

Research Article

Semi-continuous Measurements of Water-soluble Organic Carbon and Ionic Composition of PM_{2.5} in Baengnyeong Island during the 2016 KORUS-AQ (Korea-United States Air Quality study)

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ABSTRACT This study characterized the water-soluble organic carbon (WSOC) and ionic components of PM_{2.5} (particles less than 2.5 µm in diameter) from April to June 2016, at Baengnyeong Island. The study utilized a particle-into-liquid sampler (PILS) coupled with a total organic carbon (TOC) analyzer and ion chromatography (PILS-TOC-IC). The PM_{2.5} mean concentration in this study was $23.8 \pm 16.7 \mu\text{g m}^{-3}$, and the mean of WSOC concentration was $1.6 \pm 1.5 \mu\text{g m}^{-3}$. Ionic compounds increased by 3.8% in the period in which the air quality standard of PM_{2.5} ($35 \mu\text{g m}^{-3}$) was exceeded because the concentration of ionic components increased due to generation by chemical reactions and emissions from a primary source in a nearby urban area. The wind direction and speed were mostly in the northwest and southwest directions and the higher concentration of PM_{2.5} was also shown in the same directions. In comparison with the previous study, the WSOC/OC ratio was 0.5 ± 0.3 in Baengnyeong Island, which was higher than that at roadside and urban sites and lower than at the background site (Sweden, Aspvreten). It was considered that insoluble OC constituted a major proportion of primary OC that was emitted in urban areas, and the higher WSOC/OC ratios of rural and background sites were affected by inflow. The ratio of nitrate and sulfate in Baengnyeong Island was lower than urban areas in China in other studies, because of emitted aerosols from coal combustion or vehicle emission. The results indicate that Baengnyeong Island was affected by formation of secondary aerosols by chemical reactions and inflow from China as well as domestic emissions. The slope of $\text{H}^+_{\text{Aerosol}}/\text{SO}_4^{2-}$ in Baengnyeong Island was 0.079, which was a result of neutralized particle acidity in ambient air. The molar ratio of nitrate and ammonium with sulfate in Baengnyeong Island showed ammonium-rich conditions because ammonium nitrate was increased to homogeneous reaction of ammonia and nitric acid in the gas-phase.

KEY WORDS PILS-TOC-IC, Water soluble organic carbon, PM_{2.5}, Semi-continuous measurements, Ionic composition

1. INTRODUCTION

The majority of Asian countries have rapid industrial growth, economic development, and population growth, and have the potential to increase their pollut-

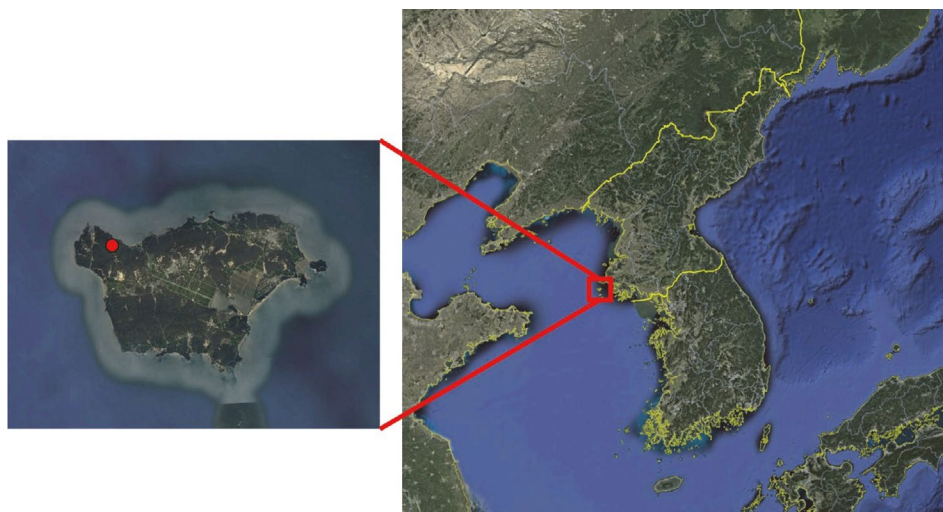


Fig. 1. The site of Baengnyeong Island.

ant emissions (Li *et al.*, 2016; Lee *et al.*, 2015; Lelieveld *et al.*, 2001). Aerosol and trace gases that are emitted in Asian countries can be transported to other continents and affect human health and the environment (Li *et al.*, 2016; Hopke *et al.*, 2008). Therefore, many studies have been reported regarding the chemical characteristics of aerosol and gases, and their sources and apportionment in Asian regions (He *et al.*, 2004).

In the pollution of ambient air, aerosols have an important effect on earth's radiative balance and directly acting as cloud condensation nuclei (Gao *et al.*, 2015; Rastogi *et al.*, 2015; Hinds, 1999). Some studies have reported that aerosols can have effects such as causing a reduction in visibility, deterioration of human health, and deposition of pollutants to ecosystems (Lim *et al.*, 2010; Lee *et al.*, 2008). Some studies have shown that organic compounds compose 10–70% of the total aerosol mass (Park *et al.*, 2013; Agarwal *et al.*, 2010; Bae *et al.*, 2009). After organic carbon (OC) was found to have effect on climate change and human health (Park and Cho, 2013), many studies were carried out on the chemical composition and sources (Park *et al.*, 2013; Bae *et al.*, 2009). Organic carbon is composed of water-soluble OC (WSOC) and water-insoluble OC (Pathak *et al.*, 2011). The WSOC constitutes 20–67% of total carbon, typically 10–70% of organic aerosols (OAs), and a maximum of 90% of OC (Park *et al.*, 2013; Agarwal *et al.*, 2010; Sullivan *et al.*, 2004), and is involved in the most unknown liquid-phase chemistry of wet aerosol and clouds from intense absorption (Facchini *et al.*,

1999). It also works as a cloud condensation nuclei (Timonen *et al.*, 2010; Decesari *et al.*, 2001; Saxena and Hildemann, 1996).

