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Original article

Characteristics of water-soluble inorganic species in PM_{10} and $PM_{2.5}$ at two coastal sites during spring in Korea

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ABSTRACT

PM_{10} and $PM_{2.5}$ were collected during spring at East ("Gangneung") and West ("Taean") coastal sites of the Korean peninsula to investigate chemical characteristics and likely formation routes of their water-soluble inorganic species. The Gangneung site is inland, about 4.5–5.0 km from the East Sea; the Taean site is about 200 m from the coastline and about 400 km from eastern China. The total water-soluble ionic species contributions to PM_{10} and $PM_{2.5}$ were respectively 28.8 and 37.4% at the Gangneung site and 46.8 and 53.1% at the Taean site. Concentrations of SO_4^{2-}, NH_4^+, and NO_3^- in both PM_{10} and $PM_{2.5}$ were found to be two times higher at the Taean site than at the Gangneung site. The potential source contribution function (PSCF) maps indicate that the enhancement of PM_{10} and its secondary aerosol species concentrations at two sites were primarily the result of atmospheric processing during long-range transport from the polluted regions of eastern China. Also upwind sources ("the capital region of Korea") and local emissions influenced the concentration levels of secondary inorganic species at Gangneung.

SO_4^{2-} events, defined by PM_{10} SO_4^{2-} concentrations exceeding the average by one standard deviation, were identified at the two sites – six at Gangneung and four at Taean – to investigate possible mechanisms for the formation of SO_4^{2-} and NO_3^-. High SO_4^{2-} and high NO_3^- at the Gangneung site were strongly associated with either high RH (89–94%) and low wind speed or high O_3 (62–103 ppb), suggesting that either gas-phase oxidation or aqueous phase oxidation played a critical role in the enhanced SO_4^{2-} production. On the other hand, at the Taean site the association was with both high RH (76–92%) and high O_3 (53–79 ppb), indicating that these conditions trigger aqueous-phase and gas-phase reactions to produce secondary SO_4^{2-} and NO_3^- particles. Also long-range transport of air masses could be one possible factor for enhanced SO_4^{2-} and NO_3^- concentrations during the events at the two coastal sites, as evidenced by PSCF maps.

1. Introduction

Atmospheric particulate matter (PM) is a complex mixture consisting of carbonaceous species, water-soluble inorganic species, elemental species, and water (Seinfeld and Pandis, 2006). The chemical compositions of atmospheric PM have significant impacts on the global climate (Facchini et al., 1999; Charlson et al., 2001; Acker et al., 2002), human health (Pope et al., 2002; Pope and Dockery, 2006; Oesterling et al., 2008; Hsieh et al., 2009), air quality deterioration and decreased visibility (Watson, 2002; Molina and Molina, 2004). Among the chemical constituents, secondary SO_4^{2-}, NO_3^-, and NH_4^+ are the major constituents of atmospheric PM (Putaud et al., 2004; Park et al., 2007, 2010; Yang et al., 2011) and control particle acidity which is an important aerosol property affecting the formation, fate, and health effects of aerosol particles (Grassian, 2001; Cao and Jang, 2009). SO_4^{2-} aerosols are almost entirely found in the particle phase (Wyers and Duyzer, 1997). However, NO_3^- can be present either in the particle

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phase or in the gas phase as nitric acid by gas-to-particle partitioning of ammonium nitrate depending on ambient temperature (Seinfeld and Pandis, 2006). In order to address the ambient PM-related issues raised above, it is necessary to understand the sources and formation pathways of major water-soluble inorganic species.

East Asia is one of the largest aerosol source regions on Earth. The aerosol downwind of the Asian continent is a complex mixture of natural and anthropogenic sources (Chung et al., 2003; Park et al., 2007; Jung et al., 2010; Park and Cho, 2013; Park et al., 2013; Son and Park, 2015). Many observations of aerosols have been conducted in Korea to investigate the impact of dust and anthropogenic aerosols originating from the China. For example, intensive and routine measurements of aerosol were conducted at clean background sites, such as Gosan, Cheju Island (Kim et al., 1998; Lee et al., 2001; Huebert et al., 2003; Han et al., 2004; NIER, 2007; Kim et al., 2009; Moon et al., 2013), Taean (He et al., 2003), and Deokjeok Island (Lee et al., 2002; Kim et al., 2009). These background sites have been considered to be ideal places to estimate the amount of air pollutants transported to Korea from China. Examination of water-soluble inorganic species concentrations in TSP, PM_{10}, and $PM_{2.5}$ particles collected at the background sites revealed that most of the aerosols measured at the sites were transported from China, rather than from the Korean peninsula (Kim et al., 1998; Lee et al., 2001, 2002; Kim et al., 2009).

