Science of the Total Environment 408 (2010) 2369–2377

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Atmospheric transport of water-soluble ions (NO_3^-, NH_4^+ and nss-SO_4^{2-}) to the southern East Sea (Sea of Japan)

Jeongwon Kang *, Byung Cheol Cho, Chang-Bok Lee

School of Earth and Environmental Sciences and Research Institute of Oceanography, Seoul National University, Seoul 151-742, Republic of Korea

ARTICLE INFO

Article history:
Received 28 August 2009
Received in revised form 24 December 2009
Accepted 11 February 2010
Available online 15 March 2010

Keywords:
Aerosol
Water-soluble ions
Nss-sulfate
Atmospheric nitrogen
Backward trajectory
East Sea (Sea of Japan)

ABSTRACT

Atmospheric deposition of different types of aerosols over the southern East Sea has received little attention in terms of seawater biogeochemistry. We investigated the concentrations of water-soluble ions (NO_3^-, NH_4^+ and nss-SO_4^{2-}) in the aerosols associated with air mass transport patterns arriving at the east coast of Korea, adjacent to the southern East Sea, in order to determine source regions affecting chemical composition of aerosols and to assess the atmospheric pathway as a significant controlling mechanism of the biogeochemistry in this marginal sea. Concentrations of certain elements (Al, Na, Ca, V, Zn and Pb) together with the water-soluble ions were measured in the aerosol samples ($n = 34$) collected during the period March 2002–February 2003. The geometric mean concentrations of the water-soluble ions were NO_3^- 2.98 (0.56–16.22), NH_4^+ 1.42 (0.37–6.73) and nss-SO_4^{2-} 2.47 (0.17–17.35) μg m^{-3}. The backward trajectories revealed that air masses passing slowly over eastern China contributed more to increases in the concentrations of water-soluble ions than those associated with fast-moving northwesterly and maritime winds. Therefore, the correlation between the NH_4^+ and NO_3^+ concentrations increased, suggesting that gas-phase NH_3 and HNO_3 was forming fine-mode NH_4NO_3. The atmospheric N input accounted for ~10% of new production over the southern East Sea on an annual scale, while it accounted for over ~25% of new production during the water column stratification seasons (summer and early fall).

1. Introduction

The East Asian region is one of the largest emitters of natural aerosol (mineral dust) and pollution precursors (SO_2, NO_x and NH_3) in the world (Streets et al., 2001; Kim et al., 2006; Kim, 2008). According to the Ace-Asia and Trace-P Modeling and Emission Support System (ACESS; http://www.cgrer.uiowa.edu/ACESS/acess_index.htm), SO_2 and NO_x emissions for 2000 in East Asia region were estimated to be 22.7 and 15.9 Tg, and those in the year 2006 were 32.9 and 25.3 Tg, respectively. An estimate of SO_2 and NO_x for 2000 accounts for around 20% of global emissions reported in that year (Cofala et al., 2007). The East Sea (Sea of Japan) is a marginal sea of the northwestern Pacific, surrounded by Korea, Russia and Japan. Atmospheric investigations along the coast and on remote islands of the southern East Sea have revealed that this region acts as a receptor for the huge natural and anthropogenic emissions from the Asian continent via long and medium-range transport under the influence of the monsoon system (Mukai et al., 1990; Mukai and Suzuki, 1996; Murano et al., 2000; Kang et al., 2009).

The increase in economic activities in East Asia, particularly in China, has been accompanied by increasing atmospheric emissions of SO_2 and NO_x (Streets et al., 2001; Hao et al., 2002). SO_2 and NO_x emitted from industrial areas are oxidized in the atmosphere to SO_4^{2-} and NO_3^-, respectively, by heterogeneous and homogeneous reactions during transport (Kai et al., 2007 and references therein). These inorganic aerosols can be neutralized by NH_4^+, which is formed from gaseous NH_3 emitted from agricultural areas. They usually exist in the form of $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3 (Nakamura et al., 2005; Kim et al., 2006; Chou et al., 2008). SO_4^{2-} and NO_3^- are the most common acidic ions in the atmosphere (Kang et al., 2004). However, in marine environments, where ecosystems are N-limited, non-sea-salt (nss)-SO_4^{2-} is considered a major possible acid species (Bates and Peters, 2007). This is because the NH_4^+ and NO_3^--containing aerosols are used by marine phytoplankton. This contributes to new production (Paerl, 1985), which is especially significant in oligotrophic regions (Owens et al., 1992; Guerzoni et al., 1999) and regions that are stratified thermally throughout the year (Jickells, 1995). The East Sea is an N-limited system, so additional N input by atmospheric deposition probably triggers new algal biomass production there (Hartmann et al., 2008).

