



## Analysis of water-soluble ions and their precursor gases over diurnal cycle



Zang-Ho Shon <sup>a</sup>, Samik Ghosh <sup>b</sup>, Ki-Hyun Kim <sup>b,\*</sup>, Sang-Keun Song <sup>c</sup>, Kweon Jung <sup>d</sup>, Nam-Jin Kim <sup>d</sup>

<sup>a</sup> Department of Environmental Engineering, Dong-Eui University, Busan 614-714, Republic of Korea

<sup>b</sup> Department of Environment and Energy, Sejong University, Seoul 143-747, Republic of Korea

<sup>c</sup> Department of Earth and Marine Sciences, Jeju National University, Jeju 690-756, Republic of Korea

<sup>d</sup> Seoul Metropolitan Government Institute of Public Health and Environment, Seoul, Republic of Korea

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### ABSTRACT

A detailed description of an interactive relationship is made between water-soluble ionic components in PM<sub>2.5</sub> and their precursor gases using the hourly resolution data measured at an urban monitoring site in Seoul during the year of 2010. Their diurnal variability was found to be correlated with their precursor gases (HNO<sub>3</sub> and NH<sub>3</sub>). In the case of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, a close similarity was seen in their diurnal trends, especially during spring. There were no noticeable differences in the formation pathway of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> aerosols between day and night. For NO<sub>3</sub><sup>-</sup> formation, heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> might play a significant role in the nighttime enhancement of the oxidation rate. In addition, the concentrations of major anions (e.g. NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup>) exhibited highly diverse seasonal patterns with their maximum values occurring in spring, summer, and winter, respectively. The overall results of this study suggest that the formation pathway of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> aerosols should be regulated by a competing relationship between the NH<sub>3</sub>-lean (spring and winter) and NH<sub>3</sub>-rich conditions (summer and fall).

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### 1. Introduction

Over recent decades, air quality has altered noticeably due to industrialization, urbanization, economic growth, and associated increases in energy demands, especially in urban areas (Kim et al., 2013; Phan et al., 2013). In recent years, air pollution by fine particles has gained a great deal of attention in urban areas, due to mortality and pulmonary effects (Lee et al., 2006; RÖösl et al., 2001). In general, particulate matter (PM) is a complex mixture of extremely small solid particles and liquid droplets found in the air; it includes fine (an aerodynamic diameter of  $\leq 2.5 \mu\text{m}$ , PM<sub>2.5</sub>) and inhalable coarse particles (<http://www.epa.gov/pm/>). It is well known that both fine and inhalable coarse particles can cause serious health problems (Mokdad et al., 2004; Reichhardt, 1995; Schwartz, 1994; Schwartz et al., 1996). In an effort to reduce atmospheric

environmental problems, the Korean Ministry of Environment (KMOE) established a special action plan for the improvement of Metropolitan Air Quality on 1 January 2005. The main objective of the plan was to suppress the annual PM<sub>10</sub> levels from 60 (in 2005) to 40  $\mu\text{g m}^{-3}$  (in 2014). However, Kim and Shon (2011) reported that the mean concentrations of PM<sub>10</sub> from the 16 major urban roadside stations in Korea increased from 51.3 (before 2000) to 70.3  $\mu\text{g m}^{-3}$  (after 2001). The identification of aerosol composition and their production pathway can play a pivotal role in reducing PM levels in urban areas.

Note that most previous studies of PM compositions had to rely on the data sets collected over daily intervals (Chung et al., 2006; He et al., 2003; Kang et al., 2004; B.-G. Kim et al., 2001; K.W. Kim et al., 2001; Kim et al., 2002, 2003, 2006; Lee et al., 1999; Lee and Kang, 2001). In this respect, our hourly measurement data should be valuable enough to describe the short-term variability of ionic constituents. The data acquisition at such short intervals is important since air pollution

\* Corresponding author. Tel.: +82 2 3408 3233; fax: +82 2 3408 4320.  
E-mail address: khkim@sejong.ac.kr (K.-H. Kim).

in Seoul is highly dependent on dynamic source activities (e.g. mobile source conditions). In addition, inorganic aerosol production pathways such as the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> aerosol (0.5 days on coarse sea-salt aerosol) in the aqueous phase (Chin et al., 2000; Martin et al., 2004) and the uptake of HNO<sub>3</sub> (or SO<sub>2</sub>) by sea-salt aerosol or dust particles (~1 h) occur in relatively short periods.

In this research, we conducted our investigations to assess the short-term, diurnal variability of ionic constituents in PM<sub>2.5</sub> and the related processes leading to their production using the data sets collected from an urban monitoring station in Seoul. In our early study, these short-term sampling data sets collected from the same monitoring site were analyzed to describe the primary factors controlling the distribution of major ionic constituents from a number of perspectives in relation to changes in the relevant environmental parameters (Shon et al., 2012). Thus, the results of this present study will help us gain further knowledge as to the environmental behavior of key chemical components of PM<sub>2.5</sub> and their distribution over a diurnal cycle.

