Different Characteristics of PM$_{2.5}$ Measured in Downtown and Suburban Areas of a Medium-Sized City in South Korea

Sung-Won Park $^{1}$, Su-Yeon Choi $^{1}$, Jin-Yeo Byun $^{2}$, Hekap Kim $^{3}$, Woo-Jin Kim $^{4}$, Pyung-Rae Kim $^{5}$ and Young-Ji Han $^{3, *}$

1 Department of Interdisciplinary Graduate Program in Environmental and Biomedical Convergence, Kangwon National University, Chuncheon 24341, Korea; pth96@kangwon.ac.kr (S.-W.P.); suycommn@kangwon.ac.kr (S.-Y.C.)
2 Division of Chemical Research, National Institute of Environmental Research, Incheon 22689, Korea; jinseo121@korea.kr
3 Department of Environmental Science, Kangwon National University, Chuncheon 24341, Korea; kimh@kangwon.ac.kr
4 Department of Internal Medicine and Environmental Health Center, Kangwon National University, Chuncheon 24341, Korea; pulmo2@kangwon.ac.kr
5 Forest Environment and Conservation Department, National Institute of Forest Science, Seoul 02545, Korea; pyungraekim@korea.kr
* Correspondence: youngji@kangwon.ac.kr; Tel.: +82-(332)-508-579

Abstract: Chuncheon, a medium-sized city in South Korea, frequently shows high PM$_{2.5}$ concentrations despite scarce anthropogenic emission sources. To identify factors increasing PM$_{2.5}$ concentrations, PM$_{2.5}$ and its major chemical components were concurrently measured at two different sites, namely, downtown and suburban areas. The average PM$_{2.5}$ concentrations at the two sites were similar, but the daily and monthly variations in PM$_{2.5}$ and its components were significantly larger at the suburban site. NH$_4^+$ was significantly higher at the suburban site than at the downtown site, whereas organic carbon (OC) showed the opposite trend. Several PM$_{2.5}$ samples showed an abrupt increase during winter at the suburban site, along with an increase in the amount of OC, NH$_4^+$, and K$^+$, and the correlations between water-soluble OC, K$^+$, and NH$_4^+$ were considerably strong, implying that local biomass burning in the suburban site was an important source of high PM$_{2.5}$ episodes. Secondary OC (SOC) concentration was generally lower at the suburban site than at the downtown site, but its contribution to OC increased during winter with an increase in relative humidity, indicating the significance of heterogeneous SOC formation reactions at the suburban site. These results indicate that relevant local measures can be put into place to alleviate the occurrence of high PM$_{2.5}$ concentration episodes even in medium-sized residential cities where medium- and long-range transport is anticipated to be significant.

Keywords: fine particulate matter; ammonium ion; biomass burning; secondary organic carbon; heterogeneous reaction

1. Introduction

Particulate matter less than 2.5 µm (PM$_{2.5}$) is a global air pollutant, categorized as Group 1 carcinogen by the World Health Organization. There have been many pieces of evidence that PM$_{2.5}$ causes adverse health effects, including respiratory and cardiovascular disease [1–4]. It has also both direct and indirect effects on climate change because it absorbs and scatters sunlight, and alters cloud formation processes [5–7]. PM$_{2.5}$ is directly emitted from primary sources such as combustion of biomass and fossil fuels or secondarily formed in the atmosphere via complex reactions; therefore, it is composed of various components, including ionic (e.g., NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$), carbonaceous (organic and elemental carbon), and metallic (e.g., Zn, Cd, and Cu) compounds [8–10]. The contribution of each component to PM$_{2.5}$ mass depends on the season and location; however, organic and ionic...
compounds generally contribute the most. Organic carbon (OC) is either emitted from both natural and anthropogenic sources or secondarily formed through homogeneous gas-phase oxidation, gas–aerosol partitioning, and heterogeneous oxidation of volatile organic compounds, and it can further be categorized as hydrocarbon-like organic aerosol, cooking-related organic aerosol, and oxygenated organic aerosol [11]. On the other hand, elemental carbon (EC) is emitted only by combustion [12]; therefore, EC is widely used as a tracer of primary OC [13]. Approximately 40–80% of OC is water soluble, and water-soluble OC (WSOC) is considered as being secondarily formed or being emitted from non-fossil fuel combustion, such as biomass burning [14]. Sulfate mainly exists within 0.1–1.0 µm size, whereas nitrate shows bimodal size distribution, existing in both accumulation (0.1–1.0 µm) and coarse (>2.5 µm) mode [15]. Sulfate and nitrate generally exist as (NH₄)₂SO₄, NH₄HSO₄, and NH₃NO₃, but other forms such as KNO₃ and K₂SO₄ can also be found in some situation [16]. Metallic elements generally exist at trace levels in the atmosphere.

Each PM₁₀ component is known to show different health effects. Toxic effects of PM are mediated by an inflammatory response resulting from PM-induced oxidative activity, and reactive oxygen species are produced when PM₁₀ interacts with epithelial cells and macrophages [17]. Carbonaceous compounds may cause arterial blood vessel size change, heart rate change, and lipid oxidation [18]. Several studies have also found that transition metals such as Fe, Mn, Cu, V, and Ni promote redox reactions in a biological system [19–21]. Therefore, it suggests that even trace elements of PM₁₀ can have a significant impact on human health.

This study’s sampling site is in Chuncheon, a medium-sized city in South Korea. The population of this city is slightly more than 280,000, and there are no large anthropogenic sources. However, PM₁₀ often exceeds its 24 h national ambient air quality standard (35 µg m⁻³) and has not satisfied its annual standard of 15 µg m⁻³ since 2015. One of the reasons for the high PM₁₀ concentration is that the city is located in a downwind area of metropolitan and major industrial cities of Korea and China [22–24]. Previous studies have identified that high PM₁₀ concentration episodes occurring in this city were derived from both regional- and long-range transport and local sources [25,26]. This study was initiated to identify factors increasing PM₁₀ concentrations at two different sites, namely, downtown and suburban areas, where the distance between two sites was only 8.3 km. Major chemical components of PM₁₀ and the size distribution of PM₁₀ were also measured to better understand the emission, transport, and formation of PM₁₀ in medium-sized residential cities in Northeast Asia.