The WSOC is composed of hydrophilic and hydrophobic fractions that are emitted directly from natural sources and combustion, and are formed through secondary processes of gas or aerosol oxidation (Yu *et al.*, 2014; Pathak *et al.*, 2011; Sullivan *et al.*, 2004). Sources of WSOC are associated with primary emissions of burning biomass and the formation of secondary organic aerosols (SOA) that react through oxidation from the photochemical reaction of organic compounds in ambient air (Sun *et al.*, 2011; Park *et al.*, 2010; Sannigrahi *et al.*, 2006). Cho and Park (2013) showed that water-soluble ionic components have high correlations with oxalate that forms through secondary particle formation processes. Chemical characteristics and source apportionment of WSOC were studied for research of SOA mechanism or formation (Sullivan *et al.*, 2004). The study of pollution sources of WSOC is an important method for study of SOA formation that has been incompletely identified (Park *et al.*, 2014; Park *et al.*, 2010). Several papers have reported on the characteristics and origins of WSOC, however, the occurrence of WSOC in aerosol particles remains insufficiently studied (Decesari *et al.*, 2001). The majority of air quality measurements in Korea focus mainly on inorganic components of PM_{2.5} (particles less than 2.5 μm in diameter) such as sulfate, nitrate, ammonium, metals, and so on (Park *et al.*, 2010). In addition, the measurements of

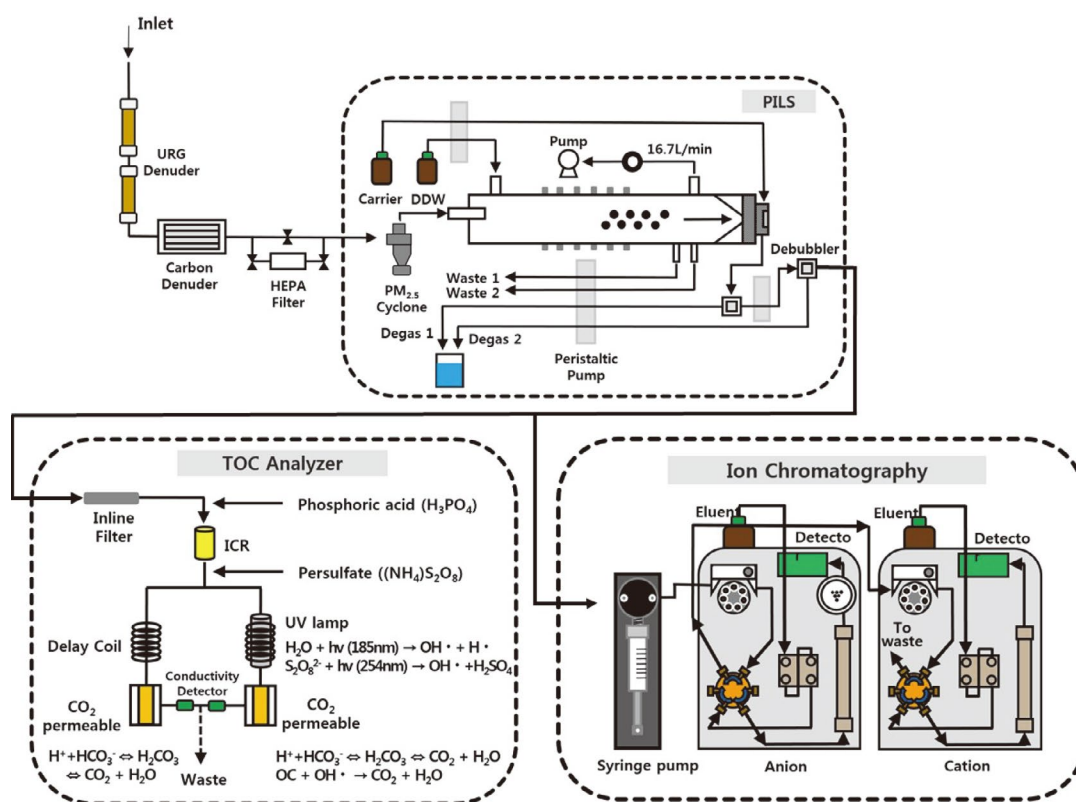


Fig. 2. Diagram of the PILS-TOC-IC (particle-into-liquid sampler [PILS] coupled with a total organic carbon [TOC] analyzer and ion chromatography [IC]) at Baengnyeong Island (Adapted from Park *et al.*, 2016).

carbonaceous species (especially WSOC) remain insufficient.

In this study, a particle-into-liquid sampler (PILS) coupled with a total organic carbon (TOC) analyzer and ion chromatography (IC) (PILS-TOC-IC) was used for semi-continuous measurements of WSOC and ionic compounds of $PM_{2.5}$ on Baengnyeong Island during the Korea United States Air Quality study (KORUS-AQ).

