increased when H$_2$SO$_4$ reacted sufficiently with NH$_3$ to produce ammonium sulfate (NH$_4$)$_2$SO$_4$.

Fig. 3 presents the molar concentrations of NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ in the atmosphere of Seongbuk, Seoul, in the summer of 2018, indicating mostly ammonium-poor conditions, with some periodic exceptions. However, during that summer, environmental conditions, specifically the high temperature, resulted in the decomposition of NO$_3^-$. Hence, SO$_4^{2-}$ had the highest percentage of WSIIs during the measurement period (Fig. 2). Therefore, it is possible that the formation of (NH$_4$)$_2$SO$_4$ through the heterogeneous reaction of the atmosphere in Seongbuk measured in summer was stronger than that measured in spring (Pathak et al., 2009).

There were relatively more NO$_2$ and NH$_4^+$ ions in the atmosphere than SO$_4^{2-}$; therefore, the conditions were considered to be ammonium-rich. As ammonium-rich conditions have been observed during most previously reported measurement periods, the generation of NH$_4$NO$_3$ through homogeneous reactions in the atmosphere is likely strong (Griffith et al., 2015).

The molar ratio (R) and SNA values were used to identify the possibility of NO$_3^-$ formation (Fig. 4). The calculation of the R-value in this study is given by Eq. (1). Xu et al. (2019) reported that the formation of NO$_3^-$ was suppressed by the reduction of ammonia owing to ammonia limitation (R < 1) and a decrease in nitric acid owing to nitric acid limitation (R > 1). The R-value was 60% of the HNO$_3$ concentration and 40% of the NH$_3$ concentration in Seongbuk (2018). In Jungnang (2019), the R-value was calculated as 74% for HNO$_3$ limitation and 26% for NH$_3$ limitation. The formation of NO$_3^-$ was likely suppressed by the reduction of HNO$_3$. However, because hydrochloric acid (HCl) was not measured during the measurement period, its concentration was not considered in the R values, and it is possible that these R values resulted in overestimation (Xu et al., 2019).

\[ R = \frac{\text{NO}_3^-}{\text{SO}_4^{2-} + \text{NO}_2^- + \text{HNO}_3} \times \frac{\text{NH}_4^+ + \text{H}^+}{\text{Cl}^- + \text{HCl}} - 2\text{Ca}^{2+} - \text{K}^+ - 2\text{Mg}^{2+} \]

Eq. (1) shows the changes in the measured constant values ($K_m$) and the theoretical equilibrium constant ($K_p$) of NH$_4$NO$_3$ to confirm whether the environment was suitable for the formation of NH$_4$NO$_3$ during the entire measurement period. The calculations for $K_m$ and $K_p$ in this study are shown in Eqs. (2) and (3), respectively. Here, the relative humidity was assumed to be solid NH$_4$NO$_3$ under the condition that the relative humidity was less than the deliquescence relative humidity and $K_p$ was simplified. In Eq. (2), $T$ is the absolute temperature (K) and $K_p$ is the unit of ppbv$^2$ (Li et al., 2014).

\[ \ln K_p = 84.6 - 24220 / T - 6.1 \times \ln(T / 298) \]

Eq. (2)

\[ K_m = [\text{NH}_4^+] \times [\text{HNO}_3] \]

Eq. (3)

In Seongbuk (2018), the NH$_3$ and HNO$_3$ were 13.08 (±5.26) and 0.53 (±0.32) ppb, respectively, at a temperature of 27.3 (±4.8) °C. In Jungnang (2019), the NH$_3$ and HNO$_3$ were 14.87 (±4.18) ppb and 0.63 (±0.36) ppb, with a temperature of 18.3 (±5.1) °C. During the 2018 measurement period in Seongbuk, the NH$_3$ and HNO$_3$ concentrations were relatively low and the temperature was higher than that in Jungnang in 2019. Hence, most of the measured constant values ($K_m$) were below the solid line ($K_p$). In July and August 2018, when high temperatures continued, SO$_4^{2-}$ concentrations increased and the environment was NH$_3$-limited; therefore, it is likely that (NH$_4$)$_2$SO$_4$ was produced first, after which NH$_3$ was consumed in the formation of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ (Stelson et al., 1979). During the 2019 measurement period in Jungnang, most $K_m$ values were higher than, and closer to $K_p$. This suggests that conditions such as NH$_3$ and HNO$_3$ concentrations and temperature were suitable for the formation of NH$_4$NO$_3$ (Li et al., 2014). As the atmospheric conditions in Jungnang were HNO$_3$-limited, if $K_m$ was lower than $K_p$ through HNO$_3$ reduction, NO$_3$ formation was likely suppressed. However, there is some uncertainty because neither the influence of the components of PM$_{2.5}$ nor relative humidity was considered.

