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Characteristics of Locally Occurring High PM_{2.5} Concentration Episodes in a Small City in South Korea

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Abstract: In this study, the ionic and carbonaceous compounds in PM_{2.5} were analysed in the small residential city of Chuncheon, Korea. To identify the local sources that substantially influence PM_{2.5} concentrations, the samples were divided into two groups: samples with PM_{2.5} concentrations higher than those in the upwind metropolitan area (Seoul) and samples with lower PM_{2.5} concentrations. During the sampling period (December 2016–August 2018), the average PM_{2.5} was 23.2 µg m^{−3}, which exceeds the annual national ambient air quality standard (15 µg m^{−3}). When the PM_{2.5} concentrations were higher in Chuncheon than in Seoul, the organic carbon (OC) and elemental carbon (EC) concentrations increased the most among all the PM_{2.5} components measured in this study. This is attributable to secondary formation and biomass burning, because secondary OC was enhanced and water soluble OC was strongly correlated with K⁺, EC, and OC. A principal component analysis identified four factors contributing to PM_{2.5}: fossil-fuel combustion, secondary inorganic and organic reactions in biomass burning plumes, crustal dust, and secondary NH₄⁺ formation.

Keywords: PM_{2.5}; biomass burning; secondary formation; water soluble organic carbon; principal component analysis

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1. Introduction

Particles less than 2.5 µm in diameter (PM_{2.5}) contribute to many serious issues, including adverse effects on human health, deteriorating visibility, and transboundary transport. PM_{2.5} has also been reported to have direct and indirect effects on climate change, as the particles effectively scatter solar radiation and act as cloud condensation nuclei [1–4]. PM_{2.5} is emitted directly from anthropogenic (such as mobile sources, coal power plants, and biomass burning) and natural sources (such as sea salt, soil re-suspension, and volcanic eruptions) or is formed secondarily in the atmosphere through complex homo- and heterogeneous reactions [5,6]. These PM_{2.5} types are primary and secondary PM_{2.5}, respectively. Many studies have identified possible sources and/or formation pathways of PM_{2.5} based on detailed chemical composition data [7–9]. PM_{2.5} mainly consists of water-soluble ionic compounds and organic and elemental carbon, with trace levels of metallic elements. Elemental carbon (EC) is emitted primarily by combustion processes [10–14]. On the other hand, organic carbon (OC) can be either directly emitted by both natural and anthropogenic sources or formed secondarily in the ambient air through homogeneous gas-phase oxidation, gas–aerosol partitioning, and/or heterogeneous oxidation of volatile organic compounds. In previous studies, secondary OC (SOC) has often been estimated using the EC tracer method [15–17]. OC can be classified into water-soluble OC (WSOC) and water-insoluble OC (WIOC). WSOC has been suggested as a proxy for SOC [18–22], but some studies have also indicated that WSOC is also emitted by non-fossil fuel combustion,

including biomass combustion [23–26]. Previous studies have shown that approximately 50–80% of $\text{PM}_{2.5}$ mass is secondary, mainly existing as NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and various forms of OC [27,28].

$\text{PM}_{2.5}$ has recently emerged as the most important air pollutant in South Korea, while concentrations of other representative pollutants, including SO_2 and CO, have decreased steadily in recent decades. According to the 2018 World Air Quality Report by AirVisual [29], South Korea is second behind Chile among the organization for economic cooperation and development (OECD) countries, and 44 Korean cities are among the worst 100 cities. Approximately 98% of the sites in the National Monitoring Network of Air Quality exceeded the South Korean annual National Ambient Air Quality Standard (NAAQS) of $15 \mu\text{g m}^{-3}$. Since $\text{PM}_{2.5}$ is a significant transboundary pollutant and due to South Korea's proximity to China, the contributions of Chinese sources to $\text{PM}_{2.5}$ concentrations in South Korea have been considered to be as large or larger than those of national sources [27,28,30,31].

In this study, we measured the atmospheric concentrations of $\text{PM}_{2.5}$ and its ionic and carbonaceous compounds in the relatively small residential city of Chuncheon, South Korea. Chuncheon is located ~100 km northeast of Seoul, South Korea. According to the National Emissions Inventory (2017), the $\text{PM}_{2.5}$ emission rate from anthropogenic sources in Chuncheon is quite low (167.3 metric tons) compared to Seoul (1629.4 metric tons). However, $\text{PM}_{2.5}$ concentrations in Chuncheon have often been similar to or higher than those in Seoul. Although the sources affecting $\text{PM}_{2.5}$ concentrations in Chuncheon are considered to be different from the major source types in metropolitan and industrial cities, only a few studies have identified potential $\text{PM}_{2.5}$ sources in small cities with low anthropogenic emissions [7,32]. Because westerly winds dominate this area, episodes of high $\text{PM}_{2.5}$ concentrations in Chuncheon are presumed to be caused by regional and long-range transport from urban and industrial areas of Korea and China; therefore, there have been few attempts to identify local $\text{PM}_{2.5}$ sources in the city. In addition, previous studies have identified $\text{PM}_{2.5}$ sources using $\text{PM}_{2.5}$ chemical compositions [33,34], relationships with other pollutants [35,36], and receptor modelling such as positive matrix factorisation (PMF) [37,38]; however, it is difficult to determine whether the identified source is local or whether it has been affected by long-range transport. In this study, $\text{PM}_{2.5}$ samples were divided into two groups: $\text{PM}_{2.5}$ concentrations that were higher and lower than those in the upwind area (Seoul). The characteristics of $\text{PM}_{2.5}$ in these two groups and their major components were then compared.

