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Source apportionment of particulate pollutants in the atmosphere over the Northern Yellow Sea

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HIGHLIGHTS

► Principle component analysis and positive matrix factorization are used.
► Secondary aerosols and soil dust are the dominant sources.
► Aerosols are influenced by ship emission and continental agricultural activities.
► Seasonal variations of the contributions of the sources are exhibited.

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ABSTRACT

Atmospheric aerosol samples were collected over the Northern Yellow Sea of China during the years of 2006 and 2007, in which the Total Carbon (TC), Cu, Pb, Cd, V, Zn, Fe, Al, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and K^+ were measured. The principle components analysis (PCA) and positive matrix factorization (PMF) receptor models were used to identify the sources of particulate matter. The results indicated that seven factors contributed to the atmospheric particles over the Northern Yellow Sea, i.e., two secondary aerosols (sulfate and nitrate), soil dust, biomass burning, oil combustion, sea salt, and metal smelting. When the whole database was considered, secondary aerosol formation contributed the most to the atmospheric particle content, followed by soil dust. Secondary aerosols and soil dust consisted of 65.65% of the total mass of particulate matter. The results also suggested that the aerosols over the North Yellow Sea were heavily influenced by ship emission over the local sea area and by continental agricultural activities in the northern China, indicating by high loading of V in oil combustion and high loading of K^+ in biomass burning. However, the contribution of each factor varied greatly over the different seasons. In spring and autumn, soil dust and biomass burning were the dominant factors. In summer, heavy oil combustion contributed the most among these factors. In winter, secondary aerosols were major sources. Backward trajectories analysis indicated the 66% of air mass in summer was from the ocean, while the air mass is mainly from the continent in other seasons.

1. Introduction

Atmospheric particulates from natural or anthropogenic sources can be transported from the continents to oceans. These particulates carry various trace metals (e.g., Fe, Zn, and Cu) and nutrients (e.g., N, P, S, and K). Atmospheric deposition is one of the major pathways for these elements in the upper layer of open oceans in contrast to river inputs (Duce and Tindale, 1991; Gao and Duce, 1997; Krishnamurthy et al., 2009, 2010). Atmospheric inputs of these elements have been hypothesized to have a profound effect on the chemical and biological dynamics of open seas (Zhang, 1994; Hand et al., 2004; Harrison and Yin, 2000). Fe has been proposed to be a limiting element in high-nitrate low-chlorophyll (HNLC) regions of oceans and control the primary productivity (Tsuda et al., 2003). Atmospheric deposition of copper derived from anthropogenic emissions may have a toxic effect on the *Synechococcus* and potentially alter patterns of marine primary production when its concentration is over the threshold of toxicity (Paytan et al., 2009). The bioavailability of these elements is partially controlled by their solubility in seawater. Moreover, the solubility of a certain element depends largely on its dominant origins (crustal or anthropogenic sources) (Hsu et al., 2005). Thus, it is necessary to obtain the details of source information of aerosols over the sea and estimate their

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contributions. These would facilitate the risk assessment for atmospheric deposition of continental materials to marine ecosystems and marine biogeochemistry.

Source apportionment of atmospheric particulates over seas has been conducted in various marine regions. Three sources (crustal, photochemical and marine) of coarse particles have been identified in the Eastern Mediterranean using a factor analysis (FA), while two additional sources (residual oil and secondary aerosol) of fine particles were identified (Koulouri et al., 2008). Aerosols over the Bohai Sea have been shown to be heavily influenced by anthropogenic air pollutants (Sheng et al., 2005). Three sources (anthropogenic, marine, and crustal sources) of aerosols over the East China Sea were identified using a principal component analysis (PCA) (Shi et al., 2011). Source apportionment results of aerosols over the Western Pacific Ocean, Southern Ocean and Prydz Bay indicated that different elements enriched in different source categories (crustal, marine, or anthropogenic) (Huang et al., 2003). Most of these studies focused on qualitative analysis rather than quantitative analysis (Vallius et al., 2003). Studies on the specific quantitative source apportionment to obtain detailed source information for limited objective conditions are rarely found.