2. EXPERIMENTAL METHODS

2.1 Site and Measurement Period

Sampling was conducted during April-June 2016 (KORUS-AQ) on Baengnyeong Island, Korea (37.967°N, 124.630°E), which is located west of the Korean Peninsula approximately 180 km from the Shandong Peninsula in eastern China (Fig. 1). The KORUS-AQ campaign was an international collaboration field study between Korea and National Aeronautics and Space

Administration (NASA) to assess the aspects of air quality research across the Korean Peninsula (Park *et al.*, 2018). The PILS-TOC-IC analyses were conducted at the Baengnyeong Island Atmospheric Research Centre, operated by the Korea National Institute of Environmental Research (NIER), which is located approximately 100 m above sea level. The population on the island is small (~5000), and the research center is located on the island's sparsely populated western side (Lee *et al.*, 2015).

2.2 Particle-into Liquid Sampler (PILS)-TOC (Total Organic Carbon)-IC (Ion Chromatography)

For analysis of WSOC and ionic $PM_{2.5}$ components, particle into liquid sampler (PILS, Metrohm AG) was connected to an ion chromatography and a total organic carbon analyzer. The operation of PILS-TOC-IC measured ambient air that was drawn through an aluminium cyclone separator (URG Corporation, $D_{50} = 2.5 \mu m$, 16.7 L/min). The PILS was heated from high-

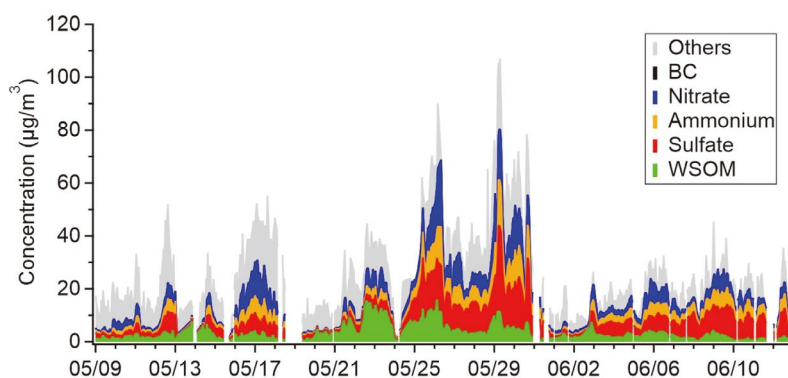


Fig. 3. Timeline of chemical composition in PM_{2.5} (particles less than 2.5 µm in diameter) (note that water-soluble organic matter [WSOM] = water-soluble organic carbon [WSOC]*organic matter /organic carbon [OM/OC] ratio from HR-ToF-AMS and the water-insoluble organic matter [WIOM] = organic matter [OM] – water-soluble organic matter [WSOM]).

temperature steam of deionized water at 150°C. When ambient air was drawn to PILS, particles were grown size up and were then collected by the impactor plate of the PILS (Park *et al.*, 2014; Orsini *et al.*, 2003; Weber *et al.*, 2001). Collected samples were divided for analyses by IC (Metrohm, 883 Basic IC, 250 µL loop) and the TOC analyzer (GE Power Water & Process Technologies, Sievers 800); IC was measured to sample that was collected from a syringe pump (Fig. 2).

2.3 Inorganic Ionic Components

To analyze inorganic ionic components (Cl^- , SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) using IC, HNO_3 and NH_3 gases in ambient air were removed from the annular denuder (URG corporation) that was coated with phosphorus acid and sodium carbonate (Park *et al.*, 2016). An ion chromatography is an instrument that analyses inorganic ionic components by a separation process involving the distribution of ionic components between stationary and mobile phases. A column of the IC separates the ionic components of samples by combination and separation between stationary phase and mobile phase. In the process of separation and combination between stationary and mobile phases, ionic components have different speeds and the following were measured in this study; retention time, peak area, and peak shape of each ionic component from the IC detector.

2.4 Carbonaceous Species (OC, EC, BC and WSOC)

Before ambient air penetrated through an aluminium cyclone separator, particles and volatile organic car-

bons (VOCs) were removed from a carbon denuder. To measure WSOC, water-insoluble organic carbon (OC) was removed from an inline filter that was installed in front of the TOC analyser. The sample of removed water-insoluble OC was analyzed using the TOC analyzer (Park *et al.*, 2016), which is capable of measuring the TOC concentration from carbon dioxide (CO_2) emitted by oxidation of organic compounds in a sample. Samples that entered the TOC analyzer were reacted with oxidizer and ultraviolet (UV) to analyze the total carbon and inorganic carbon (which was calculated from the difference between total carbon and inorganic carbon concentrations).

For comparison of carbonaceous species concentration at each site (Park *et al.*, 2011), an organic carbon (OC) / elemental carbon (EC) analyzer (4F-semi-continuous carbon filed analyzer, Sunset Laboratory Inc.) was used to measure OC and EC concentration. It analyzed to OC and EC concentration from thermal optical transmittance and non-dispersive infrared method based on NIOSH protocol (Bauer *et al.*, 2009). The OC and EC of PM_{2.5} were collected on the quartz filter at the flow rate of 8 L/min through a PM_{2.5} inlet and analyzed using the NIOSH protocol.