2. Methods

2.1. Sample Collection

$\text{PM}_{2.5}$ samples were collected on the roof of a 4 story building at Kangwon National University in Chuncheon, South Korea, from December 2016 to August 2018. Chuncheon is a small residential city with no large anthropogenic sources because the city has been designated as a water resource protected area. The city is located ~100 km northeast of Seoul (the capital and largest city in South Korea) and is along the border of Gyeonggi Province, where various large industries are located. Therefore, air pollutants emitted by Seoul and the adjacent industrial areas are likely transported to Chuncheon by the prevailing westerly winds (Figure 1). Samples were collected for 24 h every 6 d from December 2016 to November 2017, and additional measurements were conducted when high $\text{PM}_{2.5}$ concentrations were forecasted. From December 2017 to August 2018, samples were continuously collected over consecutive 71 h periods (for example, one sample was collected from 11 am on December 3 to 10 am on 6 December 2017). A 47 mm Teflon filter with a supported polypropylene ring (2.0 μm pore size, Pall Co., Port Washington, NY, USA) was used in a PMS-103 sampler (APM Engineering, Bucheon-si, Korea) at a flow rate of 16.7 L min^{-1} to determine the $\text{PM}_{2.5}$ mass concentrations. A 47 mm quartz filter (2.2 μm pore size, Whatman International Ltd., Maidstone, UK) that was previously baked in a furnace at 500°C for 24 h was used at a flow rate of 16.7 L min^{-1} to measure the

carbonaceous compounds in the PM_{2.5}. A carbon denuder was connected to the system between a cyclone and a filter pack to remove possible artefacts after February 2018.

Figure 1. Sampling site used in this study. Location of South Korea (left). Map of South Korea (right). Red star indicates the location of the PM_{2.5} sampling site in Chuncheon, and the blue circle indicates the national ambient air quality monitoring station in Seoul.

To collect ionic compounds, a cyclone (URG-2000-30EN), two 3 channel annular denuders (242 mm length, URG Co., Chapel Hill, NC, USA), and a 3 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/or negative artefacts. The filter pack contained Zeflour (1 µm pore size, Pall Co., Port Washington, NY, USA), nylon (1 µm pore size, Pall Co., Port Washington, NY, USA), and paper filters (2 µm pore size, Whatman International Ltd., Maidstone, UK) that were soaked in 10% citric acid prior to deployment. HNO₃ and NH₃ volatilised from NH₄NO₃ that collected on the Zeflour filter were collected using the nylon and paper filters, respectively [28]. The annular denuder was coated with a mixture of 50 mL of ethanol, 1 g N₂CO₃, 1 g of glycerol, and 50 mL of deionised water to collect acidic gases (SO₂, HNO₃, HNO₂), and with a mixture of 100 mL of ethanol, 1 g of citric acid, and 1 g of glycerol to collect basic gas (NH₃).

2.2. Analyses

The Teflon filters were stored in controlled temperature (20 °C) and relative humidity (50%) conditions for at least 24 h before and after sampling, and were weighed at least twice using an analytical balance (Sartorius, Germany, 10^{−5} g accuracy). After sampling, all of the filters were wrapped in aluminium foil and stored in a freezer until analysis. For the carbonaceous compounds, the quartz filters were punched to a size of 1.5 cm² and analysed using the National Institute of Occupational Safety and Health (NIOSH) method 5040 for thermal-optical analysis (Sunset Laboratory Inc., Tigard, OR, USA) to measure the OC and EC concentrations (Sunset Laboratory Inc., Tigard, OR, USA) [39]. A detailed description of the analytical protocol can be found in previous studies [40]. The remaining quartz filters were extracted using a sonicator with ultra-pure water for 1 h, followed by filtration through 0.2 µm PTFE syringe filters (Pall Co., Port Washington, NY, USA), and were then analysed using a total organic carbon (TOC) analyser (Sievers 5310C Laboratory, GE Analytical Instruments, Boulder, CO., Boulder, CO, USA) to quantify the WSOC. The TOC analyser is based on the oxidation of organic compounds to form CO₂ using UV radiation and a chemical oxidising agent (NH₄)₂S₂O₈, and the CO₂ is measured using a selective membrane-based conductivity detection technique [9]. Total inorganic carbon (TIC) concentrations were first quantified, and the total carbon (TC) contents were measured after oxidising the organic compounds. The total organic carbon (TOC) concentrations were then calculated as the difference between the TC and TIC [9,20]. In this study, water insoluble organic carbon (WIOC) was calculated by subtracting the

WSOC from OC. For the ionic compounds, the Zeflour, nylon, and paper filters were extracted using a sonicator with ultra-pure water for 2 h, filtered using a 0.45 µm syringe filter (PVDF, Pall Co., Port Washington, NY, USA), and analysed using ion chromatography (Thermo Dionex ICS-5000+ system, Thermo Fisher Scientific, Waltham, MA, USA).

