



Sulfur isotope and chemical compositions of the wet precipitation in two major urban areas, Seoul and Busan, Korea



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ABSTRACT

The seasonal variations of $\delta^{34}\text{S}$ together with major ions in snow and rainwater samples were measured in urban areas. Precipitation samples were collected from metropolitan city, Seoul and large port city, Busan, Korea, for about one year from June 2002 to June 2003. The $\delta^{34}\text{S}$ values of sulfate in precipitation ranged from -4.3‰ to $+6.6\text{‰}$ (mean: 3.72‰) and $+1.0\text{‰}$ to $+18.6\text{‰}$ (mean: 5.55‰) in Seoul and Busan, respectively. Even though both of the study areas have large populations and transportation infrastructure, $\delta^{34}\text{S}$ values of sulfate in Seoul precipitation originate more from anthropogenic sources relative to that of Busan. The elevated anthropogenic sources in Seoul might be influenced by human activities from surrounding industrial cities, while the scatter of $\delta^{34}\text{S}$ values in Busan may be influenced by marine air. During the study, $\delta^{34}\text{S}$ values are high in the fall season and low in the spring season. It may be inferred from this data that spring time $\delta^{34}\text{S}$ values are affected more by biogenic sources compared to the fall season. As such, Seoul and Busan showed significant differences in chemical compositions, such as $\delta^{34}\text{S}$ and nss-SO_4^{2-} . Especially, $\delta^{34}\text{S}$ values in the Seoul show very good relationship with anthropogenic emissions (e.g., emission from coal combustion) and $\delta^{34}\text{S}$ values in the Busan may be influenced by sea spray from the oceanic surface micro-layer. This correlation and the $\delta^{34}\text{S}$ values indicate that the major source in this region is likely to be anthropogenic source in Seoul and sea spray in Busan, rather than traditionally suggested sources such as soil resuspension, stratospheric air intrusion, volcanic emissions, and biogenic emissions.

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1. Introduction

Fast growing industry-based economic development has caused many environmental problems over the world. Industrial belts emit many types of contaminating gases into the atmosphere, causing acid rain and excess ozone. Acid rain has been one of the major issues in the studies of atmospheric environment in the twenty-first century and recently has troubled East Asia. To understand this problem, scientists have been studying the origins and composition of acidic precipitation. The major element and isotopic composition analyses of precipitation have provided useful information on sources and aerial transport processes of atmospheric pollutants. In this study, chemical composition and sulfur isotopes in urban precipitation were used to understand atmospheric transportation and origin.

Major sources of element in rainwater are marine (sea spray), terrestrial (soils, biological emissions), and anthropogenic (indus-

trial, biomass burning) (Junge, 1963; Mason, 1971; Granat et al., 1976; Stallard and Edmond, 1981). The importance of marine source varies with distance from the coast. A “hierarchy of ions” can be established (after Means et al., 1981 and Stallard and Edmond, 1981) based on relative importance of marine sea-salt sources and continental (terrestrial or pollutive) sources. Major ions of rainwater are from both natural (marine, terrestrial and biogenic emission) and anthropogenic (industries, vehicle emission and others) sources. In general, the chemical composition of atmosphere has the following patterns. The “hierarchy of ions”, $\text{Cl}^- = \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- = \text{NH}_4^+$, was established by Means et al. (1981) and Stallard and Edmond (1981), illustrating from left to right the decreasing importance of the marine source relative to the terrestrial or pollutant sources (Panettiere et al., 2000).

Among principal cations, Na^+ is the major cation in marine-influenced rain, while Ca^{2+} is dominant in inland rain due to NaCl solution in the ocean and CaSO_4 solution in the continent. In the coastal area, precipitation has generally similar sea-salt ratios as Na^+ , Cl^- and Mg^{2+} , but Ca^{2+} and K^+ ratios may be different

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depending on continental inputs (Bernier and Bernier, 2012). A majority of sodium might be derived from marine source but it sometimes comes from particularly an arid, dusty area of igneous rocks (over most sedimentary rocks), saline dry lake beds, and soil dust from agriculturally developed areas (Munger, 1982). Chlorine also is mainly from a marine source. The decrease of chlorine content inland is explained by rapid deposition of sea salt in precipitation and air mixing (Junge, 1963). However, all Cl^- in rainfall is not originated from sea salt; some come from chlorine-containing gases from automobiles, coal combustion, and burning of polyvinyl chloride in incinerators (Paciga and Jervis, 1976).