2. Materials and Methods

2.1. Sampling

PM₁₀ samples were collected from two sampling sites in Chuncheon, Korea. One site is located on the roof of a four-story building in Kangwon National University (KNU), which is situated in the city center (Figure 1). The KNU site is surrounded by a residential area, and the general industrial complex is located approximately 2 km north of the KNU site (Figure S1). The other site is located on the roof of a three-story building of Kangwon Business Incubation Center (KBIC), located on the outskirts of the city (Figure 1). On the west side of the KBIC site, there is farmland and cattle shed. The biggest driveway in this city starts on the east side of the KBIC site and extends to the south (Figure S1). In addition, an approximately 1.5 km long dense area of charcoal-grilled meat cooking restaurants is located approximately 1 km south and southeast of the KBIC site. The KNU and the KBIC sites are approximately 8.5 km apart. At the KNU site, PM₁₀ samples were collected every 6 days for 24 h, from 26 August 2017 to 27 November 2017, and were continuously collected over a consecutive 71 h period from 30 November 2017 to 29 January 2018. At the KBIC site, PM₁₀ samples were collected every 6 days for 24 h (00:00–00:00) from 26 August 2017 to 29 January 2018.
A 47 mm Teflon filter (pore size of 2.0 μm, Pall Co., Port Washington, NY, USA) was used to collect samples at a flow rate of 16.7 L min⁻¹ to determine PM₂.₅ mass concentration. A 47 mm quartz filter (pore size of 2.2 μm, Whatman International Ltd., Maidstone, UK) that was previously baked at 500 °C for 24 h was used at a flow rate of 16.7 L min⁻¹ to measure carbonaceous compounds. For ionic compounds, two three-channel annular denuders (242-mm length, URG Co., Chapel Hill, NC, USA) and a three-stage Teflon filter pack (URG Co., Chapel Hill, NC, USA) were connected in sequence at a flow rate of 10 L min⁻¹ to eliminate any positive and negative artifacts [27]. The first denuder was coated with a mixture of 50 mL of ethanol, 1 g of N₂CO₃, 1 g of glycerol, and 50 mL of ultrapure water to collect acidic gases (SO₂, HNO₃, and HNO₂), and the second denuder was coated with a mixture of 100 mL of ethanol, 1 g of citric acid, and 1 g of glycerol to collect basic gas (NH₃). The three-stage filter pack was equipped with a 47 mm PTFE filter (pore size of 1.0 μm, Pall Co., Port Washington, NY, USA), a nylon membrane filter (pore size of 1.0 μm, Pall Co., Port Washington, NY, USA), and a paper filter (pore size of 2 µm, Whatman International Ltd., Maidstone, UK) soaked in 10% citric acid before deployment. The nylon and paper filters were used to capture nitric acid (HNO₃) and ammonia (NH₃) volatilized from NH₄NO₃ collected on the PTFE filter, respectively.

To determine the size-segregated concentration of PM₂.₅, an optical particle sizer 3330 (OPS) (TSI Incorporated, Minnesota, USA) was used at both sites from August to November 2017. It measured particles from 0.3 to 10 μm in 16 adjustable size channels (0.3–0.35, 0.3–0.4, 0.3–0.45, 0.3–0.5, 0.3–0.55, 0.3–0.6, 0.3–0.7, 0.3–0.8, 0.3–1.0, 0.3–1.5, 0.3–2.5, 0.3–3, 0.3–4, 0.3–6, 0.3–8, and 0.3–10 μm). In this study, the number and volume concentrations of particles were measured in a 1 h resolution.

Meteorological data, including temperature, wind speed, wind direction, and relative humidity, were measured every 5 min using a meteorological tower (Instruments 6152 Wireless Vantage Pro2 Weather Station, Davis Instrument, Hayward, CA, USA) at both sampling site. In this study, the meteorological data were averaged to match the temporal resolution of the PM₂.₅ samples.

2.2. Chemical Analysis

Before and after sampling, Teflon filters were stored in a desiccator at constant temperature (20 °C) and relative humidity (50%) for 24 h. The filters were then weighed using a microbalance (Satorius, CP22SD, detection limit = 10⁻⁵ g) after eliminating static

![Sampling sites of this study: location of South Korea with adjacent countries (left); map of South Korea (middle); map of Chuncheon (right); red and blue starts indicate KNU (latitude: 37.872, longitude: 127.743) and KBIC (latitude: 37.940, longitude: 127.784) sites, respectively.](image)
electricity to determine PM$_{2.5}$ mass concentration. To analyze ionic compounds, the filters were extracted with ultrapure water in a sonicator for 2 h, and the extract was filtered through a 0.45 µm PTFE syringe filter ( Pall Co., Port Washington, NY, USA) and was analyzed using ion chromatography. To determine OC and EC concentration, a small piece (1.5 cm$^2$) of the quartz filter was analyzed using the National Institute of Occupational Safety and Health method 5040 protocol for thermal–optical analysis in which a sample is heated in pure helium (He) and subsequently in 2% oxygen and He atmosphere. Detailed analysis was provided by Byun (2020) [25]. The remaining portion of the quartz filter was extracted using ultrapure water in a sonicator for 1 h, filtered through a 0.2 µm PTFE syringe filter (Pall Co., Port Washington, NY, USA), and analyzed using a total OC analyzer (Sievers 530IC Laboratory, Boulder, CO, USA) to determine WSOCC concentration. Water-insoluble OC (WSOC) was then calculated by subtracting the WSOCC concentration from the OC concentration.

### 2.3. QA/QC and Statistical Analysis

Field blanks (FB) were collected once every six samples, and the method detection limit; relative percent difference (RPD) between the triplicate (or duplicate) analyses are shown in Table 1.

