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Molecular marker characterization and source appointment of particulate matter and its organic aerosols

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HIGHLIGHTS

- Trace elements, ions, OC/EC and molecular markers in TSP and $PM_{2.5}$ were analyzed.
- The seasonal variation of the chemical compositions in particulate matters was observed.
- The correlations between TSP and $PM_{2.5}$ constituents were observed.
- The source contributions of organic aerosols in TSP were quantified using a MM-PMF.

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ABSTRACT

This study was carried out to identify possible sources and to estimate their contribution to total suspended particle (TSP) organic aerosol (OA) contents. A total of 120 TSP and $PM_{2.5}$ samples were collected simultaneously every third day over a one-year period in urban area of Incheon, Korea. High concentration in particulate matters (PM) and its components (NO_3^-, water soluble organic compounds (WSOCs), and n-alkanoic acids) were observed during the winter season. Among the organics, n-alkanes, n-alkanoic acids, levoglucosan, and phthalates were major components. Positive matrix factorization (PMF) analysis identified seven sources of organic aerosols including combustion 1 (low molecular weight (LMW)-polycyclic aromatic hydrocarbons (PAHs)), combustion 2 (high molecular weight (HMW)-PAHs), biomass burning, vegetative detritus (n-alkane), secondary organic aerosol 1 (SOA1), secondary organic aerosol 2 (SOA2), and motor vehicles. Vegetative detritus increased during the summer season through an increase in biogenic/photochemical activity, while most of the organic sources were prominent in the winter season due to the increases in air pollutant emissions and atmospheric stability. The correlation factors were high among the main components of the organic carbon (OC) in the TSP and $PM_{2.5}$. The results showed that TSP OAs had very similar characteristics to the $PM_{2.5}$ OAs. SOA, combustion (PAHs), and motor vehicle were found to be important sources of carbonaceous PM in this region. Our results imply that molecular markers (MMs)-PMF model can provide useful information on the source and characteristics of PM.

1. Introduction

Atmospheric aerosols play a key role in many environmental processes at local and global scales. These aerosols affect visibility, air quality, the climate system, and human health, including respiratory symptoms, bronchitis, cardiovascular effects, and premature deaths. Fine particles can penetrate the human respiratory tract and lungs. Several epidemiological studies have reported a link between elevated atmospheric particle concentrations and increased mortality and morbidity (Laden et al., 2000; Ito et al., 2006).

Atmospheric aerosols originate from a wide range of sources and atmospheric processes. OAs have important influences on atmospheric physicochemical and biochemical properties, including radiative forcing, hygroscopicity, and toxicity. Organic species account for a large fraction of PM, especially in $PM_{2.5}$ (Seinfeld and Pankow, 2003). The organic compound fraction of atmospheric aerosols in both rural and urban environments consists of complex

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mixtures including n-alkanes, n-alkanoic acid, polycyclic aromatic hydrocarbons (PAH), alcohols, saccharides, among others (Rogge et al., 1993, 1997; Schauer et al., 2002; Zheng et al., 2002; Park et al., 2006).

Primary organic aerosols (POA) are directly emitted from several sources including anthropogenic sources (e.g., vehicular emissions, wood burning, industrial processes, and cooking operations) and natural sources (e.g. vegetative detritus) (Dutton et al., 2010; Pindado and Perez, 2011). Additionally, OAs form in the atmosphere through a photochemical reaction between gas-phase precursors, resulting in SOAs (Robinson et al., 2007). SOAs are a major contributor to carbonaceous particulate matter in many areas, and an important contributor to air quality degradation, visibility degradation, climate forcing, and adverse impacts on human health (Jacobson, 2002; Pope et al., 2004; Tabazadeh, 2005).

Researchers have recently become interested in developing methods for the source apportionment of air pollutants (Lee and Hopke, 2006; Robinson et al., 2007; Zhang et al., 2009). Accurate apportioning of pollutant sources and their components is a critical step toward developing efficient control strategies and reducing the harmful effects of particulate matter. Common receptor models can be categorized into univariate models such as chemical mass balance (CMB) models, and multivariate models such as principal components analysis (PCA), PMF, and the EPA's Unmix model.

Both CMB and MM models have been used for source apportionment in various studies in the United States, in locations including the southeast (Zheng et al., 2002), the Los Angeles Basin (Schauer et al., 1996), and San Joaquin Valley in California (Schauer and Cass, 2000). However, CMB models have limited application because they require prior knowledge about source profiles. Therefore, uncertainty always arises as to the accuracy of source profiles and the ability to quantify errors associated, because source profiles may not realistically represent the sources affecting receptor sites. In contrast, PMF models do not require source profiles as model inputs, but they do require information about source profiles to interpret factors derived from the model as air pollution sources (Jaeckels et al., 2007). Recently, PMF source apportionment has been applied to investigate sources of OA with one year of MM data collected in St. Louis, Missouri (Jaeckels et al., 2007) and Pittsburgh, Pennsylvania (Shrivastava et al., 2007). Other studies have also coupled PMF results with surface wind direction and air-mass back trajectories to obtain reasonable estimates of possible source locations (Kim et al., 2006; Gildemeister et al., 2007; Rizzo and Scheff, 2007). However, few studies have used a source apportionment methodology incorporating organic molecular marker (MM) data, due to the time and effort required to collect detailed measurements and accommodate associated uncertainties. Also, if MM datasets are not large enough for PMF analysis, thus source apportionment can be only limited to CMB models. Therefore, the identification of the source contributions of organic aerosols (OAs) using a PMF model coupled with MM data is a quite challenge.