Black carbon (BC) was measured by an aethalometer (AE33, MAGEE Scientific) for analysis of long-range transport and biomass burning with carbon monoxide (CO). The aethalometer captures PM_{2.5} to the filter and measures the transmission of the light passing through the collected filter. It analyses to BC concentration by conversion to mass concentration from the change of light attenuation and intensity.

Table 1. Concentrations of chemical species of PM_{2.5} (particulate matter < 2.5 µm) (Unit*: µg/m³; Unit**: ng/m³)

| | Mean ± SD | High loading ± SD | Low loading ± SD |
|---------------------|-------------|-------------------|------------------|
| PM _{2.5} * | 23.8 ± 16.7 | 50.4 ± 15.2 | 22.7 ± 18.6 |
| WSOC* | 1.6 ± 1.5 | 3.0 ± 2.0 | 0.8 ± 0.5 |
| Nitrate* | 3.6 ± 3.6 | 8.7 ± 4.4 | 2.4 ± 2.0 |
| Sulfate* | 5.6 ± 4.7 | 11.0 ± 6.4 | 4.3 ± 3.1 |
| Ammonium* | 3.2 ± 2.7 | 6.8 ± 3.3 | 2.3 ± 1.7 |
| OC* | 3.0 ± 2.0 | 5.5 ± 2.2 | 2.4 ± 1.4 |
| EC* | 0.9 ± 0.6 | 1.6 ± 0.5 | 0.8 ± 0.4 |
| BC** | 158 ± 80.1 | 193 ± 91.9 | 112 ± 89.6 |

Standard deviation: SD

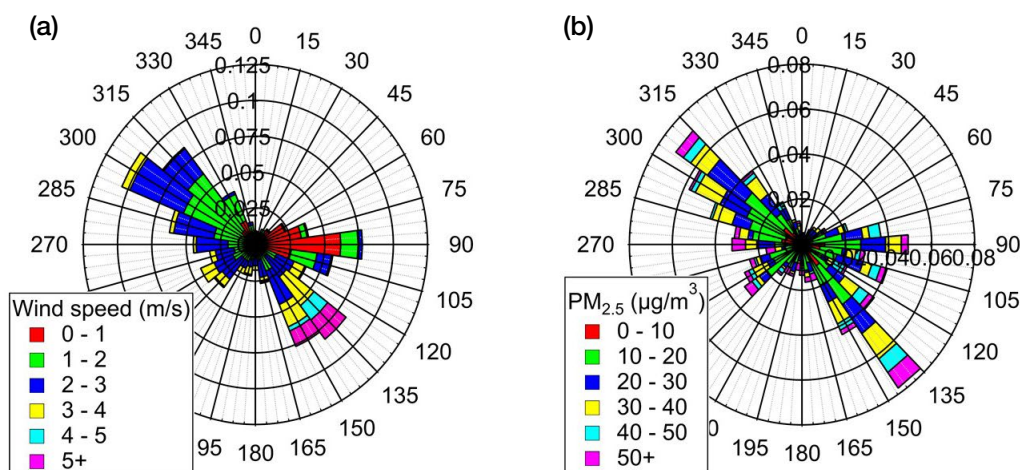


Fig. 4. Rose plot of; (a) wind speed, and; (b) PM_{2.5} (particles less than 2.5 µm in diameter) concentration at Baengnyeong Island.

3. RESULTS AND DISCUSSION

3.1 General Characteristics of PM_{2.5}

The timeline of PM_{2.5} and WSOC in Baengnyeong Island during the KORUS-AQ campaign is shown in Fig. 3. The water-soluble organic matter (WSOM) concentration was calculated to the value by multiplying the real-time organic matter/organic carbon (OM/OC) ratio from high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.) with WSOC concentration. The water-insoluble organic matter (WIOM) concentration was calculated to subtract WSOM from organic matter (OM). The mean concentrations of PM_{2.5} species in the total period was summarized to Table 1. It also was shown to mean concentration of PM_{2.5} species under and over the air quality standard (below 35 µg m⁻³ of PM_{2.5} per hour). This study was set up at both high and

low PM_{2.5} episodes, such as periods during which the concentrations were above and below the air quality standard. The mean concentration of PM_{2.5} was 23.8 ± 16.7 µg m⁻³, and mean concentrations of WSOC, OC, elemental carbon (EC) and black carbon (BC) were 1.6 ± 1.5 µg m⁻³, 3.0 ± 2.0 µg m⁻³, 0.9 ± 0.6 µg m⁻³, and 158 ± 80.1 ng m⁻³, respectively, in the experiment period. Concentrations of ionic compounds such as nitrate, sulfate, and ammonium were 3.6 ± 3.6 µg m⁻³, 5.6 ± 4.7 µg m⁻³, and 3.2 ± 2.7 µg m⁻³ respectively. The mean concentration of metal (Xact-series 600, Cooper Environmental Services, K, Ca, V, Mn, Fe, Ni, Zn As, Tl and Pb) in Baengnyeong Island was 0.5 ± 0.5 µg m⁻³. Sulfate constituted the largest portion (27.6%) in PM_{2.5}.