#### Table 1. Monthly average concentration of PM$_{2.5}$ and its components at the KNU and KBIC sites.

|    | Month | PM$_{2.5}$ | OC | EC | WSOC | WSOCC | NH$_4$$^+$ | NO$_3$$^-$ | SO$_4^{2-}$ | OC/EC | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ |
|----|-------|-----------|----|----|------|--------|------------|------------|-------------|--------|------|--------|-------|
| KNU | SEP   | 25.1 ± 22.3 | 8.6 ± 2.9 | 5.0 ± 4.0 | 3.5 ± 2.5 | 1.4 ± 2.4 | 1.0 ± 0.41 | 0.70 ± 0.12 | 1.69 ± 0.46 | 0.4 ± 0.0 | 2.3 ± 2.0 | 1.6 ± 0.9 | 0.5 ± 0.2 | 0.9 ± 0.4 | 1.2 ± 0.9 |
|     | OCT   | 19.7 ± 21.5 | 8.2 ± 2.1 | 4.9 ± 1.5 | 3.4 ± 1.8 | 2.8 ± 1.0 | 3.6 ± 0.31 | 1.35 ± 0.60 | 2.94 ± 0.22 | 6.7 ± 0.4 | 154.9 ± 21.5 | 107.1 ± 0.4 | 62.9 ± 13.2 | 77.9 ± 10.2 | 195.2 ± 10.2 |
|     | NOV   | 30.5 ± 23.9 | 7.2 ± 2.6 | 5.4 ± 1.9 | 3.7 ± 1.8 | 2.3 ± 0.8 | 4.9 ± 0.35 | 1.1 ± 0.4 | 3.01 ± 0.19 | 7.1 ± 0.6 | 32.3 ± 12.1 | 17.2 ± 3.0 | 33.0 ± 6.9 | 69.4 ± 15.8 | 49.3 ± 10.3 |
|     | DEC   | 30.5 ± 23.9 | 7.2 ± 2.6 | 5.4 ± 1.9 | 3.7 ± 1.8 | 2.3 ± 0.8 | 4.9 ± 0.35 | 1.1 ± 0.4 | 3.01 ± 0.19 | 7.1 ± 0.6 | 32.3 ± 12.1 | 17.2 ± 3.0 | 33.0 ± 6.9 | 69.4 ± 15.8 | 49.3 ± 10.3 |
|     | JAN   | 30.5 ± 23.9 | 7.2 ± 2.6 | 5.4 ± 1.9 | 3.7 ± 1.8 | 2.3 ± 0.8 | 4.9 ± 0.35 | 1.1 ± 0.4 | 3.01 ± 0.19 | 7.1 ± 0.6 | 32.3 ± 12.1 | 17.2 ± 3.0 | 33.0 ± 6.9 | 69.4 ± 15.8 | 49.3 ± 10.3 |

Field blanks; method detection limit; relative percent difference.

All of the statistical analysis including correlation was conducted using the SPSS (Statistical Package for the Social Science, Ver. 23, IBM, Armonk, NY, USA). Most of the data in this study are not normally distributed. However, if the number of data points exceeded 30, it was assumed to be a normal distribution on the basis of the central limit theorem [32].

### 3. Results

#### 3.1. General Characteristics of PM$_{2.5}$ at Two Locations

The average PM$_{2.5}$ concentrations at the two locations were similar, showing 28.3 µg m$^{-3}$ and 28.8 µg m$^{-3}$ at the KNU and the KBIC sites, respectively (Table 1). However, the standard deviation was much higher at the KBIC site than at the KNU site (Table 1), indicating the larger daily variation at the KBIC site. PM$_{2.5}$ was highest in December at both sites, and the average PM$_{2.5}$ in December was about 1.2 times and 1.7 times higher than the overall average values at the KNU and the KBIC sites, respectively (Table 1). At both sites, OC showed the highest contribution to PM$_{2.5}$ mass, and it was statistically higher at the KNU site than at the KBIC site ($p = 0.004$). At the KNU site, there was no significant difference between the monthly average OC concentration, although it showed the highest average
in January. On the other hand, at the KBIC site, OC concentration was found to be very high in December and considerably low from September to November, with large monthly fluctuations (Table 1). OC was highly correlated with EC at both sites \((p < 0.001)\); however, the correlation coefficient at the KBIC site (Pearson \(r = 0.89\)) was much higher than at the KNU site \((r = 0.69)\), suggesting that the primary OC was more important at the KBIC site [33]. EC concentration was also significantly higher in December than in other months at the KBIC site.

WSOC, known to be emitted from non-fossil fuel combustion [34] or secondarily formed in the atmosphere [35], was high in December at the KBIC site, and the difference in WSOC concentrations at the KNU and KBIC sites was also highest in December (Table 1). While the percentage of WSOC to total OC (average of ratio) remained consistent throughout the sampling period, showing 48% and 44% at the KNU and KBIC sites, respectively, the WSOC variation to the OC variation differed at the two sites. The WSOC concentration predicted the OC distribution much better at the KBIC site than at the KNU site (Figure 2). In addition, the WSOC/OC ratio increased as the OC concentration increased at the KBIC site, whereas no correlation was observed between these two variables (Figure 2). The Pearson correlation coefficient between OC and the WSOC/OC ratio was 0.42 at the KBIC site, but it increased to 0.56 when one point (sample with a WSOC/OC ratio of 0.75 in Figure 2) was excluded. Better correlations between WSOC and OC and between OC and the WSOC/OC ratio at the KBIC site suggest that the major emission sources (or formation pathways) of WSOC significantly affected the total OC concentration and that WSOC became more important with increasing OC at the KBIC site. On the other hand, WIOC provides a better explanation of the OC variation than WSOC at the KNU site \((r^2 = 0.66)\) (Figure S2), possibly indicating the significant effect of fossil-fuel combustion at the KNU site [36].