3.2. Estimation of urban high-concentration PM$_{2.5}$ sources

3.2.1. Conditional probability function analysis

During the research period, wind direction and speed were measured using an automatic weather system (AWS). The wind directions in the

Fig. 3. The molar concentrations of NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ at Seoul. The gray dashed line indicates the value of nitrate formation separating ammonium-poor and ammonium-rich conditions, that is, a ratio of 1.5 for [NH$_4^+$/[SO$_4^{2-}$] via the gas-phase reaction between ammonia, nitric acid, and ammonium nitrate (Pathak et al., 2009).
spring in Jungnang were mainly from the west, and the average wind speeds at both sampling sites were similar, at 2.05 m s\(^{-1}\). Because Seongbuk was measured during the summer, the high average temperature and relative humidity promoted the thermal decomposition of NO\(_3\) and SO\(_4^{2-}\) because of the aqueous oxidation of SO\(_2\). Such conditions render the analysis of emission sources difficult; therefore, only the spring period in Jungnang was considered for CPF and cluster analysis (Khoder, 2002; Wang et al., 2016).

As shown in Fig. 6, during the 2019 measurement period in Jungnang, the main emission sources of PM\(_{2.5}\), NO\(_3\), and CO were identified as coming from the southwest (wind speed of 1.5–2.0 m s\(^{-1}\)) and the west (wind speed of 3.5–4.0 m s\(^{-1}\)). In winds with speeds of 1.5–2.0 m s\(^{-1}\), the concentration ranges of PM\(_{2.5}\), NO\(_3\), and CO were 43–92 μg m\(^{-3}\), 10–36 μg m\(^{-3}\), and 642–1003 ppb, respectively. In winds with a speed of 3.5–4.0 m s\(^{-1}\), the concentration ranges of PM\(_{2.5}\), NO\(_3\), CO, and SO\(_2\) were 33–38 μg m\(^{-3}\), 6–8 μg m\(^{-3}\), 454–514 ppb, and 5–16 μg m\(^{-3}\), respectively. Sulfate (SO\(_4^{2-}\)) and SO\(_2\) emission sources located in the west and southwest were the most significant contributors to the high concentrations, and they were estimated to be generated over a larger area than the other pollution sources. Furthermore, it seems that the long-range transport of air pollutants from China also affected Seoul, along with pollutants emitted from industrial complexes located in the metropolitan area (Fig. 6).

3.2.2. Polar annulus plot analysis
To examine the temporal changes in concentration according to the wind direction for each pollution source, the 2019 measurement period in Jungnang was visualized concerning the time and day of each week through a polar annulus plot (Fig. 7). A polar annulus plot was used to visualize the average concentration of pollutants and how the concentrations varied with time by color mapping wind direction as a continuous surface (Harrison et al., 2012; Masiol et al., 2017). As shown in Fig. 7b, the NO\(_3\) concentration reached its maximum in dawn when the insolation increased and showed a flow in all directions. This phenomenon is a known characteristic of urban environments in spring. As surface temperatures decrease, NO\(_3\) concentration in lower boundary layer height increases. In addition, nitrogen dioxide (NO\(_2\)) is converted to NO\(_3\) by photochemical reactions, thus increasing its concentration (Wang et al., 2019). After 10 a.m., the NO\(_3\) concentration decreased because of the rising mixed layer and increasing temperature. During the
measurement period, high concentrations of PM$_{2.5}$, NO$_3$, CO, SO$_2$, and NO$_2$ were observed in the air flowing southwest in the morning. In this study, air from the southwest was estimated to flow through central Seoul, leading to higher concentrations here than those in other areas (Fig. 6a). According to previous research, due to the increase in CO and NO$_2$ concentrations, which are from local sources, there were more dominant NO$_3$ sources than photochemical sources in the high-concentration cases, and atmospheric stagnation led to the accumulation and inflow of high concentrations of pollutants (Kim et al., 2022). Seoul reported it is a major emission source of urban air pollutants such as CO and NO$_2$ (Seo et al., 2018). The NO$_X$ supplied to the atmosphere by vehicles in Jung-gu (downtown) and the southwest, which is located on the Jungnangcheon and Dongbu Expressways from Jungnang, is likely to contribute to the increase in NO$_3$ concentration on Saturdays.

High concentrations of pollutants flowing from west of Jungnang were observed mainly in the afternoon (Fig. 7). Sulfate (SO$_4^{2-}$) flowed over a larger area than NO$_3$, mainly originating from the west, at relatively high concentrations (Fig. 7b and c). Low-concentration PM$_{2.5}$ and relatively high wind speeds were observed flowing from the southwest (Fig. 7a and g). These results were possibly influenced by the Incheon industrial complex, which is located approximately 35 km west of Jungnang, and long-range transport from China (Kim et al., 2016, 2018d).

### 3.2.3. Cluster analysis

To confirm the air trajectories during the measurement period, 72-h backward trajectories in spring from March 29 to May 31, 2019, were calculated using the HYSPLIT model (https://www.arl.noaa.gov/hysplit/). Meteorological data from the Global Data Assimilation System were used, and the modeling point was analyzed at an altitude of 500 m at the KT Plaza Jungnang sampling site (14 m above sea level, 37.590889° N, and 127.078232° E).