All instruments used in the analyses were washed using Alconox and acetone, then rinsed with ultra-pure water. A filtered blank was collected every sixth sample, and the concentrations reported in this study have been field-blank corrected. The method detection limit (MDL) was calculated as three times the standard deviation of the field blank, and concentrations below the MDL were replaced with $0.5 \times \text{MDL}$. The quality assurance/quality control (QA/QC) results, including the relative percent differences between the triplicate analyses, are shown in Table 1.

Table 1. Summarized QA/QC results for PM_{2.5} components.

	NO ₃ [−]	SO ₄ ^{2−}	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	OC	EC	WSOC
F.B. (µg m ^{−3})	0.11	0.15	0.05	1.08	0.02	0.002	0.05	0.36	0.001	1.83
MDL (µg m ^{−3})	0.20	0.23	0.07	0.81	0.05	0.003	0.04	0.42	0.093	1.42
<MDL * (%)	21.1	6.2	21.4	14.8	16.8	12.2	13.8	0.5	0.5	7.3
RPD (%)	2.37	1.67	0.47	0.38	0.30	0.18	0.19	5.11	6.46	1.28

* indicates the percentage of samples below the method detection limit (MDL).

2.3. Meteorological and Other Data

Meteorological data, including temperature, wind speed, wind direction, and relative humidity (RH) were measured by a meteorological tower (Vintage Pro2, Davis Instruments, Hayward, CA, USA) at the sampling site every 5 min. The concentrations of other air pollutants, including PM₁₀, SO₂, NO₂, CO, and O₃, were obtained from the national ambient air quality monitoring station, which is located approximately 1.5 km south of the PM_{2.5} sampling site used in this study.

Three day backward trajectories were calculated using the NOAA-HYSPLIT with Global Data Assimilation System (GDAS) meteorological data, which consist of 3 h, global 1° latitude by 1° longitude datasets of pressure surfaces [9]. The backward trajectories were then calculated every 3 h and every 6 h for the 24 h averaged and 71 h averaged samples, respectively. An arrival height of 500 m was used to describe the regional transport meteorological pattern.

A principal component analysis (PCA) was performed using the Statistical Package for the Social Sciences ((SPSS) Ver. 24, IBM, Armonk, NY, USA) to better understand potential PM_{2.5} sources. The PM_{2.5} concentrations and chemical compositions were transformed into a standardised form, then Varimax rotation was used to redistribute the variance and provide an interpretable structure to the factors [37]. The lowest eigenvalue for the extracted factors was limited to more than 1.0. All other statistical analyses were conducted using SPSS.

3. Results and Discussion

3.1. PM_{2.5} and Its Chemical Species

The average PM_{2.5} concentration was $23.2 \pm 14.2 \mu\text{g m}^{-3}$ for the entire sampling period, which exceeds the current annual national ambient air quality standard (NAAQS) for PM_{2.5} ($15 \mu\text{g m}^{-3}$). Approximately 16% of the samples ($N = 31$) exceeded a 24 h NAAQS ($35 \mu\text{g m}^{-3}$), and more than 50% of the high concentration episodes were observed during winter (December, January, and February) ($N = 20$). There were distinct seasonal variations, with average concentrations of 23.4 ± 11.8 , 16.3 ± 10.3 , 18.4 ± 11.2 , and $32.5 \pm 16.4 \mu\text{g m}^{-3}$ in spring (March, April, and May), summer (June, July, and August), fall (September, October, and November), and winter, respectively (Figure 2). According to previous studies in Chuncheon [7,9,28], PM_{2.5} concentrations in the summer are typically much lower than in spring or winter, mainly because the prevailing westerly winds that transport

material from the polluted areas of South Korea and China are dominant during the spring and winter. Relatively clean air masses are transported from the east and the south during the summer. In this study, $\text{PM}_{2.5}$ was low in the summer of 2018 as anticipated; however, it was quite high in June and July of 2017, along with OC and NH_4^+ (Figure 2). In order to identify regional meteorological transport patterns, the backward trajectories for June and July of 2017 and 2018 were compared. Most of the backward trajectories came from Eastern China in 2017. However, in 2018, they originated from all directions, including southern and eastern areas of relatively clean air (Figure S1). In July 2017, when monthly $\text{PM}_{2.5}$ concentrations were the lowest of the entire study period, the backward trajectories originated from the East and South Seas and passed through the southern and eastern regions of Korea. There is evidence that $\text{PM}_{2.5}$ is typically enhanced when air masses are transported from China [31,41–43], which is also supported by these findings.