![Figure 2](image)

**Figure 2.** Linear regression between WSOC and OC concentrations at KNU site (upper panels) and KBIC site (lower panels). The figures on the right side represent the relationship between OC concentration and WSOC/OC ratios at both sites. The dashed lines indicate the 95% confidence interval for the regression.
The average concentration of $K^+$, which is often used as an indicator of biomass burning [37,38], was similar at both sites (Table 1). However, the daily and monthly variations in $K^+$ were larger at the KBIC site than at the KNU site. While both average concentration and standard deviation of $K^+$ were the highest in December at the KBIC site, the highest monthly average $K^+$ appeared in January at the KNU site (Table 1). The highest $K^+$ was observed on 30 December 2017 and on 14 January 2018 at the KBIC and KNU sites, respectively, and the day with the highest $K^+$ concentration coincided with the day with the highest PM$_{2.5}$ concentration at both sites. This result possibly indicates the significant impact of the $K^+$ source on PM$_{2.5}$ concentration at both sites.

Among the PM$_{2.5}$ constituents, OC and WIOC were statistically higher at the KNU site than at the KBIC site ($p$-values are 0.004 and 0.013 for OC and WIOC, respectively), whereas NH$_4^+$ was the only component showing statistically higher concentration at the KBIC site than at the KNU site ($p < 0.001$). During the entire sampling period, the average NH$_4^+$ concentration at the KBIC site was approximately two times higher at the KNU site than at the KBIC site (Table 1). NH$_4^+$, similar to the majority of other PM$_{2.5}$ components, was the highest in December at the KBIC site, but its contribution to PM$_{2.5}$ mass was most significant in September and November, showing 22% and 24%, respectively. NO$_3^-$ and SO$_4^{2-}$ were measured only in September and October at the KBIC site, and their average concentrations during these two months were higher than those at the KNU site; however, the differences were not statistically significant ($p > 0.05$).

PM$_{2.5}$ and its chemical constituents were compared with those observed in other studies (Table 2). PM$_{2.5}$ concentrations in this study were generally lower than those measured in metropolitans in India, China, and Korea. However, in this study, OC showed higher concentrations than those in Seoul, while EC did not, resulting in a higher OC/EC ratio than in Seoul. The OC/EC ratio in this city was significantly higher than those observed in New Delhi, India, and major cities in China (Table 2). Considering the low OC/EC ratio generally in metropolitans in India, China, and Korea due to the large contribution of mobile source [39], the high OC/EC ratio might be caused either by other combustion sources such as biomass burning than mobile sources or by large fractions of aged aerosol [40]. K$^+$ concentrations, a possible tracer of biomass burning, were significantly lower in this study than in New Delhi, India, and in Zhengzhou and Beijing, China. Since K$^+$ is also emitted from crustal sources [41], more evident tracers such as levoglucosan should be measured in the future. NH$_3$(g) emissions are likely to be important for PM$_{2.5}$ in this city.

### Table 2. Comparisons of measured concentrations of PM$_{2.5}$ and its chemical constituents with those reported in other studies. Unit of concentration is µg m$^{-3}$.

| Site          | Chuncheon KNU | Chuncheon KBIC | India (New Delhi) | China (Zhengzhou) | China (Beijing) | Korea (Seoul) (2013–May 2015) | Reference |
|---------------|---------------|----------------|-------------------|-------------------|----------------|-----------------------------|-----------|
| Period        | 26 August 2017–29 January 2018 | June 2017 | 2017 | June 2016–June 2017 | 2017 | September 2013–May 2015 |
| PM$_{2.5}$    | 28.3          | 28.8           | 91.5              | 70.5              | 134.7          | 31.3                        | [42]     |
| OC            | 8.63          | 7.46           | 20.3              | 10.5              | 24.2           | 6.01                        | [43]     |
| EC            | 1.16          | 1.10           | 4.92              | 4.4               | 6.0            | 0.80                        | [44]     |
| WSOC          | 3.81          | 3.56           | -                 | -                 | -              | -                           | [45]     |
| NH$_4^+$      | 2.50          | 4.94           | 3.78              | 8.8               | 7.8            | 7.1                         | [46]     |
| NO$_3^-$      | 3.19          | 1.52           | 0.09              | 11.7              | 21.4           | 8.0                         |         |
| SO$_4^{2-}$   | 1.97          | 2.20           | 0.81              | 7.9               | 20.2           | 7.4                         |         |
| K$^+$         | 0.19          | 0.21           | 3.17              | 0.9               | 1.9            | -                           |         |
| Mg$^{2+}$     | 0.01          | 0.01           | 1.09              | -                 | 0.3            | -                           |         |
| Ca$^{2+}$     | 0.07          | 0.05           | 0.69              | -                 | 2.32           | -                           |         |
3.2. Relationship of PM$_{2.5}$ Components between Two Locations

When PM$_{2.5}$ concentrations measured at the two locations on the same days were compared, they were similar, except for five samples, where PM$_{2.5}$ concentrations at the KBIC site were significantly higher than that at the KNU site (Figure 3). The highest correlations between the two sites were found for NO$_3^-$ and SO$_4^{2-}$, indicating that these components appeared to be affected by regional sources rather than local sources during the measurement periods of September and October. NO$_3^-$ and SO$_4^{2-}$ were generally higher at the KBIC site than at the KNU site during these two months (Figure 3). All PM$_{2.5}$ components showed a significant correlation between the concentrations measured at the two sites, except for OC and EC, which showed relatively weak correlations (0.01 < $p < 0.05$), compared to other components ($p < 0.01$). OC showed higher concentrations at the KNU site than at the KBIC site ($p = 0.004$), whereas EC did not show any trend. There was a relatively strong correlation of NH$_4^+$ between the two locations, and NH$_4^+$ was statistically higher at the KBIC site than at the KNU site ($p < 0.001$) (Figure 3). These results suggest that there were significant primary or secondary sources of NH$_4^+$ near the KBIC site and that these sources were also likely to affect the NH$_4^+$ concentrations at the KNU site. The correlation between K$^+$ concentrations measured at the KNU and KBIC sites, as well as NH$_4^+$ concentrations, was relatively strong (Figure 3).