In the period above Korea air quality standard, PM_{2.5}, WSOC, nitrate, sulfate, and ammonium mean concentrations were 50.4 ± 15.2 µg m⁻³, 3.0 ± 2.0 µg m⁻³, 8.7 ± 4.4 µg m⁻³, 11.0 ± 6.4 µg m⁻³, and 6.8 ± 3.3 µg m⁻³,

Table 2. Carbonaceous species concentrations at each site (Park and Cho, 2011).*Unit: $\mu\text{g}/\text{m}^3$

| Site | Sampling location | | OC* | EC* | WSOC* | WSOC/OC |
|-------------|-------------------|-------------|-------|------|-------|---------|
| Korea | This study | Baengnyeong | 3.0 | 0.9 | 1.6 | 0.46 |
| Sweden | Background | Aspvreten | 2.16 | 0.10 | 1.74 | 0.81 |
| Korea | Urban | Gwangju | 3.04 | 1.27 | 1.73 | 0.48 |
| China | | Nanjing | 15.63 | 3.33 | 4.70 | 0.30 |
| Japan | | Tokyo | 3.98 | 1.69 | 1.28 | 0.35 |
| France | Roadside | Paris | 34.6 | 13.6 | 4.4 | 0.12 |
| Hong Kong | | Hung Hom | 10.20 | 5.90 | 2.1 | 0.22 |
| Netherlands | | Amsterdam | 3.9 | 1.6 | 1.0 | 0.34 |

OC: organic carbon, EC: Elemental Carbon, WSOC: water-soluble organic carbon, and WSOC/OC: water-soluble organic carbon/organic carbon ratio

respectively, which were twice the overall mean values. The results showed that ionic compounds increased by 2.6%, but WSOC had decreased to 5.6% in the period above Korea air quality standard than the period under the standard. The WSOC had decreased to the fraction in PM_{2.5} because the concentration of ionic components was increased to higher than the WSOC. Ionic components were mainly a result of chemical reactions in the atmosphere, rather than being derived from a primary source. The pollution source is smaller in Baengnyeong Island than in urban areas. Therefore, the concentration of ionic components was increased greatly by chemical reactions of pollutants that was emitted from the primary source of the urban area around island (Li *et al.*, 2010).

Wind speed and direction in Baengnyeong Island were used for analysis of pollutant inflow. During the measurement period, the wind direction was mostly northwest and southeast directions (Fig. 4). This suggested that the air pollutant concentrations were increased by the inflow of air pollutants from long-range transport or domestic stagnation.

3.2 Characteristics of Carbonaceous Components in PM_{2.5}

Park and Cho (2011) summarized the OC, EC, and WSOC concentrations and the WSOC/OC ratios during summer and winter in various urban, rural, roadside and supersite areas (Table 2). Baengnyeong Island recorded a higher OC concentration, a lower WSOC concentration, and a similar EC concentration compared to Aspvreten, Sweden (background) (Park and Cho, 2011). Baengnyeong Island had the lowest OC and EC concentrations in comparison with several

urban and roadside sites. The WSOC/OC ratio of Gwangju (Korea) was 0.48, which was similar to that on Baengnyeong Island. The mean of WSOC/OC ratios in Nanjing (China), Tokyo (Japan), and Barcelona (Spain) were 0.3, 0.29, and 0.38, respectively, about summer and winter. In roadside areas such in Paris (France), Hong Hom (Hong Kong), and Amsterdam (Netherlands), the WSOC/OC ratios were 0.12, 0.22, and 0.34 (Park and Cho, 2011), respectively, which were lower than in Baengnyeong Island. On the other hand, the background site in Aspvreten (Sweden) had a WSOC/OC ratio of 0.81, which was the highest value. Rural sites of Hok Tsui (Hong Kong) and the Pearl River region (China) recorded WSOC/OC ratios of 0.56 and 0.6, respectively. The WSOC/OC ratio was lower in urban and roadside areas compared to the background and rural sites. It was considered that insoluble OC constituted a major proportion of primary OC that was emitted in urban areas (Park *et al.*, 2010). In this study, the WSOC/OC ratio in Baengnyeong Island was 0.5 ± 0.2 higher than at roadside and urban areas, and lower than at the background site. Salma *et al.* (2001) reported that the higher WSOC/OC ratios of rural and background sites were affected by inflow. The EC (which is a typical marker of a primary source) was decreased by a dilution effect by transportation to the background site in Salma *et al.* (2001). In addition, it was reported that urban and roadside areas had higher OC concentrations and lower WSOC/OC ratios than the background site because urban and roadside were emitted the insoluble primary OC. Therefore, Baengnyeong Island is possible that it was influenced by atmospheric pollutants of domestic inflow and long-

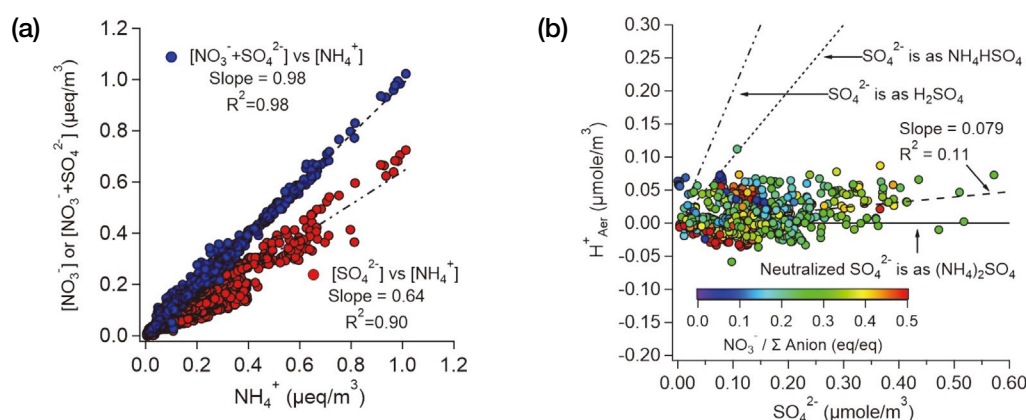


Fig. 5. (a) The comparison of ammonium with the sum of the sulfate and nitrate, and (b) the concentration comparison of H^+ Aerosol and SO_4^{2-} in $PM_{2.5}$ (particles less than $2.5 \mu m$ in diameter).

range transport of China.