Figure 2. Monthly concentrations of $\text{PM}_{2.5}$ and its major components expressed as arithmetic means. Units are $\mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ and its species.

Among the $\text{PM}_{2.5}$ constituents, OC exhibited the highest concentration ($6.7 \pm 4.3 \mu\text{g m}^{-3}$), while the EC concentration ($0.9 \pm 0.5 \mu\text{g m}^{-3}$) was quite low (Table 2). The average WSOC concentration was $4.3 \pm 2.2 \mu\text{g m}^{-3}$, comprising a significant portion of OC . Both OC and EC exhibited their highest concentrations during the winter and their lowest concentrations during the summer, while WSOC was observed to be high during the spring (Table 2).

Table 2. Seasonally averaged PM_{2.5} constituent concentrations ($\mu\text{g m}^{-3}$).

	Spring	Summer	Fall	Winter	Annual
OC	6.3 ± 4.3	5.1 ± 4.0	6.0 ± 3.4	8.9 ± 4.5	6.7 ± 4.3
EC	0.8 ± 0.5	0.5 ± 0.3	0.8 ± 0.5	1.2 ± 0.6	0.9 ± 0.5
WSOC	5.1 ± 2.5		3.2 ± 2.0	4.5 ± 1.9	4.3 ± 2.2
SO ₄ ^{2−}	2.2 ± 1.6	2.8 ± 1.8	0.9 ± 0.8	2.2 ± 1.7	2.1 ± 1.7
NO ₃ [−]	2.1 ± 2.3	0.4 ± 0.6	1.7 ± 2.2	4.5 ± 3.4	2.4 ± 3.0
NH ₄ ⁺	2.8 ± 1.5	2.2 ± 1.5	1.2 ± 1.0	2.6 ± 1.5	2.3 ± 1.5
Na ⁺	0.23 ± 0.33	0.17 ± 0.13	0.14 ± 0.18	0.29 ± 0.43	0.22 ± 0.31
K ⁺	0.16 ± 0.14	0.07 ± 0.01	0.14 ± 0.10	0.26 ± 0.15	0.16 ± 0.14
Mg ²⁺	0.06 ± 0.06	0.01 ± 0.01	0.02 ± 0.01	0.05 ± 0.05	0.01 ± 0.05
Ca ²⁺	0.18 ± 0.23	0.04 ± 0.02	0.28 ± 0.68	0.15 ± 0.13	0.16 ± 0.36

The average correlation coefficient (*Pearson r*) between OC and EC was 0.85 (Figure 3), indicating that the major sources of both carbonaceous species overlapped considerably throughout the study period. The correlation coefficient between OC and EC was higher during the spring ($r = 0.91$) and winter ($r = 0.90$), and lower during the summer ($r = 0.76$) and fall ($r = 0.83$) (Figure S2), likely because SOC was actively forming in strong solar radiation and high temperature conditions [21,44,45]. The correlations of WSOC with both OC and EC were statistically significant (*Pearson r* = 0.67 for OC and EC) (Figure 3). EC has been used previously as a tracer for anthropogenic combustion sources [46–48], while OC is either emitted by combustion and biogenic sources or formed secondarily in ambient air [49]. WSOC is also emitted by biomass burning [23,24,34,50] or is formed secondarily in ambient air [51]. The strong correlations between OC and EC and between WSOC and EC indicate that the carbonaceous compounds were likely influenced by primary combustion sources. Previous studies have suggested that the OC/EC ratio is 1.0–4.2 for a mobile source, ~7.7 for biomass burning, and 2.5–10.5 for coal combustion [52]. Based on the results of this study, which exhibited high OC/EC ratios (7.8 average) throughout the entire sampling period (7.4, 9.9, 7.2, and 7.2 for spring, summer, fall, and winter, respectively), the main combustion source was anticipated to be biomass burning. However, secondary OC was also likely important during warm months, given the highest OC/EC ratio and the lower correlation coefficient between OC and EC during the summer (Figure S2). It should be noted that OC concentrations from the initial part of the sampling period were likely overestimated (due to sorption of organic vapour) because the carbon denuder was not deployed upstream of the filter until February 2018. Subramanian et al. (2004) [53] observed an almost constant positive artefact of $0.5 \mu\text{g m}^{-3}$ for 24 h bare quartz samples without a denuder throughout the study period. Kim (2016) [54] and Cheng et al. (2012) [55] also showed that OC concentrations were overestimated by approximately 10% during the spring and fall and by approximately 15% during the summer, respectively, due to a positive sampling artefact.

