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A five-year observation of atmospheric metals on Ulleung Island in the East/Japan Sea: Temporal variability and source identification

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ABSTRACT

We investigated seasonal characteristics (concentration, enrichment factors, and correlation coefficients) of chemical constituents, including sources for sea salt-corrected metals (Al, Fe, K, Ca, Mg, S, As, Cd, Co, Cu, Li, Mn, Mo, Ni, Pb, Sn, Sr, Ti, V, and Zn), in 334 aerosol samples collected during October 2003–October 2008 at Ulleung Island in the southern East/Japan Sea. High Al concentrations were found in spring (geometric means of 1.23 and 1.28 μg m^{-3} in March and April, respectively) due to Asian dust (yellow sand) originating from northeastern China. The dust mineral transport by strong winds resulted in a change of metal composition showing soil-dominated condition. In the rainy period (June–September), the aerosol metal concentrations and composition were influenced largely by wet deposition and the summer monsoon, together with anthropogenic aerosol transport. The correlation coefficients in the summer period (July and August) showed a positive correlation of Al with K ($r = 0.74$) and As ($r = 0.63$), probably reflecting anthropogenic-originated Al coming from coal burning. In autumn (October and November) and winter (December and January), mixed sources of soil and anthropogenic-originated aerosols were pronounced by the development of northwesterly winds from the Asian continent. Especially, the soil-originated proportion was relatively higher in autumn than in winter when the anthropogenic-originated aerosols from heating fuels predominated. Anthropogenic As, Sn, Mo, Zn, Pb, and Cd between low- and high-dust periods that had similar air–mass movements in spring were at similar concentrations, but higher in the air masses including eastern China trajectories and/or slow movement at lower height during high-dust periods.

1. Introduction

The East Asian region emits massive amounts of pollutant aerosol precursors (SO_2, NO_x, and NH_3) and anthropogenic particles, and such emissions are increasing rapidly with expanding economic and industrial activities (Richter et al., 2005; Fang et al., 2009; Kang et al., 2010). In addition, East Asia has large natural aerosol sources, including mineral dust from several deserts and loess areas (upper basin of the Yellow River) and sea salts from the marine environment (Zhang et al., 2006; Kim, 2008; Liu et al., 2009). During continental outflow events, which are most frequent in spring, dust particles are transported out over the Pacific Ocean where they mix with marine air masses. In addition, the gaseous pollutants from urban and industrial activities in eastern China, South and North Korea, and Japan, and their oxidation products (H_2SO_4 and HNO_3), interact with mineral and sea-salt particles during the transport process (Nakamura et al., 2005). Because the marginal seas around the Korean peninsula are the first receptors of emissions of natural and anthropogenic aerosols and a transit area to the open ocean, a detailed investigation of the aerosols over these seas may provide important data to evaluate the role of atmospheric pathways in the marine biogeochemical cycles of terrigenous materials.

Particulate trace metals in aerosol have been investigated extensively in continentally bound seas (*e.g.*, Gao et al., 1992; Injuk et al., 1998; Herut et al., 2001; Koçak et al., 2005) to evaluate the relative importance of source intensities to marine aerosols. In East Asia, Asian dust (yellow sand) events generated from arid and semiarid North China and southern Mongolia (Wang et al., 2009) result in higher atmospheric metal concentrations, especially for crust-originated metals such as Al, Mg, Ti, Fe, and Ca, and are the major factor affecting the compositional changes of atmospheric

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particulate matters (Kim et al., 2003). During Asian dust transport, anthropogenic components are also entrained through scavenging (up-take) processes, indicating that dust minerals can serve as a vector for pollution transport (Mori et al., 2003; Marx et al., 2008). In addition, dust particles could be transported with antecedent pollutants containing anthropogenic-originated particles such as road dust and deposited fly ash (Guo et al., 2007; Marx et al., 2008). Along with windblown dusts, pollutants arising from increased industrial development and coal consumption are delivered out of China (Fang et al., 2009). A portion of each of the natural and anthropogenic components is subject to long-distance transport and may thus affect downwind regions in East Asia (*e.g.*, Mukai and Suzuki, 1996; Han et al., 2004; Hsu et al., 2005; Kang et al., 2009).

The East/Japan Sea is a marginal basin of the northwestern Pacific Ocean, surrounded by Korea, Russia, and Japan. Atmospheric investigations along the coast and on remote islands of the southern East/Japan Sea have revealed that this region acts as a receptor for massive 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). In the region between 33° and 45°N, which covers the southern East/Japan Sea, the seasonal variation of atmospheric metal concentrations is related to Asian dust transport, entrainment of anthropogenic components in the northwestern monsoonal winds, and wet deposition; these factors increase the atmospheric metal concentrations in spring and winter and reduce them in the summer (Gao et al., 1992; Hao et al., 2007; Kang et al., 2009). Therefore, the metal composition of the atmosphere over the southern East/Japan Sea could be considered to be constrained by the extent to which the continuous supply of anthropogenic aerosol is perturbed by sporadic mixing with injections of dust mineral from desert/loess sources, as found for the Mediterranean Sea (Chester et al., 1993). However, to characterize the seasonal evolution of metal composition in aerosols, a more detailed atmospheric investigation is needed. Specifically, it is necessary to characterize the changes in metal composition during the northwest monsoon periods with and without Asian dust transport, as well as the metal composition during the rainy periods (summer monsoon), and examine the differences and similarities between these periods.

