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Distribution of inorganic nitrogen-containing species in atmospheric particles from an island in the Yellow Sea

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ABSTRACT

In this study, total suspended particles (TSP) and size-segregated atmospheric aerosol samples were measured on Qianliyan Island in the Yellow Sea in spring (April–May), summer (July–August) and fall (October–November) of 2006 and in water (January–February) of 2007. The mass concentration of the TSP varied from 75.6 to 132.0 μg/m^3. The average concentration were 9.37 ± 7.56 μg/m^3 and 5.32 ± 4.25 μg/m^3 for nitrate and ammonium in the TSP, respectively. TSP concentration showed a significant correlation with those of nitrate (n = 27, r = 0.73) and ammonium (n = 27, r = 0.60). The mass-size distribution of atmospheric particles exhibited two modes with an accumulation mode at 0.43–1.1 μm and a coarse mode at 3.3–4.7 μm throughout the sampling months. A bi-modal size distribution of nitrate in concentration occurred in the April–May, October–November and January–February, but a uni-modal size distribution occurred in the August. The uni-modal size distribution of ammonium at 0.43–0.65 μm was observed throughout the sampling months. The average of inorganic nitrogen in mass concentration accounted for 4.0% of the total mass of aerosol particles while ammonium-N was the dominant fraction of TIN (Total Inorganic Nitrogen), contributing to 62–71% of the TIN.

1. Introduction

Atmospheric deposition is one of the most important nitrogen sources for ocean ecosystems (Baker et al., 2007; Clark and Kremer, 2005; Duce et al., 1991; Zhang et al., 2007). Due to the influence of human activity, the total nitrogen deposition increases at a rate of 0.26 kg N ha^{-1} per decade in the last century (Bowen and Valiela, 2001). Estimates of annual atmospheric nitrogen emissions will increase up to 132 Tg N year^{-1} in 2030 and anthropogenic atmospheric nitrogen (ANN) emissions will be 113 Tg N year^{-1} (Duce et al., 2008).

Particulate inorganic nitrogen-containing compounds have been reported to account for 66.2% (on average) of the atmospheric deposition of total nitrogen (Shi et al., 2006, 2010). The mass concentration of inorganic particulate nitrogen often exhibit different size distributions spatially and temporally. The mass concentration of nitrate was reported to uniquely distribute in the coarse mode over the northwest Pacific Ocean (Matsumoto et al., 1998). However, other researchers (Kumar et al., 2010; Lestaria et al., 2003; Li et al., 2011; Moya et al., 2004; Zhao and Gao, 2008) observed that particulate nitrate exhibited a bi-modal size distribution, and that the dominant mode occurred at both the submicron and supermicron sizes.

On the other hand, most of the ammonium has been reported to exist in the accumulation mode in urban area (Moya et al., 2004; Zhao et al., 2011) and over the northwest Pacific Ocean (Matsumoto et al., 1998). However, significant coarse-mode fractions of ammonium (~19–45%) were found in aerosol samples at coastal sites in the United Kingdom, and dissolution and coagulation processes are thought to give rise to the size-distribution shifting of aerosol ammonium (Yeatman et al., 2001). It is obvious that size distribution of inorganic

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nitrogen in mass concentration is the important parameter to estimate atmospheric nitrogen deposition.

The Yellow Sea is on the passageway path of continent aerosols to the Pacific Ocean. Compared with data for other ocean areas, information on the variation in concentration and mass-size distribution of inorganic nitrogen in the marine atmosphere over the Yellow Sea is limited. Therefore, TSP and size-segregated aerosol samples were collected on Qianliyan Island in the Yellow Sea in April–May, July–August and October–November of 2006 and again in January–February 2007. Inorganic nitrogen (NH_4^+, NO_3^-) was analyzed, and the variations that were found in concentrations and size distribution are discussed in this paper.

2. Material and methods

2.1. Sampling

Atmospheric aerosol samples were collected at Qianliyan Island (36°15′N, 121°23′E) of the Yellow Sea (Fig. 1) in April–May, July–August and October–November of 2006 and again in January–February 2007. The sampling site is about 93.5 m above sea level and 110 km northeast of Qingdao (about 8,190,000 inhabitants in Qingdao). The samplers were mounted and secured on a high platform during the entire sampling period. The TSP (Total Suspended Particles) samples was collected on quartz microfiber filters (Whatman QM-A) using a high volume air sampler (Model KC-1000, Qingdao Laoshan Electronic Instrument Complex Co., Ltd.). The filters were preheated to 450 °C for 4.5 h in an oven to remove the organic compound to avoid the pollution of organic nitrogen. The KC-1000 samplers were operated for about 24 h within each sampling period. The sampling information for each TSP sample is listed in Appendix A.