Trans-boundary air pollution is one of the key issues in East Asia (Murano et al., 2000; Kim et al., 2005). A few studies have attempted to apply backward trajectory modeling in combination with chemistry to identify trans-boundary sources of polluted air masses that may affect air quality in western Japan, adjacent to the southern East Sea (*e.g.*, Mukai and Suzuki, 1996; Murano et al., 2000). However,

---

* Corresponding author.
E-mail address: jwkhang5@snu.ac.kr (J. Kang).

0048-9697/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2010.02.022

there has been little consideration of the atmospheric deposition of chemical materials from the Asian continent into the sea during transport (Kang et al., 2009). As studies of the Yellow and East China Seas have shown (Gao et al., 1992; Chen and Wang, 1999), atmospheric investigations are essential for understanding mass balances and biogeochemical cycles in the southern East Sea (Kang et al., 2009).

We performed cluster analysis to classify the aerosol observation dates using the concentrations of water-soluble ions (NO_3^-, NH_4^+ and nss-SO_4^{2-}). Other chemical species, including crustal elements (Al and Ca) and those from continental (Zn and Pb) and marine sources (Na), were also included. Then, we investigated the transport patterns of aerosols using backward trajectories and the associated concentrations of those ions on the east coast of Korea adjacent to the southern East Sea. We also discuss the chemical characteristics of water-soluble ions in the classified groups in relation to their formation. Finally, we calculate atmospheric nitrogen deposition and discuss its potential impact on the biogeochemistry of the southern East Sea including comparison with results from the other sea area of East Asia.

2. Methods

2.1. Aerosol sampling and chemical analysis

Thirty-four aerosol samples for chemical analyses were collected during the period from March 2002 to February 2003 on the east coast of Korea (37.58°N, 129.11°E; RIO in Fig. 1). A high-volume sampler (Kimoto Inc., Japan) was installed on the rooftop of the Research Institute of Oceanography of Seoul National University (RIO, SNU) in Donghae City, approximately 30 m above sea level. Total suspended particulates (TSP) were collected on Whatman 41 filter at flow rates of 700–800 l min^{-1}. The run time of sampler was 24 h for most samples. Except in April, July and December 2002 and February 2003, three to five samples were analyzed per month (Table 1).

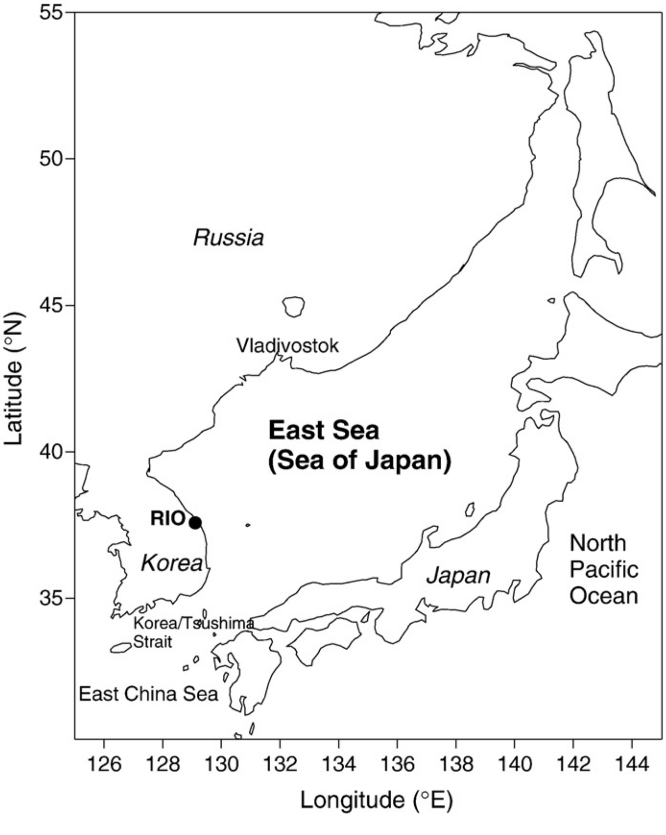

Fig. 1. Location of the Research Institute of Oceanography of Seoul National University (RIO, SNU) aerosol observation site in Korea.