The total contributions of the 7 ionic components (SO₄^{2−}, NO₃[−], NH₄⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺) to PM_{2.5} mass was 32.0%, and NO₃[−] was the largest contribution to PM_{2.5} mass, followed by NH₄⁺ and SO₄^{2−} (Table 2). As reported by previous studies, the contribution of NO₃[−] was high in cold months due to active gas–particle conversion at low temperatures [9,56]. However, SO₄^{2−}, which is mostly formed secondarily, was the largest contributor to PM_{2.5} mass in the summer because of vigorous photochemical reactions that produce H₂SO₄, which is the intermediate species to the SO₄^{2−} aerosol [57]. NH₄⁺ did not exhibit any seasonal variations because it is mostly present as NH₄NO₃ and (NH₄)₂SO₄ [58], although the average concentration was the highest during the winter (Table 2). The trends in the NO₃[−], SO₄^{2−}, NH₄⁺, and K⁺ concentrations were all very similar from November to March, indicating the effect of the same source (Figure 2).

Figure 3. Correlations between EC and OC (left) and between WSOC and EC (green squares) and between WSOC and OC (orange circles).

3.2. Comparison with $\text{PM}_{2.5}$ in Seoul

Since Chuncheon is ~ 100 km east of the metropolitan area of South Korea (Seoul), its air quality is anticipated to be affected by Seoul and nearby areas via the prevailing westerly winds. In this study, we compared $\text{PM}_{2.5}$ concentrations between Chuncheon and Seoul. $\text{PM}_{2.5}$ concentration data from Seoul were obtained from the national ambient air quality monitoring station located at the centre of Seoul (Jung-Gu) (Figure 1). Samples from Chuncheon had $\text{PM}_{2.5}$ concentrations more than 1.2 times higher than those in Seoul on day 49 during the sampling period (higher concentration in Chuncheon, HC), while samples from Chuncheon had $\text{PM}_{2.5}$ concentrations more than 1.2 times lower than those in Seoul on day 106 during the sampling period (lower concentration in Chuncheon, LC). In this study, the HC sample was assumed to represent a locally occurring episode of high concentration in Chuncheon. There were 60 d with no significant difference between the two sites during the sampling period. HC samples generally were observed in 2017, while LC samples were observed in 2018 (Figure 4). It should be noted that samples were taken for 24 h until November 2017 and collected for 71 h thereafter. Therefore, the frequent occurrence of HC samples only in 2017 may suggest that high $\text{PM}_{2.5}$ concentration episodes in Chuncheon were unlikely to have lasted longer than 3 d.

Figure 4. Monthly occurrence rates of higher concentration (HC) and lower concentration (LC) samples throughout the sampling period.

3.2.1. Differences between HC and LC Samples

In this study, we compared the characteristics of PM_{2.5} and its chemical constituents in the HC and LC samples collected at the sampling site in Chuncheon. Concentrations of most of the constituents, as well as PM_{2.5} mass, were higher in the HC samples than in the LC samples (Table 3). However, except for OC, the percentage of each element in the PM_{2.5} mass was lower in the HC samples, resulting in a higher contribution of an undetermined portion in the HC samples (Figure 5). Metallic elements that were not measured in this study are typically considered as core constituents of PM_{2.5}. These elements are directly emitted by natural and anthropogenic sources and are not formed secondarily [59]. Therefore, a higher contribution of an undetermined PM_{2.5} composition indicates the potential significance of primary emission sources when PM_{2.5} concentrations were higher in Chuncheon than in Seoul. Excluding the undetermined fraction, the highest mass contributors were OC and EC in the HC samples, with increases of 1.8 and 1.5 times their contributions to the LC samples, respectively (Figure 5).

Table 3. Average PM_{2.5} concentrations of HC, LC, and other samples and their major chemical components.

Type	PM _{2.5}	PM ₁₀	NO ₃ [−]	SO ₄ ^{2−}	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	OC	EC	WSOC
HC	32.1 ± 15.9	43.2 ± 21.4	2.5 ± 3.2	2.3 ± 1.6	0.24 ± 0.35	2.5 ± 1.4	0.17 ± 0.12	0.03 ± 0.05	0.13 ± 0.12	9.3 ± 4.3	1.1 ± 0.6	4.0 ± 2.1
	18.4 ± 11.7	44.5 ± 22.4	1.9 ± 2.3	2.0 ± 1.5	0.19 ± 0.20	2.2 ± 1.6	0.15 ± 0.15	0.03 ± 0.05	0.15 ± 0.31	5.2 ± 3.6	0.7 ± 0.5	4.8 ± 2.2

Figure 5. Concentrations of PM_{2.5} components (left) and the fraction of each component in the PM_{2.5} mass (right) for HC and LC samples. Green circles in the left plot indicate the concentration ratios of HC to LC samples for each PM_{2.5} component.