Sea salt aerosol plays an important role in atmospheric chemistry and physics. The sea salt particle may influence the radiative balance of the atmosphere (Murphy et al., 1998) and cloud formation (Pierce and Adams, 2006), raising climate issues. Furthermore, sea salt constituents interact with other chemical substances, contributing to halogen and sulphur chemistry, and have a corrosive effect (Anwar Hossain et al., 2009). Also a correlation between sea salt and mortality was found, although with a substantial time lag (Mar et al., 2006). Since sea salt particles are generated at the surface of the ocean by the bursting of white-cap bubbles, the concentration is highest at the shore and falls rapidly as a distance from the coastline increases (Chow et al., 1996; Kim et al., 2000; Tsai et al., 2011). The concentrations vary significantly with wind speed, direction, elevation and topography. The sea salt concentration in PM_{10} was 53.4% at Point Reyes, Central CA (Chow et al., 1996), 24.7% at San Nicolas Island in South Coast Air Basin of Southern California (Kim et al., 2000), and 11.2–15.8% at the coastal region of Southern Taiwan (Tsai et al., 2011). In studies in coastal regions of Korea, the contribution of sea salt concentration to PM_{10} was 3.1–13.5% at Gosan, Jeju (Han et al., 2003; NIER, 2007), 3.0% at Deokjeok Island (NIER, 2007), and 3.6% (0.5–15.8%) at Seokmori, Incheon (NIER, 2009). Also the Cl^-/Na^+ mass ratio varies significantly with locations-high at coastal locations and low at inland and urban locations (Chow et al., 1996; Kim et al., 2000; Dasgupta et al., 2007).

In this study, both PM_{10} and $PM_{2.5}$ were measured during spring at eastern and western coastal sites of the Korean peninsula, which is greatly impacted by long-range transport of air pollutants from China. The purpose of the observations aimed to investigate the difference in the concentration levels and likely formation processes of water-soluble inorganic species in PM_{10} and $PM_{2.5}$ between the two coastal sites, which are about 350 km apart, and also to improve the knowledge on sea salt concentrations in PM and the relative contribution of sea salt to PM concentrations. The observations were compared with observations of sea salt in PM from previous studies. In addition, PM_{10} SO_4^{2-} events were classified at the two sites and discussed to examine likely formation processes of the SO_4^{2-} and NO_3^-.

2. Methodology

2.1. Study areas and aerosol measurements

Measurements of PM_{10} and $PM_{2.5}$ were carried out on two coastal sites, i.e., Gangneung (128.90E, 37.76N) and Taean (126.15E, 36.75N). Both sampling locations are shown in Fig. S1 (see Supporting Material (SM)). Two sites adjacent to the seashores were selected to investigate PM_{10} and its water-soluble inorganic species levels at costal sites, and the contribution that sea salt particles make to PM_{10}. Gangneung site is located on the eastern side of the Korean peninsula and is about 4.5–5.0 km westward from the coastline of the East Sea. A two-lane road is in front of the site. Thus it is expected that the particulate matter at the Gangneung site is influenced by a mixture of both local anthropogenic and natural (marine air) sources. Taean site, "a national background monitoring site", is located on western side of the Korean peninsula and is considered to be an appropriate place to monitor air pollutants transported from China because there are few local anthropogenic emission sources. The site is about 200 m eastward from the coastline and approximately 350–400 km from Shandong peninsula in China. Air masses there were expected to contain a mixture of particles from both natural and long-range transported sources.

The measurements of PM_{10} and $PM_{2.5}$ at the Gangneung site were made using PM_{10} and $PM_{2.5}$ impactor samplers (R&P, PM_{10} inlet 57-00596, USA) at flow rates of 16.7 l/min between April 18 and May 18, 2009. Aerosol sampling was conducted twice a day (09:00–21:00 and 21:00–09:00). The reason for 12-hr integrated measurements of aerosol particles at the site is to investigate the difference in the sea salt contribution to particulate matter between daytime and nighttime, and to find out the corrosive effect of sea salt particles from the sea on the inside of the PM_{10} impactor inlet (nozzle outlet, impaction plate, and walls) of the beta-gauge monitor that is currently in operation at the site. Salt is present in the ambient air and is derived from seawater aerosols carried by the wind. The mineral content of seawater consists of more than 85% sodium chloride. It is reported that chlorides can deposit on metals including Al and may result in stress corrosion attack and/or cause corrosion pitting (Evans, 1960; Rozenfeld, 1972). However, this corrosion issue is not discussed in this paper. PM_{10} and $PM_{2.5}$ particles were collected using 47-mm-diameter Teflon membrane filters (Zefluor, 2.0 μm, Gelman PJ0047). The collected samples were analyzed for mass and water-soluble inorganic species. For the Taean site, daily PM_{10} and $PM_{2.5}$ samples were collected using PM_{10} and $PM_{2.5}$ sequential samplers (two PMS-103, APM Eng., Korea), respectively, at flow rates of 16.7 l/min between April 23 and June 10, 2009, and analyzed for mass and water-soluble inorganic species. PM_{10} and $PM_{2.5}$ measurements were made between 09:00 and 09:00 and 47-mm-diameter Teflon membrane filters (Zefluor, 2.0 μm, Gelman PJ0047) were used to collect aerosol samples. Field blanks were also collected and used to correct their background concentrations. In this study, the measured nitrate concentrations are expected to be lower than actual values due to evaporation of semi-volatile ammonium nitrate during the sampling ($NH_4NO_3 \Leftrightarrow NH_{3(g)} + HNO_{3(g)}$).

2.2. Prevailing meteorology

Fig. S2 (see SM) shows wind rose plots over the study period at the Gangneung and Taean sites. For the Gangneung site, the 12-hr average wind speed, ambient temperature and relative humidity (RH) were 2.8 m/s (0.7–7.1), 16.3 °C (6.1–27.7), and 54.4% (16.3–96.6), respectively. The winds during the daytime were predominantly from the southwest, the direction in which residential and commercial areas are located, and from the northeast