Size-segregated samples were collected using an Andersen impactor sampler (Model AN-200, Sibata Scientific Technology Ltd.) installed with PTFE membranes. The cut-points of eight stages include >11 μm, 7.0–11 μm, 4.7–7.0 μm, 3.3–4.7 μm, 2.1–3.3 μm, 1.1–2.1 μm, 0.65–1.1 μm, and 0.43–0.65 μm. The Andersen sampler generally was operated for 60–72 h, except three samples. Sampling was interrupted because the electrical machine was incapable of working continuously. The information about the samples is listed in Appendix B. In this study, we define coarse particle as particles larger than 2.1 μm for discussion.

The meteorological data (including temperature, relative humidity, wind velocity, wind direction, pressure, and rainfall) were measured by using an automatic weather station.

2.2. Sample analysis

The aerosol samples were ultrasonically extracted with ultra-pure water in an ice water bath for 30 min. The concentrations of ammonium and nitrate were then analyzed

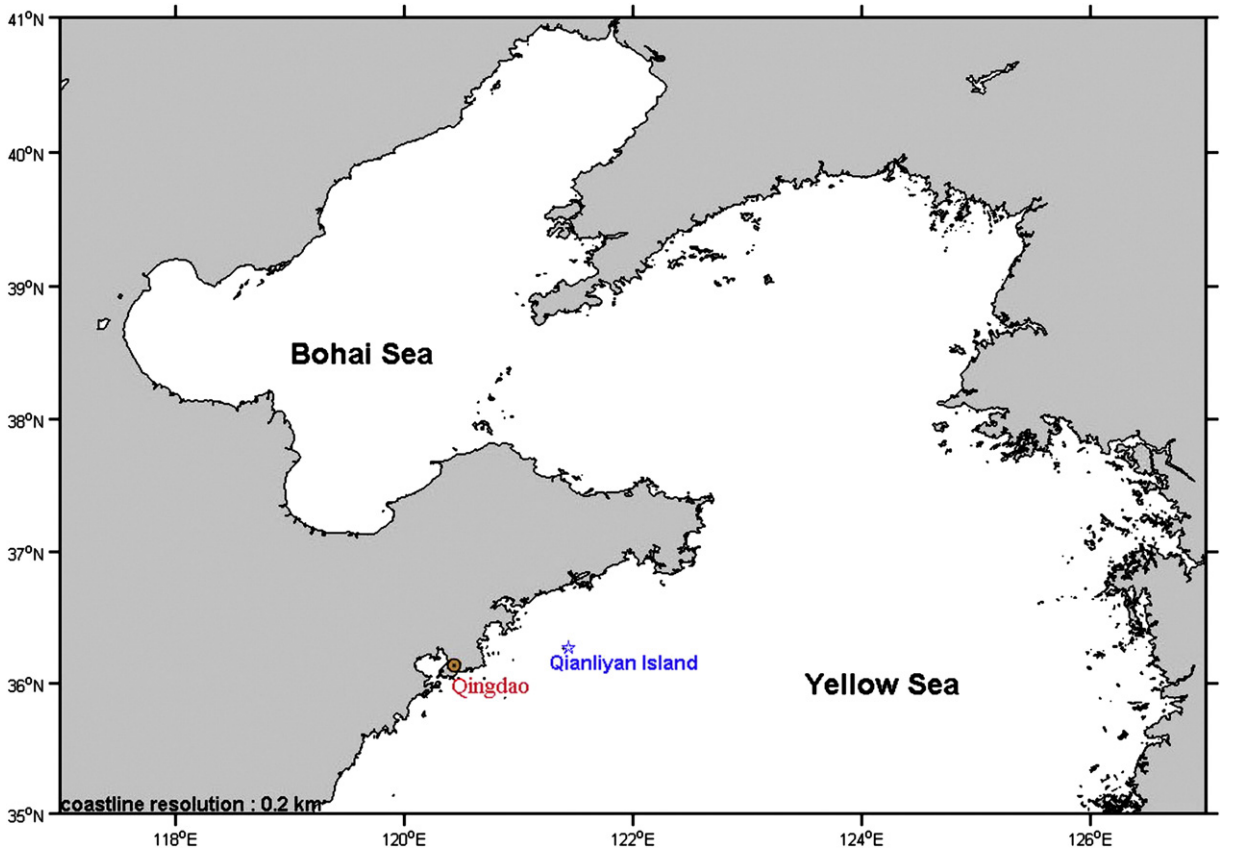

Fig. 1. Location of the sampling site.