While PM_{2.5} concentrations of the HC samples were 1.7 times higher than the LC samples, the PM₁₀ concentrations of the HC samples ($43.2 \pm 21.4 \mu\text{g m}^{-3}$) were very similar to those of the LC samples ($44.5 \pm 22.4 \mu\text{g m}^{-3}$), resulting in a much higher PM_{2.5}/PM₁₀ ratio for the HC samples (74.3%) than the LC samples (41.4%). Considering that the average PM_{2.5}/PM₁₀ ratio was 49.8% for the entire sampling period, the elevated PM_{2.5}/PM₁₀ ratios of the HC samples suggest that primary sources and/or secondary formation pathways that generated only PM_{2.5} and not PM_{2.5–10} caused the local high concentration episodes in Chuncheon. In addition, the correlation between PM_{2.5} and PM_{2.5–10} was statistically significant in the LC samples ($r = 0.471$, $p < 0.001$), but was not significant in the HC samples ($r = 0.225$, $p\text{-value} = 0.193$), indicating that the major sources of PM_{2.5} were likely different from those of PM_{2.5–10} when the PM_{2.5} concentrations in Chuncheon were higher than in Seoul.

3.2.2. Possible Sources for HC Samples

The total contributions of the seven ionic components to the $PM_{2.5}$ mass were 23.1% and 40.0% for the *HC* and *LC* samples, respectively, although the $PM_{2.5}$ concentrations of the *HC* samples were higher than those of the *LC* samples (Table 3). The contributions of NO_3^- , SO_4^{2-} , and NH_4^+ were 6.0, 7.2, and 8.1% in the *HC* samples and 8.9, 13.7, and 13.6% in the *LC* samples, respectively. The major contribution of NH_4^+ among the ionic components indicates an NH_4^+ surplus existed when the $PM_{2.5}$ concentrations were higher in Chuncheon than in Seoul. This suggests that NH_3 emissions from agricultural areas, which comprise a large portion of land cover in Chuncheon, were important to increased $PM_{2.5}$ concentrations. Since NH_3 is not likely to undergo long-range transport due to its short atmospheric residence time [58,60], it would be useful to reduce NH_3 emissions from local sources in order to reduce $PM_{2.5}$ concentrations. The contribution of SO_4^{2-} to the $PM_{2.5}$ mass was approximately two times greater in the *LC* samples than the *HC* samples because the *LC* samples were often collected during warm months (the fraction of *LC* samples collected in spring and summer was 75% of the total samples, while the fraction of *HC* samples was 30%) when the formation of H_2SO_4 occurs due to the high concentrations of hydroxyls (OH^-) [18,61].

OC and EC concentrations were higher in the *HC* than in the *LC* samples, with average values of $9.3 \pm 1.1 \mu g m^{-3}$ and $1.1 \pm 0.6 \mu g m^{-3}$, respectively (Table 3). The correlation coefficient between OC and EC was much higher for *LC* samples ($r = 0.94$) than for *HC* samples ($r = 0.71$) (Figure 6). In addition, the OC/EC ratios were 9.7 ± 5.2 and 7.0 ± 1.8 for the *HC* and *LC* samples, respectively. These results, including higher OC concentrations, lower correlation coefficients between OC and EC, and higher OC/EC ratios for *HC* samples, suggest that carbonaceous compounds were affected by diverse sources including secondary formation during high concentration episodes that occurred locally in Chuncheon. The OC/EC ratios in the *HC* samples during the summer were more than two times larger (16.6 ± 5.7) than those of the *LC* samples (7.3 ± 2.3), indicating that OC in the *HC* samples was mainly formed secondarily either in situ in Chuncheon, or during regional or long-range transport to Chuncheon during the summer. The secondary formation of OC is also supported by the relatively low correlation coefficients between OC and EC in the *HC* samples (Figure 6).

SOC was estimated indirectly using the EC tracer method [62], which assumes that primary OC can be calculated from EC concentrations using the following equation:

$$POC = b \cdot EC + a \quad (1)$$

where b is the fraction of POC emitted along with EC from the combustion source and a indicates non-combustion-derived POC [63]. The slope, b , and the offset, a , were determined from a regression line of plotted OC vs. EC data, including points aligned at the lower end of the graph (Figure 6) [17,63,64]. The concentrations of SOC were then estimated using the following equation:

$$SOC = OC - POC = OC - (b \cdot EC + a), \quad (2)$$

In both *HC* and *LC* samples, the fractions of POC emitted along with EC from the combustion source (slope b) were almost identical, and the non-combustion-derived POC (offset a) was negligible (Figure 6). The slope obtained in this study was somewhat larger than those obtained in previous studies (-1.0 – 2.5) [17,64], likely because of a smaller influence of mobile sources (with low OC/EC ratios) than other combustion sources [65] in this small city. SOC was more important in the *HC* samples ($SOC = 4.4 \pm 3.0 \mu g m^{-3}$, SOC/OC ratio = 47%) than in the *LC* samples ($1.8 \pm 1.7 \mu g m^{-3}$, 35%), which is also supported by the lower correlation coefficient between OC and EC for the *HC* samples than the *LC* samples (Figure 6). The SOC concentrations and SOC/OC fractions increased to $7.5 \mu g m^{-3}$ and 71% during summer in the *HC* samples. Relative humidity had a major impact on SOC formation [63], as aqueous phase chemistry is a major pathway for SOC

formation, particularly under high NO_x conditions [66,67]. Galindo et al. (2019) [63] observed significant increases in SOC concentrations when RH > 70%. In this study, the impact of RH on SOC concentration was significant only in the *HC* samples, and the coefficient of determination (r^2) increased further when only winter data were considered (Figure 7). This result indicates that the gas–particle partitioning of organic compounds via aqueous phase reactions is important, especially during the winter, for locally occurring high concentration episodes. During other seasons, volatile organic compounds are likely converted into low-volatility products through active gas phase photochemical oxidation and condensed into the particulate phase [63,68].