3.3 Characteristics of Water-soluble Ionic Components in $PM_{2.5}$

Lee *et al.* (2016) reported that the NO_3^-/SO_4^{2-} ratio was used to apportion mobile and stationary sources of $PM_{2.5}$. The mean of NO_3^-/SO_4^{2-} ratio was 0.64 in Baengnyeong Island. Previous studies in urban sites in China have reported NO_3^-/SO_4^{2-} ratios of 0.71 in Beijing, 0.60 in Shanghai, and 0.95 in Seoul (Ko *et al.*, 2015; Shen *et al.*, 2009). The NO_3^-/SO_4^{2-} ratio of Baengnyeong Island was lower than other urban sites, although Baengnyeong Island is a background site in Korea. It has been considered that aerosols that were emitted from coal combustion or vehicle emission in China were contained within the ambient air in Baengnyeong Island (Lee *et al.*, 2016; Cao *et al.*, 2009; Shen *et al.*, 2009).

In this study, ionic components were compared to equivalent concentrations of ammonium, nitrate, and sulfate. Ammonium concentrations were similar to the sum of the sulfate and nitrate concentrations (Fig. 5(a)), indicating that the ammonium concentration was sufficient to neutralize sulfuric acid and nitric acid. It was considered that the ambient air was neutralized because the ammonia gas concentration was adequate to generate ammonium sulfate or ammonium nitrate from reactions with sulfuric acid or nitric acid, respectively (Kang *et al.*, 2018; Pathak *et al.*, 2009). A previous study compared the molar concentrations of hydrogen ion and sulfate to understand particle acidity (Zhang *et al.*, 2007). In the present study, the slope of

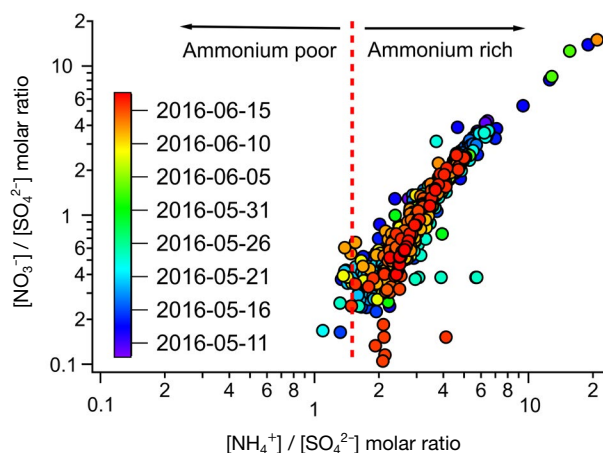


Fig. 6. Comparison of the molar ratios of NO_3^- , SO_4^{2-} and NH_4^+ in Baengnyeong Island.

H^+ Aerosol/ SO_4^{2-} in $PM_{2.5}$ was 0.079 as a result of neutralized particle acidity in ambient air (Fig. 5(b)), which was similar to the result of Zhang *et al.* (2007) that compared NH_4^+ with NO_3^- and SO_4^{2-} .

The molar ratio of nitrate and ammonium with sulfate is shown in Fig. 6. Pathak *et al.* (2009) reported on results of ammonium-poor and ammonium-rich conditions by the molar ratio (1.5) of ammonium and sulfate because the ammonium nitrate was formed clearly to the reaction of nitric acid and ammonia when the molar ratio of ammonium and sulfate was 1.5. The ammonium-poor condition that is below 1.5 of $[NH_4^+]/[SO_4^{2-}]$ occurred mainly to the heterogeneous reaction that was the reaction between two different phases. The ammonium-rich condition that is