The contribution of sea salt to Ca^{2+} in inland rain is very trivial. Instead, Ca^{2+} comes dominantly from the dissolution of calcium carbonate (CaCO_3) in soil dust. HCO_3^- and Ca^{2+} are formed by dissolving CaCO_3 in the rain. Ca^{2+} in rain is also derived CaSO_4 (gypsum) soil dust and occasionally from CaCl_2 (road salt) (Butler et al., 1984). In addition, Ca^{2+} can be produced by pollution from coal burning and from cement manufacture (Pearson and Fisher, 1971). Magnesium is correlated with calcium, presumably due to a similar soil source (Munger and Eisenreich, 1983). Except for coastal areas or areas of strong marine influence such as the Amazon, Mg is not an importance source for sea salt (Stallard and Edmond, 1981). Non-marine sources of potassium are soil dust, K-bearing fertilizers, biogenic aerosol, pollen seed, and forest burning, particularly in tropical areas (Junge, 1963; Gillette et al., 1992; Munger, 1982). From the partial reaction between ammonia gas (NH_3) and water, ammonium can be formed. This reaction raises the pH of rainwater. Atmospheric ammonia can be produced

from the bacterial decomposition of animal and human excreta, fertilizer release, burning coal, and biomass burning (Bernier and Bernier, 2012). Agricultural sources are seasonal, being at a maximum in the spring and summer. Ammonia is a very minor product of coal combustion. In fact, well-burned coal releases no NH_3 at all (Stedman and Shetter, 1983), with all of the nitrogen appearing as N_2 instead as NO_x . However, some data show little areal correlation with other fuel combustion products such as SO_2 (Healy et al., 1970; Junge, 1963). Nitrate in atmosphere originates from natural sources (lightning, photochemical oxidation in the stratosphere, chemical oxidation of ammonia to NO_x and soil production of NO) and anthropogenic sources (fossil fuel combustion and biomass burning).

Sulfur in the atmosphere originate from sea spray, organic compounds from sulfur reducing bacteria, volcanic gases, combustion of fossil fuels, and other human activities (Newman et al., 1991). The ratio of ^{34}S to ^{32}S in the rainwater is used to identify and trace the source of sulfur in atmospheric fallout. Generally, sea spray sulfate contributes to only a minor fraction of the total atmospheric sulfate content, especially in urban conditions (Na et al., 1995; Lim et al., 2012). The sources of NSS (Non-Sea Salt) sulfate are either anthropogenic sulfur dioxide originating from oil and fossil fuel combustion, or natural biogenic reduced sulfur gases (Junge, 1963; Bonsang et al., 1980; Bernier and Bernier, 1987; Gammon and Charlson, 1993; Herut et al., 1995).

The purpose of this study is to examine and compare the S isotope and chemical compositions of the wet precipitation in Seoul and Busan to determine the possibility of using sulfur as a tracer in evaluating the sources of atmospheric pollution in these areas.

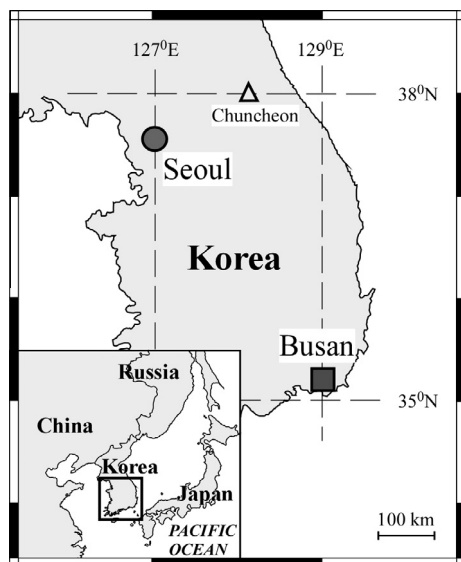


Fig. 1. Map of the sampling location of study area in Seoul (black circle) and Busan (black square) and reference area in Chuncheon (open triangle; Yu et al., 2007).

2. Study area

The two largest cities in Korea, Seoul and Busan, were selected for this study because the effects of pollution from anthropogenic sources in these areas are expected to be maximized within the Korean peninsula in recent years compared to reference rural site Chuncheon (Yu et al., 2007) during rain and snow events from June, 2002 to June, 2003 (Fig. 1).

Seoul accommodates around ten million people with about three million vehicles and numerous industrial belts. The sampling site is located at Seoul National University in the southern part of the Seoul metropolitan area. The locations of the sampling site are presented in Fig. 1. The Gwanaksan granite is a stock-size pluton which belongs to the Jurassic Daebo granite series, and placed in the southern Seoul granitic batholith (Kwon et al., 1995).

Busan is the second largest city in Korea with nearly four million people and about one million vehicles. Busan is located on the southeastern end of the peninsula and is a harbor city. Samples were collected in Pukyong National University. Both of the sampling areas are in the metropolitan city and samples were acquired from a roof of a school building. The Busan region, located

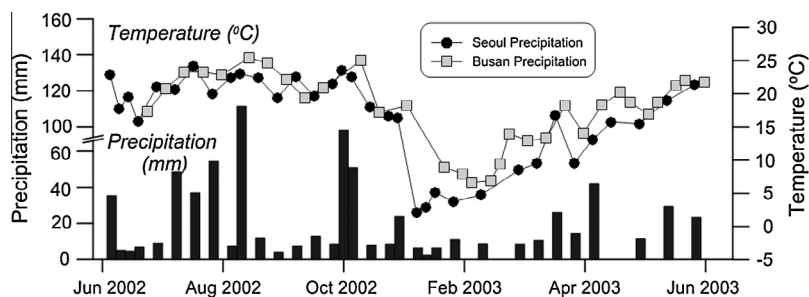


Fig. 2. Seasonal variations of precipitation and air temperature in Seoul and Busan.

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