Figure 6. Correlations between carbonaceous compounds in the *HC* (left panels) and *LC* (right panels) samples.

Meanwhile, WSOC had a much stronger correlation with EC, as well as with OC, in the *HC* samples than the *LC* samples (Figure 6), indicating that primary combustion emissions had a significant influence on the PM_{2.5} carbonaceous component as a local source in Chuncheon. WSOC is known to be either directly emitted by combustion sources or formed by the oxidation of volatile organic compounds (VOCs) in the atmosphere [69]. Although secondary formation is believed to be the major formation pathway of WSOC, a number of studies have found that non-fossil fuel sources, such as biomass burning, are a major source of WSOC [70]. On the other hand, WIOC usually better represents primary OC emitted directly by fossil-fuel combustion [70]. In this study, WSOC was better correlated with EC in the *HC* samples than the *LC* samples (Figure 6), indicating that it was mainly emitted by primary combustion sources in the *HC* samples because EC is not a secondary pollutant [71]. WSOC was also highly correlated with secondary inorganic aerosols including NO₃[−], SO₄^{2−}, and NH₄⁺ as well as with K⁺, a marker for biomass burning, in the *HC* samples (Table 4), while it showed weak correlations only with OC and EC in the *LC* samples (Table 5). These results suggest that the strong co-emissions or

common source (or formation pathway) of the highly correlated species were significant local sources in Chuncheon. It has been suggested that the particles derived from the burning of fresh biomass can be readily converted to KNO_3 and K_2SO_4 via heterogeneous reactions [72,73]. In the *HC* samples, K^+ was strongly correlated with NO_3^- (Table 4), as well as with WSOC, suggesting that biomass burning was likely an important local source for both WSOC and $\text{PM}_{2.5}$ in Chuncheon.

Figure 7. The effect of RH on SOC concentrations for all *HC* samples (left) and only winter *HC* samples (right).

Table 4. Pearson correlation coefficients between $\text{PM}_{2.5}$ components in *HC* samples. Number in bold with two stars and with one star indicate that the correlations were significant at the 0.01 and 0.05 levels, respectively.

	NO_3	SO_4	Na	NH_4	K	Mg	Ca	OC	EC	WSOC
$\text{PM}_{2.5}$	0.71 **	0.32	0.44 **	0.64 **	0.64 **	0.53 **	0.16	0.83 **	0.79 **	0.86 **
NO_3	1									
SO_4	0.28	1								
Na	0.37	0.20	1							
NH_4	0.53 *	0.70 **	0.42 **	1						
K	0.94 **	0.24	0.20	0.41 **	1					
Mg	0.46	−0.17	0.76 **	0.36 *	0.29	1				
Ca	0.18	−0.29	0.55 **	0.04	0.25	0.59 **	1			
OC	0.72 **	0.34	0.44 **	0.42 *	0.50 **	0.37 *	−0.02	1		
EC	0.72 **	0.08	0.32	0.27	0.60 **	0.55 **	0.10	0.71 **	1	
WSOC	0.91 *	0.86 *	0.45 *	0.71 **	0.76 **	0.56 **	0.21	0.83 **	0.83 **	1

Table 5. Pearson correlation coefficients between $\text{PM}_{2.5}$ components in *LC* samples. Number in bold with two stars and with one star indicate that the correlations were significant at the 0.01 and 0.05 levels, respectively.

	NO_3	SO_4	Na	NH_4	K	Mg	Ca	OC	EC	WSOC
$\text{PM}_{2.5}$	0.70 **	0.53 **	0.12	0.72 **	0.67 **	0.37 **	0.09	0.69 **	0.67 **	0.23
NO_3	1									
SO_4	0.33 *	1								
Na	0.18	0.14	1							
NH_4	0.54 **	0.60 **	0.09	1						
K	0.76 **	0.40 **	0.05	0.66 **	1					
Mg	0.24	0.10	0.33 **	0.16	0.01	1				
Ca	0.21	−0.06	0.39 **	−0.01	0.10	0.26 *	1			
OC	0.52 **	0.21	0.27 *	0.39 **	0.40 **	0.47 **	0.10	1		
EC	0.54 **	0.19	0.26 *	0.38 **	0.44 **	0.46 **	0.08	0.94 **	1	
WSOC	−0.40	−0.04	−0.02	0.04	−0.15	0.44 *	0.19	0.43 *	0.39 *	1