![Figure 3](image-url)

**Figure 3.** Correlations between PM$_{2.5}$ components measured at the KNU and at the KBIC sites. All concentration units are in $\mu g m^{-3}$, and the green dotted line represents the 1:1 line. Correlation coefficient, $r$ with two-star (**) and one-star (*) indicates that the correlation was significant at the 0.01 and 0.05 levels, respectively.

3.3. Higher PM$_{2.5}$ Samples at the KBIC Site Than at the KNU Site

Although the average PM$_{2.5}$ concentration during the entire sampling period was lower than at the KNU site, the daily variation in PM$_{2.5}$ concentrations was considerably large at the KBIC site (Figure 4a). In particular, significantly higher PM$_{2.5}$ concentrations at the KBIC site than at the KNU site were often observed in December and January (Figure 4b). PM$_{2.5}$ concentrations measured on 3 December, 4 December, 30 December, 17 January, and 30 January were approximately 1.3 to 2.9 times higher at the KBIC site than at the KNU site (Figure 4b,c). This result strongly indicates that sources affecting PM$_{2.5}$ at the KBIC site were different from those influencing PM$_{2.5}$ at the KNU site. The concentration variations of OC, NH$_4^+$, and K$^+$ followed the PM$_{2.5}$ variation very well (Figure 4c) during the period, with significantly higher PM$_{2.5}$ at the KBIC than at the KNU sites, which is shaded in yellow in Figure 4b,c, indicating that high PM$_{2.5}$ concentrations appearing locally at the KBIC site were related to the emission sources and/or secondary formation pathways of NH$_4^+$, OC, and K$^+$. As shown in Figure 4c, from 30 November...
2017 to 23 January 2018, the concentrations of PM$_{2.5}$ components were compared on the five days when the PM$_{2.5}$ concentrations were significantly higher at the KBIC site than at the KNU site (3 December 2017; 24 December 2017; 30 December 2017; 17 January 2018; 23 January 2018), as well as other days, and all PM$_{2.5}$ components were increased at high rates on days with significantly higher PM$_{2.5}$ concentrations at the KBIC site (Figure 4d). Mg$^{2+}$ and Ca$^{2+}$, the representative crustal elements, increased at the highest rate; however, from 24 November 2017 to 23 January 2018 (the area shaded in yellow in Figure 4b), they were below the MDL, except in the five days, showing significantly higher PM$_{2.5}$ concentration at the KBIC than at the KNU sites. Even in these five days, the concentrations of both Mg$^{2+}$ and Ca$^{2+}$ were lower than in September and October. In addition, the concentration variations of Mg$^{2+}$ and Ca$^{2+}$ were not the same as PM$_{2.5}$ ($t^2$ between Mg$^{2+}$ and PM$_{2.5}$ and Ca$^{2+}$ and PM$_{2.5}$ was 0.19 and 0.13, respectively). K$^+$ is often used as an indicator of biomass burning [38] but is also emitted from soil dust [41]. In this study, high PM$_{2.5}$ episodes locally appearing at the KBIC site were unlikely to be affected by the crustal emission source because OC, especially WSOC, and NH$_4^+$ increased significantly in these five samples (Figure 4d). The contribution of NH$_4^+$ to PM$_{2.5}$ increased from 16% to 19% for the significantly higher PM$_{2.5}$ samples at the KBIC site than at the KNU sites, compared to the PM$_{2.5}$ samples obtained on other days. The concentrations of NO$_3^-$ and SO$_4^{2-}$ were not measured at the KBIC site during the period shown in Figure 4c. Therefore, it is unknown whether the increased NH$_4^+$ concentration existed as NH$_4$NO$_3$ or (NH$_4$)$_2$SO$_4$.

Figure 4. (a) Box plots of PM$_{2.5}$ at two sites; (b) daily PM$_{2.5}$ concentrations at two sites. The period in which significantly higher PM$_{2.5}$ concentrations were often observed at the KBIC site than at the KNU site is shaded in yellow; (c) concentrations of PM$_{2.5}$ (shown as bars), OC (shown as a red line), and NH$_4^+$ (shown as a green line) at the KBIC site during the period shaded in yellow in (b). PM$_{2.5}$ concentrations significantly higher at the KBIC site than at the KNU site are indicated by blue bars, and the rest by gray bars; (d) the increment ratio of each PM$_{2.5}$ component was obtained by dividing the average concentration of component measured on the days when PM$_{2.5}$ was significantly higher at the KBIC site than the KNU site (during the five days represented in the blue bars in (c)) by the average concentration of chemical component on other days represented by the gray bars in (c).

Although the mineral content of biomass ash depends on several factors such as the type of biomass and combustion temperature, K is typically the main alkali, and Ca and Mg are the main alkaline earth metal [47,48]. Therefore, when the contribution of biomass burning to PM$_{2.5}$ is significant, the concentrations of both Ca$^{2+}$ and Mg$^{2+}$ could be increased
with K⁺, even when the effect of crustal dust is minimal. These results suggest that biomass burning and NH₄⁺-related sources are likely to be an important local source on the outskirt area of the city under study, resulting in abrupt increases in PM₂.₅ concentrations at the suburban site rather than at the downtown site.