After the sampling was completed, the sample filter was stored in a clean vinyl bag. Replicate analyses of portions of a filter media had indicated precision ≤5% for certain elements (Fe, Mn, Cu and Zn). This result is comparable to that reported by Herut et al. (2001), suggesting that the aerosols are likely to be homogeneously loaded on the filter during the sampling. For the water-soluble ion analysis, the filters were cut into small pieces, approximately 16% of the aerosol-loaded area (387 cm^2), and placed into 50-ml conical plastic tubes. The solution for analyzing water-soluble ions was made by extraction with 20 ml of purified water, which was produced from a Milli-Q system (specific resistivity > 18 MΩ cm, Millipore), after 3 h on a rotary shaker at an ambient temperature (*e.g.*, Fernández et al., 2002). Soluble phases were separated from insoluble ones by centrifugation at 3200 rpm for 10 min. After extraction and centrifugation, the tube was used to decant the solution by pipette into 20-ml vials. The concentrations of the ionic components were determined using a Dionex series 4500 ion chromatograph equipped with an ion exchange column (IonPac AS14A) and an ASRS-ULTRA suppressor, which was operated at the Institute of Environmental Protection and Safety of Seoul National University. A mixture of 8.0 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ at a flow rate of 1.0 ml min^{-1} was used to elute NO_3^- and SO_4^{2-}. For the NH_4^+ analysis, we used the nesslerization method with an ammonium ion selective electrode (Phoenix Electrode) and an Istek pH/ISE meter Model 730p (*e.g.*, Clarke et al., 1999).

Whatman 41 filters ($n = 6$) were analyzed to assess the blank contribution to sample concentration. The blank values subtracted from the samples were 0.22 ± 0.09, 0.26 ± 0.05 and 0.28 ± 0.10 mg kg^{-1} for NO_3^-, NH_4^+ and SO_4^{2-}, respectively. The contribution of average blanks was found to be less than 10% for the lowest samples of the ions. Using 3σ of the blanks and the average-sampled volume of 1120 m^3 for a sampling time of 24 h, the calculated detection limits were 0.031, 0.017 and 0.034 μg m^{-3} for NO_3^-, NH_4^+ and SO_4^{2-}, respectively. For NO_3^- and SO_4^{2-}, duplicate analysis showed results with differences of 7–8%.

Another filter section was prepared for the trace elements. Measurements were made using inductively coupled plasma atomic emission spectrometry (ICP-AES; Shimadzu ICP-1000IV) for Al, Na and Ca, and inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer, ELAN 6100) for V, Zn and Pb. These procedures were performed at the National Center for Inter-University Facilities of Seoul National University. Details of the sample acid-digestion were given in Kang et al. (2009). The blank values ($n = 4$; μg kg^{-1}) were found to be Al 365 ± 244, Ca 825 ± 640, Na 950 ± 54, V 29.3 ± 18.1, Zn 4.6 ± 1.8 and Pb 3.9 ± 0.4. The average blanks of Zn and Pb occupied 5 and ~10% of the lowest samples, respectively, and around 20% for Al and Ca. For Na and V, the blank contributions were up to ~50 and ~70% of the lowest samples, respectively. But the subtracted blank values were less than 5% of the average values for the analytes of interest except for V (~30%). The detection limits were defined as lower blank values with the analytical reproducibility < 10% from analytical batch. The calculated detection limits in aerosol samples (ng m^{-3}) were Al 11.58, Ca 55.01, Na 76.43, V 0.62, Zn 0.30 and Pb 0.43. The accuracy was checked against marine sediment reference material (SRM) of the United States Geological Survey (USGS), otherwise known as MAG-1, and the recovered values for all target elements were in the range of 94 (Ca)–122% (Zn) based on average.

2.2. Calculations of marine-Na, and non-sea-salt (nss) SO_4^{2-} and Ca in aerosols

The concentration of marine-Na was calculated from the total Na concentration using (Zieman et al., 1995)

$$[Na]_{Marine} = [Na]_{total} - \{([Na]/[Al])_{soil} \times [Al]_{total}\}, \quad (1)$$