A PCA analysis was performed for the HC samples to interpret the PM_{2.5} sources using PM_{2.5}, its chemical constituents, and meteorological parameters. Four factors were extracted, which accounted for 98.5% of the total variance (Table 6). Factor 1, which contributed −63.2% of the total variance, was interpreted as fossil fuel combustion during the winter because NO₂, CO, SO₂, and WIOC exhibited high factor loadings, while temperature had a negative loading. Factor 2, which accounted for −20% of the total variance, exhibited high loadings of NO₃[−], SO₄^{2−}, NH₄⁺, K⁺, and WSOC, and was presumed to be biomass burning. This implies that the formation of WSOC is associated with secondary inorganic reactions in biomass burning plumes [9,72–74]; hence, secondary OC can also be considered to be explained by Factor 2. Factor 3 was interpreted as crustal dust, as PM_{2.5–10}, Na⁺, Mg²⁺, and Ca²⁺ were all enriched. Factor 4 exhibited high loadings of temperature, RH, and NH₄⁺, indicating secondary NH₄⁺ formation during warm days when NH₃⁺ emissions typically increase due to fertiliser application and cattle farming [75]. Both NO₃[−] and SO₄^{2−} did not exhibit high loadings in Factor 4, indicating that NH₄⁺ may have existed in other forms (e.g., NH₄Cl) [9] as well as (NH₄)₂SO₄ and NH₄NO₃, as shown by Factor 2.

Table 6. Factor loadings in PM_{2.5} components with representative gaseous pollutants and meteorological parameters from principal component analysis (PCA).

	Factor 1	Factor 2	Factor 3	Factor 4
PM _{2.5}	0.478	0.602	0.185	0.591
PM _{2.5–10}	0.206	0.190	0.919	0.190
O ₃	−0.870	−0.301	0.016	0.381
NO ₂	0.886	0.444	−0.025	0.129
CO	0.859	0.489	−0.120	0.026
SO ₂	0.845	0.428	−0.069	0.174
T	0.044	0.101	0.504	0.842
RH	0.641	0.516	0.088	0.557
WS	−0.871	−0.038	−0.161	−0.448
NO ₃ [−]	0.391	0.911	0.018	0.089
SO ₄ ^{2−}	0.205	0.962	0.148	−0.006
Na ⁺	−0.008	0.271	0.958	0.049
NH ₄ ⁺	0.253	0.726	0.166	0.612
K ⁺	0.398	0.915	0.062	0.016
Mg ²⁺	0.378	−0.110	0.841	0.353
Ca ²⁺	−0.469	0.020	0.878	0.048
OC	0.637	0.666	0.256	0.270
EC	0.874	0.382	0.137	0.258
WSOC	0.445	0.789	0.213	0.321
WIOC	0.758	0.544	0.279	0.220
Variance explained (%)	63.2	83.0	92.2	98.5

4. Conclusions

In this study, PM_{2.5} and its major chemical compositions were measured in Chuncheon, South Korea, a small residential city, which experiences local high PM_{2.5} concentration episodes that cannot be linked to particulate transport from upwind urban and industrial areas. Of the 215 samples collected in Chuncheon, 49 had PM_{2.5} concentrations of at least 1.2 times higher than those in the upwind metropolitan area of Seoul. While PM_{2.5} concentrations were clearly higher in the HC samples than in the LC samples, the PM₁₀ concentrations were very similar to each other, suggesting that there were certain primary sources and/or secondary formations that generated only PM_{2.5}, and not PM_{2.5–10}. For the HC samples, PM_{2.5} was strongly correlated with carbonaceous compounds, including OC and EC, and the SOC fraction contributed to OC was much higher than in the LC samples, indicating the significance of the formation of secondary organic aerosols in locally occurring high PM_{2.5} episodes in Chuncheon. However, WSOC, a potential indicator of secondary OC or non-fossil fuel sources, was highly correlated with EC and K⁺ in the

HC samples, suggesting that biomass burning was also an important local source in Chuncheon. A PCA analysis identified four possible factors: fossil-fuel combustion during the winter, represented by high loadings of NO₂, CO, SO₂, and WIOC (Factor 1); secondary inorganic and organic reactions in biomass burning plumes (Factor 2); crustal dust (Factor 3); and secondary NH₄⁺ formation during warm days (Factor 4). Factors 2 and 4 exhibited high PM_{2.5} loading values, suggesting that secondary organic/inorganic formation and biomass burning were the most significant sources of variation in PM_{2.5} concentrations in Chuncheon. Based on the results of this study, it is clear that local policies to reduce biomass burning and NH₃ emissions should be applied to decrease the PM_{2.5} concentrations in Chuncheon. In addition, high RH and low WS conditions in the city are suitable for the formation of secondary aerosols; therefore, cooperation with adjacent regions and countries to reduce NO_x and SO₂ emissions is also very important because these precursor gases can undergo long-range transport.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4433/12/1/86/s1>, Figure S1: Backward trajectories for June and July in 2017 (a) and 2018 (b); Figure S2: Relationship between OC and EC in spring (top left), summer (top right), fall (bottom left), and winter (bottom right).

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