3.4. Correlations of PM₂.₅ Components with PM₂.₅ Mass and Relative Humidity

Correlations between each PM₂.₅ component and PM₂.₅ mass were identified at the two sampling sites. PM₂.₅ showed a high correlation with OC and EC at both sites, but the correlations were much stronger at the KBIC site (Table 3). PM₂.₅ was also highly correlated with NH₄⁺ and K⁺ at the KBIC site, indicating that it was significantly affected by the sources related to OC, EC, NH₄⁺, and K⁺. The significantly higher correlations of PM₂.₅ with OC, EC, NH₄⁺, and K⁺ at the KBIC site than at the KNU site also indicate that these sources locally influenced PM₂.₅ measured at the KBIC site, considering that the distance between the two sampling sites was only 8.3 km. NH₄⁺ showed significantly strong correlations with OC, EC, and K⁺ at the KBIC site, whereas, at the KNU site, NH₄⁺ was better correlated with NO₃⁻ and SO₄²⁻. In addition, K⁺, an indicator of biomass burning, showed a high correlation coefficient with WSOC, another indicator of biomass burning, at both sites, but a significantly stronger correlation was found at the KBIC site (Table 3). Previous studies have shown that NH₃ is largely emitted from biomass burning [49], and there is also active secondary organic and inorganic aerosol formation in the plume of biomass burning. Xiao (2020) measured a stable nitrogen isotope ratio (δ¹⁵N) of aerosol NH₄⁺ in central China [50]. NH₄⁺ concentration increased as the temperature decreased close to winter, whereas the δ¹⁵N did not show this pattern. The increase of NH₄⁺ was concluded to be attributed not to fossil fuel sources but biomass burning. Other studies also suggested the active secondary inorganic aerosol formation, including KNO₃ and K₂SO₄, in biomass burning plumes [51]. In this study, both NO₃⁻ and SO₄²⁻ concentrations were measured only during September and October at the KBIC site. Therefore, the presence of nitrate and sulfate aerosols was not confirmed in December and January when high PM₂.₅ episodes occurred at the KBIC site. However, strong correlations of PM₂.₅ with K⁺ and WSOC, and between WSOC, K⁺, and NH₄⁺ possibly indicate that local biomass burning had a significant impact on high PM₂.₅ episodes at the KBIC site.

Table 3. Correlation coefficient between PM₂.₅ component at KNU site (upper table) and KBIC site (lower table). Correlation coefficient with two-star (**) and one-star (*) superscript indicates that the correlation was significant at the 0.01 and 0.05 levels, respectively.

|        | PM₂.₅ | OC     | EC     | WSOC   | NH₄⁺ | K⁺    | Mg²⁺  | Ca²⁺  | NO₃⁻ | SO₄²⁻ |
|--------|--------|--------|--------|--------|------|-------|-------|-------|-------|-------|
| KNU    |        |        |        |        |      |       |       |       |       |       |
| PM₂.₅  | 0.620 **| 0.582 **| 0.560 **| 0.699 **| 0.616 **| 0.194 | 0.347 *| 0.6350 **| 0.837 **|
| OC     | 0.692 **| 1      |        |        |      |       |       |       |       |       |
| EC     | 0.660 **| 0.773 **| 1      |        |      |       |       |       |       |       |
| NH₄⁺   | 0.441 * | 0.336 * | 0.441 * | 1      |      |       |       |       |       |       |
| K⁺     | 0.483 **| 0.447 **| 0.611 **| 0.784 **| 1    |       |       |       |       |       |
| Mg²⁺   | 0.193  | 0.273  | 0.183  | 0.160  | 0.378 *| 1     |       |       |       |       |
| Ca²⁺   | 0.347  | 0.339  | 0.409 *| 0.534 **| 0.719 **| 0.606 **| 1    |       |       |       |
| NO₃⁻   | 0.635 **| 0.372  | 0.468 *| 0.940 **| 0.904 **| 0.321 | 0.751 **| 1    |       |       |
| SO₄²⁻  | 0.837 **| 0.425 *| 0.496 *| 0.851 **| 0.746 **| 0.307 | 0.590 **| 0.775 **| 1    |       |
| KBIC   |        |        |        |        |      |       |       |       |       |       |
| PM₂.₅  | 0.930 **| 0.832 **| 0.906 **| 0.813 **| 0.890 **| 0.194 | 0.416 *| 0.388 | 0.815 **|
| OC     | 1      |        |        |        |      |       |       |       |       |       |
| EC     | 0.890 **| 1      |        |        |      |       |       |       |       |       |
| WSOC   | 0.958 **| 0.870 **| 1      |        |      |       |       |       |       |       |
| NH₄⁺   | 0.759 **| 0.655 **| 0.720 **| 1      |      |       |       |       |       |       |
| K⁺     | 0.889 **| 0.740 **| 0.843 **| 0.719 **| 1    |       |       |       |       |       |
| Mg²⁺   | 0.012  | 0.155  | 0.029  | 0.111  | 0.185 | 1     |       |       |       |       |
| Ca²⁺   | 0.298  | 0.411 *| 0.306  | 0.393 *| 0.405 *| 0.688 **| 1    |       |       |       |
| NO₃⁻   | 0.652 *| 0.599 *| 0.307  | -0.204 | 0.483 | 0.106 | 0.007 | 1    |       |       |
| SO₄²⁻  | 0.306  | 0.526  | 0.471  | 0.620 *| 0.181 | 0.325 | 0.593 *| 0.094 | 1    |
Relative humidity (RH) often shows good correlations with secondary aerosol, indicating the importance of aqueous phase reactions [26,52,53]. A previous study conducted at the KNU site found a statistically significant regression equation for PM$_{2.5}$ concentration using RH and wind speed during winter, showing positive and negative contributions of RH and wind speed to PM$_{2.5}$ concentration, respectively [25]. In this study, no relationship was found between RH and PM$_{2.5}$ during the entire sampling period. However, from November to January, the Pearson correlation coefficient between RH and PM$_{2.5}$ was 0.74 ($p < 0.001$) at the KNU site, and secondary inorganic components such as NO$_3^-$ ($r = 0.78$), SO$_4^{2-}$ ($r = 0.70$), and NH$_4^+$ ($r = 0.65$) showed a strong correlation with RH among PM$_{2.5}$ components. At the KBIC site, RH showed a good correlation with PM$_{2.5}$ ($r = 0.84$) and NH$_4^+$ ($r = 0.75$) from November to January even though RH was measured concurrently with only nine PM$_{2.5}$ samples (NO$_3^-$ and SO$_4^{2-}$ were not measured during this period). Comparing RH measured on the same days at the KNU and KBIC sites, the average RH was 71% at the KBIC site, which was higher than the average RH (68%) at the KNU site. If restricted to winter data only, the average RH was 71% and 66% at the KBIC and KNU sites, respectively. The significantly higher concentration at the KBIC site than at the KNU site, which often appeared in December and January (Figure 4b), was possibly affected by the higher RH at the KBIC site. The studied city, Chuncheon, is famous for a large number of lakes, and there is a large lake (the largest lake in this city) near the KBIC site (Figure S1), leading to a higher RH than at the KNU site in the downtown area. The high RH most likely provided suitable conditions for NH$_3$ (and also possibly HNO$_3$ and SO$_2$) to be condensed on humid particles in winter, as suggested in other studies [25,54–56], resulting in the active formation of secondary inorganic PM$_{2.5}$ at the KBIC site.