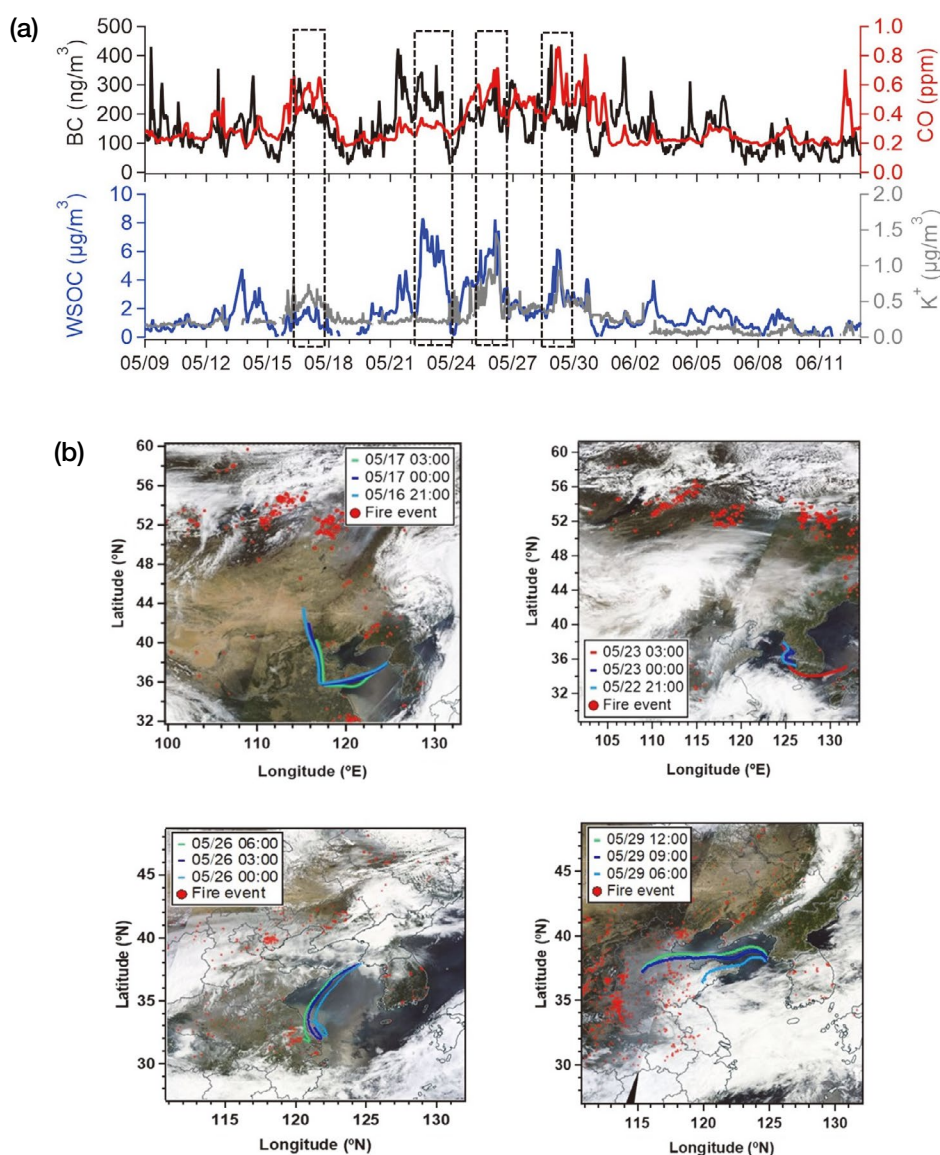


Fig. 7. (a) Timeline of water-soluble organic carbon (WSOC), CO, Black Carbon (BC), and potassium (K⁺) and (b) back-trajectories with the fire event in four cases (May 16–17, May 22–23, May 26, and May 29).

upper 1.5 of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ was shown to the homogeneous reaction that was reacted between the same phases. The heterogeneous reaction was formed the ammonium nitrate after the ammonium sulfate was created priorly in the aqueous phase. The homogeneous reaction was increased the ammonium nitrate formation with the ammonia and NO_x concentration after the sulfuric acid and ammonia in ambient air were reacted enough to the formation of ammonium sulfate. Formation processes between ammonia and nitric acid were shown in different sulfate concentrations (Pathak

et al., 2009; Seinfeld and Pandis, 2006). In this study, the Baengnyeong Island was observed as having ammonium-rich conditions, indicating that the ammonia concentration was adequate for neutralization of nitric acid and sulfuric acid. Therefore, this result indicated that ammonium nitrate was increased due to homogeneous reactions of ammonia and nitric acid in the gas-phase.

3.4 Case Analysis

Potassium and WSOC concentrations were checked

Table 3. Concentrations and fractions of chemical species of PM_{2.5} with the fire event in four cases (particulate matter < 2.5 μm) *Unit: μg/m³

| | Case 1 (May 16 th –17 th) | Case 2 (May 22 th –23 th) | Case 3 (May 26 th) | Case 4 (May 29 th) |
|---------------------|---|---|-----------------------------------|-----------------------------------|
| WSOM* | 2.34 ± 0.90 | 9.93 ± 3.93 | 8.47 ± 3.21 | 5.90 ± 2.63 |
| Nitrate* | 8.04 ± 3.32 | 3.39 ± 2.39 | 9.05 ± 5.17 | 9.75 ± 4.79 |
| Sulfate* | 4.98 ± 1.37 | 3.01 ± 0.77 | 13.2 ± 3.34 | 16.18 ± 7.22 |
| Ammonium* | 4.46 ± 1.53 | 2.33 ± 1.03 | 7.57 ± 2.23 | 8.97 ± 3.95 |
| BC* | 0.20 ± 0.04 | 0.22 ± 0.09 | 0.25 ± 0.06 | 0.22 ± 0.07 |
| PM _{2.5} * | 38.8 ± 9.17 | 30.5 ± 9.83 | 46.9 ± 18.0 | 59.9 ± 23.2 |

from biomass burning in the measurement period (Fig. 7(a)). In this study, four cases were selected by the fire event with the back-trajectories and concentration of chemical species (Table 3). Many studies have reported that K⁺ is a tracer for biomass burning emissions (Rastogi *et al.*, 2015; Cheng *et al.*, 2013). To confirm biomass burning emissions in Baengnyeong Island, K⁺ was compared with CO, BC, and WSOC. Biomass burning was measured in Russia on May 16th (Case 1), when WSOC, K⁺, CO, and BC had increased compared to May 15th. When the fire event occurred in Russia, the back-trajectory of 48 h was shown to move from Russia to Baengnyeong Island. The result indicated that Baengnyeong Island was affected by atmospheric pollutants of biomass burning from Russia (Fig. 7(b)). Biomass burning was also measured in Russia on May 22th (Case 2). The highest WSOC value was measured and ionic components with PM_{2.5} were shown lower concentration in this period, however, K⁺ was 50% lower than on May 16th. Baengnyeong Island was observed to the air flow that was moved from Japan to the south sea of Korea from the back-trajectory. This result showed that biomass burning emission of Russia did not influence Baengnyeong Island and the potassium concentration was low in contrast with the high WSOC concentration due to secondary organic matter.