## 2. Materials and methods

In this study, ambient air samples were collected on an hourly basis for a one-year period (1 January to 31 December, 2010) at an air quality monitoring station located in Gwangjin district (127° 05.44', 37° 32.40') of Seoul, Korea (Fig. 1S in Supplementary material). Air quality in this area is known to be affected by traffic activities from adjacent roads but with no other major sources. Detailed information of our study site has been described elsewhere (Shon et al., 2011). In this study, 8 major ionic components of PM<sub>2.5</sub> including 5 cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) and 3 anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) were continuously measured. Relevant parameters were also monitored concurrently to include both criteria air pollutants (e.g. NO<sub>2</sub>, O<sub>3</sub>, and SO<sub>2</sub>), acidic and basic gases (HNO<sub>3</sub>, HCl, HNO<sub>2</sub>, and NH<sub>3</sub>), and basic metrological parameters (temperature, relative humidity (RH), wind speed, and UV radiation).

The chemical composition analysis of PM<sub>2.5</sub> and gaseous compounds other than the criteria pollutants was continuously made by a model ADI 2080 online beta ray analyzer (MARGA, Applikon Analytical B.V Corp., Netherlands). This system consists of a sampling box and an analytical box with the particle collection efficiency of 99.7%. Ambient air is drawn into the sampling box at a flow rate of 1 m<sup>3</sup> h<sup>-1</sup> through the impactor inlet. The gaseous components are also trapped by the liquid film (0.0035% H<sub>2</sub>O<sub>2</sub>) formed by one Wet Rotating Denuder (WRD). In the meantime, particles in residual airflow go through the supersaturated steam (0.0035% H<sub>2</sub>O<sub>2</sub>, 120–140 °C). They erupt out from the Steam Jet Aerosol collector (SJAC) and pooled into its collector. These liquefied samples flow through glass filters and are stored in syringe pumps of the analytical box for final detection by Ion Chromatography (IC). As such, MARGA utilizes a WRD to collect acid gases and ammonia by diffusion into an aqueous film, while particles passing through the WRD are collected in a SJAC. A supersaturated environment is created within the SJAC, which grows particles by deliquescence; it then allows them to be subsequently collected by inertial separation. As cooling takes place, steam condenses and washes the collected particles into an aqueous sample stream. The soluble ionic species in

aqueous solutions from the WRD and SJAC are subsequently analyzed by IC. The columns used for the analysis of cation and anion species were C4 and A support Metrohm (Switzerland), respectively. The eluent for cation and anion species was prepared as HNO<sub>3</sub> (3.5 mM) and a mixture of sodium bicarbonate (8 mM) and disodium carbonate (3.5 mM), respectively.

The analysis of ionic components for the MARGA system is made by comparison of equivalent conductivity between standard and unknown samples. As the basic quality assurance for the analytical setups used in this study, the system performance was examined with respect to detectability, reproducibility, and blank levels. For the computation of the method detection limit (MDL), 500 and 250 μL of standard solutions (prepared at equimolar concentration of 250 ppb for all target ions) were analyzed for cation and anion species, respectively. The MDL for each target component was calculated as three times of standard deviation derived from the 7 replicate analyses. The MDLs initially derived from liquid phase standard (μg L<sup>-1</sup>) can be expressed in absolute mass (ng) by multiplying the volume of standard consumed for the calibration. These absolute terms (ng) can then be used to derive the corresponding airborne concentration (ng m<sup>-3</sup>) by considering the volume of air taken for the sampling duration (e.g. 1 m<sup>3</sup> for an hour). The resulting MDL values for cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) were 0.16 ng (0.35 neq m<sup>-3</sup>), 0.16 ng (0.44 neq m<sup>-3</sup>), 0.20 ng (0.26 neq m<sup>-3</sup>), 0.20 ng (0.82 neq m<sup>-3</sup>), and 0.16 ng (0.40 neq m<sup>-3</sup>), respectively. The MDL values for anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) were 0.17 ng (0.47 neq m<sup>-3</sup>), 0.17 ng (0.27 neq m<sup>-3</sup>), and 0.08 ng (0.17 neq m<sup>-3</sup>), respectively. Likewise, the MDL values for their gaseous counterparts (HCl, HNO<sub>2</sub>, SO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub>), if expressed in nmole mole<sup>-1</sup> (or ppb), were calculated as 0.007, 0.008, 0.008, 0.004, and 0.023, respectively. Blank levels of ionic species were determined by running the double deionized water (like standard calibration) and commonly fell in the range of 4 (Na<sup>+</sup>) to 98 ng L<sup>-1</sup> (NH<sub>4</sub><sup>+</sup>).

Influence of RH (deliquescence RH, DRH) on the formation of the secondary inorganic aerosol (SIA) such as NH<sub>4</sub><sup>+</sup> was evaluated. The temperature dependence of DRH for NH<sub>4</sub>NO<sub>3</sub> was calculated according to the formula of Seinfeld and Pandis (2006):

$$\ln(\text{DRH}) = \frac{723.7}{T} + 1.6954 \quad (1)$$

where T is temperature in °K.

The oxidation ratios were used to identify the processes and extent of conversion from gaseous precursors (e.g. SO<sub>2</sub> and NO<sub>x</sub>) to SIA (SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) (Wang et al., 2005). Nitrate oxidation ratio (NOR, molar ratio) and sulfate oxidation ratio (SOR, molar ratio) were also defined in Eqs. (2) and (3), respectively:

$$\text{NOR} = \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + [\text{NO}_2]} \quad (2)$$

$$\text{SOR} = \frac{[\text{SO}_4^{2-}]}{[\text{SO}_4^{2-}] + [\text{SO}_2]} \quad (3)$$

Principal component analysis (PCA) has been demonstrated to be a useful tool to reduce the dimensionality of a

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