3.5. Secondary Organic Carbon

SOC is often quantified using an EC tracer method, as shown in Equation (1) [57].

$$\text{POC} = \text{EC} \times \left( \frac{\text{OC}}{\text{EC}} \right)_{\text{pri}} + a$$  

(1)

where POC is primary organic carbon, $(\text{OC}/\text{EC})_{\text{pri}}$ indicates the OC/EC ratio directly emitted from combustion sources, and the offset, $a$, represents the POC emitted from a non-combustion source. In this study, the $(\text{OC}/\text{EC})_{\text{pri}}$ and the offset, $a$, were calculated from a regression line of plotted OC vs. EC data including points aligned in the lower end of the graph (Figure 5) [58]. SOC concentration was calculated by subtracting POC concentration from the total OC concentration. The total OC concentration was significantly higher at the KNU site than at the KBIC site. However, POC concentration at the KBIC site was $5.1 \pm 1.5$ $\mu g$ m$^{-3}$ on average, which was slightly higher than $4.9 \pm 0.9$ $\mu g$ m$^{-3}$ found at the KNU site, indicating the POC contribution to OC was clearly higher at the KBIC site. Average SOC concentrations were $3.8 \pm 2.5$ $\mu g$ m$^{-3}$ and $2.4 \pm 2.2$ $\mu g$ m$^{-3}$ at the KNU and KBIC sites, respectively. A stronger correlation between EC and OC at the KBIC site than at the KNU site (as shown in Figure 5) indicates the importance of POC at this site, which is consistent with the lower SOC concentration and smaller SOC/OC ratio observed at the KBIC site than at the KNU site. The contributions of POC to OC were 57% and 68% at the KNU and KBIC sites, respectively. The monthly average SOC/OC ratio was 46%, 36%, 34%, 44%, and 47% from September 2017 to January 2018 at the KNU site, whereas it showed a relatively low ratio during September (18%) and October (24%) and increased up to 31%, 43%, and 32% at the KBIC site in November, December, and January, respectively, which shows increased SOC contributions in winter at both sites.
Secondary organic aerosols (SOAs) are formed from the complex oxidation of volatile organic compounds, followed by gas–particle partitioning or heterogeneous reactions of carbonyls [59,60]; therefore, it is known to be actively formed in summer because of abundant oxidants in ambient air [61–64]. In addition, some species of POA evaporate into the air and repartition into aerosol after being further oxidized, forming SOA [65–67]. In Korea, because of a high aerosol concentration during wintertime, gas–particle partitioning of semivolatile gaseous organic compounds is probably active, resulting in a high concentration of SOC in winter. Previous studies also found high PM$_{2.5}$ episodes in wintertime, driven by secondary organic aerosol formation caused by aqueous and photochemical reactions [60,68]; they also identified the oxidation and partitioning of POA treated as semivolatile as the most important SOA formation in winter. There was a strong correlation between SOC and RH ($r = 0.79$) and the SOC/OC ratio and RH ($r = 0.81$) during late fall and winter (from November to January) only at the KBIC site, suggesting the significance of heterogeneous reactions forming SOA in winter. This result can support the result in which PM$_{2.5}$ concentrations at the KBIC site were often significantly high in December and January (Figure 4b).

### 3.6. Size Distribution

OPS was used to determine the size distribution of atmospheric particles at the two sampling sites. Since OPS can measure particles of 0.3–10 $\mu$m sizes, particles less than 0.3 $\mu$m were estimated using the ratio obtained from the previous research [69] conducted using a micro-orifice uniform deposit impactor at the KNU site. In the study by Kim (2017), PM$_{0.32}$/PM$_{0.32-10}$ ranged from 0.07 to 0.54, with an average of 0.26 (Table S1), and the average ratio of PM$_{0.32}$/PM$_{10}$ was 0.20, which was similar to that found in another study [70]. PM$_{0.32}$ was assumed to be the same as PM$_{0.3}$ in this study, and PM$_{0.3}$ was estimated using Equation (2). PM$_{0.3}$ was then added to PM$_{0.3-2.5}$ and PM$_{0.3-10}$ measured by OPS to determine PM$_{2.5}$ and PM$_{10}$, respectively.

$$\frac{PM_{0.3}}{PM_{0.3-10}} = 0.26$$

(2)

OPS uses light scattering to determine the particle size, amount, and volume concentration. Therefore, particle density should be determined to convert volume concentrations to mass concentrations. In this study, PM$_{0.3}$ calculated using Equation (2) was added to the OPS measurement of volume concentration of PM$_{0.3-2.5}$, and the estimated OPS PM$_{2.5}$ volume concentration was compared with the PM$_{2.5}$ concentration measured using a gravimetric method at the KNU site to determine particle density. Particle density was determined to be 2.17 g cm$^{-3}$ in this study (Figure 5a); therefore, all OPS results reported in this study were corrected using PM$_{0.3}$ and particle density. It should be noted that there might be some uncertainty in estimating particle density in this study because particle

**Figure 5.** Correlation between EC and OC at KNU site (left) and KBIC site (right).
density may vary with the sources and continuously changed through aging processes in the atmosphere [71].