A maximum K⁺ value was measured on May 26th (Case 3). Concentrations of WSOC, CO, and BC increased from May 24th to 26th, and there were increased WSOC, CO, BC, and K⁺ concentrations on May 29th (Case 4). During both periods, inorganic ionic components (nitrate, sulfate, and ammonium) increased. In Case 4, the PM_{2.5} and ionic components were measured to highest concentration than other cases. However, K⁺ in May 22th was decreased by biomass burning emissions from Russia and back-trajectory from Japan compared to May 26th and 29th (Case 3

and Case 4). This result indicated that atmospheric pollutants were generated by biomass burning in China and were transported to Baengnyeong Island from back-trajectories. Case 3 and Case 4 were shown the back-trajectories from the eastern china with higher concentration of ionic components than Case 1 and Case 2 that were indicated inflow from Russia and Japan. On the other side, the highest WSOC concentration was measured in Case 2 that was indicated the back-trajectories moved from Japan to the south sea of Korea. In addition, Case 1, Case 3 and Case 4 were shown the inflow that was passed from eastern China and occurred the chemical reaction and emission of pollutants from the primary sources in the ambient air. In Case 2, it is possible that the atmosphere pollution matter was affected by dilution effect by inflow from the southern sea of Korea which was lower concentration of pollutants than the eastern China. Therefore, the WSOC of Case 2 was the highest concentration than other cases. It was considered that biomass burning and long-range transport from China affected Baengnyeong Island from the emission of primary sources and the secondary chemical reaction in the ambient air.

4. CONCLUSIONS

In this study, the PILS-TOC-IC was used for semi-continuous measurement of WSOC and ionic components of PM_{2.5} in Baengnyeong Island from April to June 2016 for analysis of chemical characteristics about WSOC and ionic composition of PM_{2.5} in Baengnyeong Island. The Baengnyeong Island is located west of the Korean Peninsula approximately from the eastern China. In addition, this study was analyzed to the characteristics of carbonaceous components (OC, EC and BC) in PM_{2.5} from OC/EC analyzer and aethalometer

and the case study with the air mass back-trajectories. The mean of PM_{2.5} concentration during the entire experimental period was $23.8 \pm 16.7 \mu\text{g m}^{-3}$, and the mean of WSOC, OC, EC, and BC concentrations were $1.6 \pm 1.5 \mu\text{g m}^{-3}$, $3.0 \pm 2.0 \mu\text{g m}^{-3}$, $0.9 \pm 0.6 \mu\text{g m}^{-3}$, and $34.3 \pm 19.5 \text{ ng m}^{-3}$, respectively. The mean of nitrate, sulfate, and ammonium concentrations were $3.6 \pm 3.6 \mu\text{g m}^{-3}$, $5.6 \pm 4.7 \mu\text{g m}^{-3}$, and $3.2 \pm 2.7 \mu\text{g m}^{-3}$, respectively. Concentrations of PM_{2.5}, WSOC, nitrate, sulfate, and ammonium increased to twice the overall mean value in the period when the air quality standard was exceeded. The results showed that ionic compounds increased by 3.8% in the higher period compared to the standard, indicating that the concentration of ionic components increased due to chemical reactions and primary source emissions from the nearby urban area.

In this study, the WSOC/OC ratio was 0.5 ± 0.3 in Baengnyeong Island, which was higher than at roadside and urban sites, and lower than the background site. The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio of Baengnyeong Island was lower than that of urban areas in China. It was considered that Baengnyeong Island was affected by the formation of secondary aerosols by chemical reactions and inflow from China and domestic emissions. The slope of $\text{H}^+_{\text{Aerosol}}/\text{SO}_4^{2-}$ in Baengnyeong Island was 0.079 as result of neutralized particle acidity in ambient air. The molar ratio of nitrate and ammonium with sulfate in Baengnyeong Island showed ammonium-rich conditions. It indicated that sufficient ammonia was present for neutralization of nitric acid and sulfuric acid and that ammonium nitrate increased due to homogeneous reactions of ammonia and nitric acid.

The comparison of K^+ , CO, BC, and WSOC was analyzed to confirm biomass burning emissions in Baengnyeong Island from the back-trajectories. In this study, the fire events were occurred in Russia and China during May–June 2016. When a fire event occurred in Russia on May 16th, the back-trajectories were shown to move from Russia to Baengnyeong Island with the increased K^+ , BC and CO. The concentrations of WSOC, CO, BC and K^+ increased at May 24th–26th and May 29th. However, K^+ in May 22th was decreased to concentration by biomass burning emissions from Russia and back-trajectory from Japan compared to May 26th and 29th. This result indicated that atmospheric pollutants were generated by biomass burning in China and were transported to Baengnyeong Island from back-trajectories.

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