According to the cluster analysis, in Korea, inflow from inland atmospheric stagnation (navy) contributed to 27.2%, with most inflows from the east coast of China (orange and blue), North China (green), and Mongolia (brown) during this period (Fig. 8). Because of the concentration of large ports, petrochemical plants, and thermal power plants in East China (comprising Shandong, Jiangsu, Zhejiang, and Fujian), it is necessary to consider the impact of coal and oil combustion (Kim et al.,

![Fig. 6. (a) Location of the major industrial facilities (A: Hakun Industrial Complex, B: Incheon West Regional Industrial Complex, C: Petrochemical plant, D: Incheon Machinery Industrial Complex, E: Juan National Industrial Complex, F: Bupyeong National Industrial Complex, G: Location of Seoun industrial complex, H: Onsu General Industry Complex, I: Seoul Digital National Industrial Complex) in the Seoul metropolitan area (SMA) and Jungnang, (b–i) Results of conditional probability function (CPF) analysis of PM$_{2.5}$, nitrate, sulfate, CO, and SO$_2$.](image-url)
2021b) and offshore ship emissions (Ledoux et al., 2018). The average annual PM$_{2.5}$ concentration was four to twelve times higher than that of major cities in developed countries such as Los Angeles, USA (Luo et al., 2018; Bie et al., 2021). A previous study on high concentrations of PM$_{2.5}$ found that 40% of the increase in secondary aerosols in Korea during westerly winds was attributable to East China (Kim et al., 2009). Researchers have also identified through an isotope analysis that SO$_4^{2-}$ was generated from coal combustion in China (Kim et al., 2018c). Furthermore, emissions from China were found to have an annual average impact of 40% on PM$_{2.5}$ concentrations in Seoul. The impact of emissions from China on NO$_3^-$ concentrations in Seoul was as high as 67% in spring (Bae et al., 2020). Therefore, these studies suggest the possibility that some pollutants are influenced by emissions in China.

4. Conclusions

In this study, the concentrations of PM and gaseous precursors were measured during the summers of 2018 and 2019 in Seongbuk and Jungnang, Seoul, respectively. Interaction analysis was conducted on the composition of PM and measurements of its gaseous precursors from sampling sites in Seongbuk and Jungnang, and the characteristics of air quality in Seoul were discussed. This study also traced the emission sources of pollution in Seoul through various analyses during spring. The main conclusions are as follows.

In Seongbuk, SO$_4^{2-}$ had the highest concentration of 4.13 μg m$^{-3}$ (48.1% of WSIIs), and in Jungnang, NO$_3^-$ had the highest concentration of 4.50 μg m$^{-3}$ (43.4% of WSIIs). This was affected by the thermal decomposition of NO$_3^-$ and oxidation of sulfate from SO$_2$ in the summer. In both spring and summer, the NO$_3^-$ concentration was highest when the PM$_{2.5}$ concentration exceeded the air quality standard in Korea (35 μg m$^{-3}$). This was attributed to the high concentration of PM$_{2.5}$, which resulted from the formation of nitrate.

Seongbuk exhibited mostly ammonium-poor conditions, with notable production of (NH$_4$)$_2$SO$_4$ through a heterogeneous reaction. This likely remained as HNO$_3$ in the atmosphere because of the high temperatures during the summer measurement period. Jungnang was measured during the spring and mostly exhibited ammonium-rich conditions, with notable production of NH$_4$NO$_3$ through a homogeneous reaction. Atmospheric conditions at the Jungnang sampling site promoted the conversion of HNO$_3$ to NO$_3^-$. During the measurement period in Jungnang, the atmospheric conditions were mostly HNO$_3$-limited. It appears that NO$_3^-$ formation was suppressed by the reduction of HNO$_3$ via the homogeneous reaction of NH$_4$NO$_3$. In Seongbuk, it was difficult to locate pollution sources because of NO$_3^-$ decomposition and extensive SO$_4^{2-}$ formation owing to the high average temperature and relative humidity. In Jungnang, high concentrations of PM$_{2.5}$ and NO$_3^-$ in the pollutants originating from the southwest were observed at dawn, probably related to atmospheric stagnation, and the mixing of NO$_3^-$ in lower planetary boundary layer height, due to an decrease in surface temperature. Pollutants flowing from the southwest showed high concentrations on Saturdays, indicating that heavy traffic volume on Fridays had an effect. It is estimated that NO$_3^-$ or SO$_4^{2-}$ generated by

Fig. 7. The polar annulus plot analysis for Jungnang, visualizing the concentration of pollutants in terms of wind direction using color mapping. The results indicate how pollutant concentrations vary overtime.
photochemical reactions were affected by many industrial facilities located approximately 35 km west of Jungnang. According to the cluster analysis of the Jungnang measurement period, air trajectories were primarily from China. This result suggests that a portion of the pollutants generated in China can affect Korea and are mixed with local sources in Korea, contributing to the increase in pollutant concentrations.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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