Here, we present a comprehensive study of the temporal variability of atmospheric metal concentrations based on 5 years (2003–2008) of observations at Ulleung Island located in the southern East/Japan Sea. Our detailed study focused on seasonal characteristics and the annual variation of atmospheric metal concentrations and composition through association among metals. Until now, such results have been poorly documented in the literature for the mid-latitudes of East Asia.

2. Methods

2.1. Soil sampling in arid and semiarid North China

Surface soil samples were collected from the Asian dust source regions (*e.g.*, Gobi, sandy, and loess areas, Fig. 1). Prior to chemical analysis, soil samples ($n = 16$) were sieved in the laboratory using a 20 μm nylon sieve with ultra-pure water (18.2 MΩ, pH 9 adjusted with ammonia). As dust particles finer than 20 μm can be transported in long-term suspensions over a great altitudinal range and long distances (Sun, 2002), particles <20 μm were collected by centrifugation. Size-separated soil samples were oven-dried and powdered using an agate mortar.

2.2. Aerosol sampling at Ulleung Island

In total, 334 aerosol samples were collected from October 2003 to October 2008 at Ulleung Island (37.29°N, 130.54°E) in the southern East/Japan Sea (Fig. 1). A high-volume air sampler (Kimoto

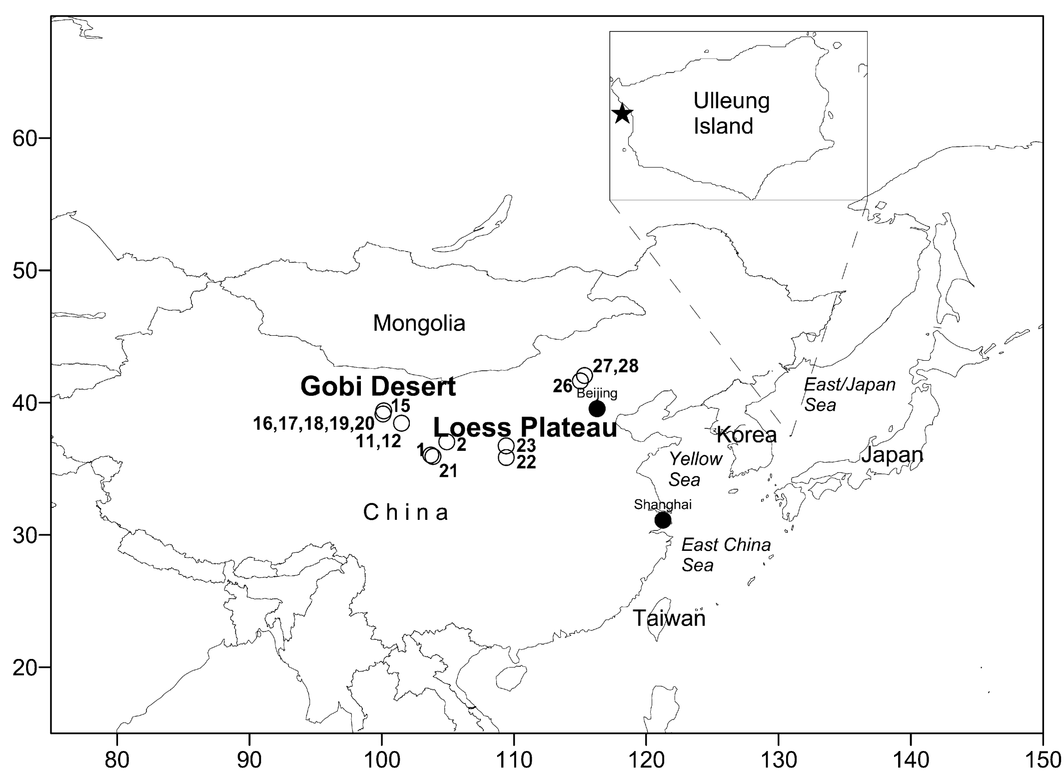

Fig. 1. Map showing sampling sites of soils in China (1 ShuiFu; 2 Jingyuan; 11,12 Shandan; 15–20 Linze; 21 Lanzhou; 22 Luochuan; 23 Ganquan; 26–28 TaibusQi) and aerosols at Ulleung Island (★).