The understanding of atmospheric aerosol composition and its major sources are important for reducing the level of ambient PM and improving air quality. This study was carried out to evaluate the sources and characteristics of OA components in TSP. We also compared the OC components in $PM_{2.5}$ on the basis of data from the TSP analysis items, and indirectly estimated the sources of organic aerosols in $PM_{2.5}$. To achieve these objectives, we (1) analyzed the chemical compounds (i.e. ions, trace elements, OC/EC, WSOCs, and individual organic species) from TSP and $PM_{2.5}$ samples collected in Incheon, an industrialized urban city in Korea; (2) examined the characteristics and seasonal variation from the analyzed chemical compositions of TSP and $PM_{2.5}$; and (3) performed the source apportionment of OAs in TSP using PMF model coupled with MM.

2. Material and methods

2.1. PM sampling

Ambient air particles were sampled in Incheon from the roof of the Nam-Gu Council building, which is situated within a mixed residential and commercial area, including the coastal area of the capital (Fig. S1). Two busy expressways are located southeast of the building, and two industrial sites (Nam-dong and Ga-jwa/Ju-an industrial complexes) are located 10 and 12 km northeast of the building, respectively. Air quality at the sampling site is also affected by pollutant emissions from the city's seaport, which is approximately 5 km to the west, and the international airport, which is approximately 20 km from the sampling site.

The samples were collected every third day from June 2009 to May 2010. All sampling periods were approximately 24 h in duration. We monitored not only the criteria air pollutants but also meteorological data on an hourly basis, including temperature, relative humidity, wind speed, and wind direction.

TSP and $PM_{2.5}$ samples were collected at the same time to investigate the composition of coarse and fine particles. TSP was collected on quartz for the analysis of the various ingredients using high volume air sampler (Thermo-MFC). This process involves drawing large volumes of air through a 20 cm × 25 cm quartz fiber filter substrate. $PM_{2.5}$ samples were collected in various types of filters (quartz filter is for carbonaceous compounds, Teflon filter for metal species, and Zeflour, Nylasorb, and paper filter for ionic items) to improve the extraction efficiency of components using a low volume air sampler (16.7 L/min). $PM_{2.5}$ sampler consists of a two-channel annular denuder system (ADS) and two channel-filter packs, which is similar to the EPA Compendium Method IO-4.2 (1999).

The quartz filters were prebaked at 550 °C for 10 h in a furnace to remove residual carbon species prior to air sampling. After collection, the samples were stored in a freezer at -10 °C until analysis. The individual TSP samples were used for the determination of OC, elemental carbon (EC), major ionic species, trace elements, and individual organic species. The component analysis of $PM_{2.5}$ samples was also carried out for each individual samples except for OC components. For the $PM_{2.5}$ organic speciation, $PM_{2.5}$ quartz samples were made into composite samples on a monthly or episode basis to obtain a sufficient number of samples for the analysis of organic components in $PM_{2.5}$.

TSP speciation results on the individual samples were utilized for the characterization and the source contribution of organic aerosols. The data for TSP component analysis were reclassified in accordance with the results of $PM_{2.5}$. We also examined the relationship between some components of $PM_{2.5}$ and TSP to indirectly estimate the sources of OAs in $PM_{2.5}$.

2.2. Analysis

The analytical procedures for chemical species have been described in our previous study (Choi et al., 2012). In brief, ionic components, such as SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, and NH_4^+ were analyzed by ion chromatography (Dionex DX-120; anion column-IONPAC AS14A, eluent-8 mM Na_2CO_3/1 mM $NaHCO_3$ at 1 mL/min; cation column-IONPAC CS12A-20 mM; MSA eluent at 1 mL/min). The filters were digested using a laboratory microwave extraction system (Microwave 3000, Anton Paar) to extract elements with a hydrochloric/nitric acid solution (US EPA Methods IO 3.1). The digest was filtered and then analyzed for 14 trace elements (Mg, Al, P, Ca, Ti, V, Cr, Fe, Mn, Ni, Cu, Zn, As, and Pb) by an inductively coupled plasma/mass spectrometry (ICP/MS, Perkin Elmer). OC/EC was analyzed based on NIOSH TOT