At both sites, particles showed bimodal distributions, but the significance of the coarse mode was more noticed at the KBIC site (Figure 6). The average PM$_{2.5}$/PM$_{10}$ ratio was higher at the KNU site (60.5%) than at the KBIC site (56.0%). The count median diameter was similar, showing 0.19 and 0.20 μm at the KNU and KBIC sites, respectively, whereas the mass median diameter was 1.86 and 2.55 μm at the KNU and KBIC sites, respectively. Standard deviations of coarse particles were also much higher at the KBIC site (Figure 6), resulting in a higher coefficient of variation (standard deviation divided by average) than at the KNU site. The largest variations were found on particles between 1.5 and 2.5 μm and between 8 and 10 μm at the KBIC site (Figure 6). All these results indicate a prominent source emitting coarse particles near the KBIC site and coarse particles were significantly more important for PM$_{10}$ mass concentrations at the KBIC site than those at the KNU site.

![Figure 6. Size distribution of PM measured at the KNU site (left) and the KBIC site (right).](image)

Based on the pollution rise of PM$_{2.5}$ at the KBIC site throughout the sampling period, PM$_{2.5}$ concentration was highly increased with the southeasterly winds (Figure S3). The KBIC site is surrounded by farm and rice paddy fields, and approximately 1.5 km long charcoal-grilled meat cooking restaurants are clustered approximately 1 km south and southeast of the KBIC site (Figure S1). In addition, there is a driveway with heavy traffic from east to south of the KBIC site (Figure S1). The size-segregated PM concentrations were determined using the OPS instrument based on the wind direction. With northeast winds (0–90°), both fine and coarse particles including PM$_{0.3}$ and PM$_{1.5−2.5}$ specifically showed high concentrations from late night to early morning (Figure 7a). There is farmland in the east and north of the KBIC site, and according to previous studies, open burning of agricultural residue and domestic waste frequently occurs in agricultural areas typically in late night and early morning hours [72]. When winds were blown from the south and southeast, where charcoal-grilled meat cooking restaurants are located, both fine and coarse particles peaked around dinner time (6–8 p.m.) and during morning time (4–10 a.m.) (Figure 7b). These peaks were probably caused by either the meat cooking restaurants or car exhaust gas and/or dust from the biggest driveway in Chuncheon (Figure S1). Coarse particles increased during rush hours, along with fine particles, because the road dust followed by tires and brake wear typically exists in the coarse mode [73,74]. On the other hand, PM concentration was increased during daytime hours with the winds from farm and paddy fields located in the west of the KBIC site (Figure 7c) (Figure S1). This daytime peak was probably caused by agricultural activities. Coarse particles during daytime were more important in this case than in other cases shown in Figure 7a,b because natural sources and mechanical processes typically emit coarse particles [75,76]. The results of size distribution
according to wind direction suggest that there are multiple sources near the KBIC site, such as mobile sources, cooking-related sources, agricultural activity, and open burning, which possibly affected the size-segregated concentrations of PM. Chemical composition data of size-segregated PM samples are needed to better identify the important sources in the future.

Figure 7. Diel variations of the size-segregated PM concentrations with (a) northerly winds, (b) easterly and southerly winds, and (c) westerly winds.

4. Conclusions

In this study, PM$_{2.5}$ and its chemical components were measured at two different sites in Chuncheon, a medium-sized city in South Korea: the city center (KNU site) and the suburbs (KBIC site). Comparison results of the concentrations of PM$_{2.5}$ components measured at the two sites showed that NH$_4^+$ was significantly higher at the KBIC site, and OC was statistically higher at the KNU site. The average POC concentration was higher at the KBIC site than at the KNU site; however, SOC contribution to OC was enhanced with an increase in RH at the KBIC site during winter, implying the significance of heterogeneous reactions forming SOC. Significantly higher PM$_{2.5}$ at the KBIC site than at the KNU site was also frequently observed in December and January, along with an increase in OC, NH$_4^+$, and K$^+$. These results support the notion that the sources of PM$_{2.5}$ at two sites differed, especially during winter, even though the distance between the two sites was only 8.3 km, and that the high PM$_{2.5}$ concentrations observed locally at the KBIC site were caused by the primary emission source and heterogeneous SOC formation. The strong correlation of PM$_{2.5}$ with K$^+$ and WSOC, as well as between WSOC, K$^+$, and NH$_4^+$ at the KBIC site, suggests that local biomass burning had a significant impact on high PM$_{2.5}$ episodes at the KBIC site. Hourly variations in size-segregated PM$_{2.5}$ concentrations were also observed at both sites. Coarse particles larger than 2.5 $\mu$m contributed more to PM$_{2.5}$ at the KBIC site probably because of agricultural activities or tires and brake wear from the nearby large driveway. In this study, the sampling duration was changed from a 24 h collection to a 71 h after 30 November 2017, and it should be noted that 71 h measurements might be somewhat biased by dilution effect, compared to 24 h measurements.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/atmos12070832/s1, Figure S1: The detailed land use information around the KBIC site, Figure S2: Linear regression between WIOC and OC concentration at KNU site, Table S1: Size-segregated mass concentrations (µg m$^{-3}$) of PM using MOUDI at the KNU site in a previous study (Kim, 2017), Figure S3: Correlation between OPS PM$_{2.5}$ volume concentration and PM$_{2.5}$ mass concentration measured by gravimetric method (left) and comparison of PM$_{2.5}$ volume concentration (ng L$^{-1}$) by OPS (green bar), PM$_{2.5}$ mass concentration (µg m$^{-3}$) measured by a gravimetric method using PMS instrument (yellow bar), and PM$_{2.5}$ mass concentration (µg m$^{-3}$) estimated by OPS.
volume concentration multiplied by particle density of 2.17 g cm$^{-3}$ (blue bar), Figure S4: Pollution rise of PM$_{2.5}$ at the KBIC site.

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