The Yellow Sea is a semi-closed area of the Northwest Pacific Ocean without large riverine inputs, and atmospheric deposition is an important source of elements in the ocean. The Yellow Sea is situated at the pathway for atmospheric particulates to be transported from Asia to the central North Pacific (Gao et al., 1992; Zhang et al., 2007). Source apportionment of atmospheric particulates over the Yellow Sea is important to understand the impact of continental sources on marine environment. In this study, the quantitative source apportionment results of aerosols over the Yellow Sea were obtained using the PCA and the positive matrix factorization (PMF). The contribution of each source in different seasons is discussed.

2. Methodology

2.1. Particulate collection

The yellow Sea, as marginal sea of Western Pacific Ocean, is surrounded by Chinese Mainland and Korean Peninsula. The maximum distance from our sampling locations to the mainland was about 110 km, while the minimum was about 30 km. Total suspended particular (TSP) samples were collected using two high-volume samplers (KC-1000, Laoshan electronic instrument company of Qingdao) during the years of 2006 and 2007. The samplers were placed on the front deck of the “DongFangHong-2” research vessel. The sampling flux was 1 m^3 min^{-1}. The duration was approximately 10 h. The samplers were turned off to avoid self-contamination when the ship anchored for other research activities. The sampling information of each sample is listed in Table 1.

Whatman 41 paper sheets were used to collect the TSP to determine the metal concentration, and Whatman QM-A quartz films were used to determine the concentration of water-soluble ions and total carbon. The quartz films were preheated at 450 °C for 5 h to remove the organic compounds. After sampling, the membrane was placed in a clean plastic bag and stored in a refrigerator (−80 °C) before weighting and chemical analysis. Clean nipper and disposable plastic gloves were used during the operation process to avoid external pollution.

2.2. Chemical analysis

The TSP samples were balanced until the weights were constant in the conditions of uniform temperature and humidity. Then, the sample films were cut into portions for the analysis of different compound concentrations.

The concentration of TC in samples collected on QM-A quartz films was determined using a TOC-5000A (Shimadzu Corporation). The samples collected on Whatman 41 papers were digested using a mixed solution of HNO_3 and $HClO_4$ in a microwave to analyze the metal concentrations. The amounts of V, Cu, Zn, Pb, and Cd were analyzed using an Atomic Absorption Spectroscopy (AAS); the detection limits were 0.2, 0.2, 3.1, 0.01, and 0.03 $\mu g\ L^{-1}$, respectively, and the recovery rates were 99.0%, 105.4%, 96.1%, 94%, and 104.6%, respectively. The concentrations of Fe and Al were measured by an Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) at a detection limit of 0.01 mg L^{-1}. The recovery rates of Fe and Al were 95.1% and 102.5%, respectively (Jin et al., 2009).

The TSP samples collected on QM-A quartz films were ultrasonically extracted with Milli-Q water in an ice-water bath to analyze the water-soluble ions. The concentrations of Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and K^+ were determined using an Ion Chromatograph (ICS-3000, Dionex). A blank sample was analyzed in the same procedure and was used to deduct the blank value. The detection limits, precision, relativity coefficient and linear ranges of ion chromatography are listed in Table 2.

2.3. Statistical analysis

Multivariate statistical analysis was performed using an SPSS software 15.0 (consultation with the free version). PCA with varimax normalized rotation was performed when the TSP data set (43 samples, and 17 variables) was used as input.

A series of backward air trajectories was calculated using the Windows version of the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Hess, 1998). In this study, the 72-h back trajectory was chosen by considering the lifetime of the different secondary species (Abdalmogith and Harrison, 2005). These trajectories at 1000 m altitude were computed at 00:00, 06:00, 12:00 and 18:00 UTC for each sampling day when the reanalysis meteorological data from the Atmospheric Research by the National Centers for Environmental Prediction/ National Center for (NCEP/NCAR) was used as input (Kong et al., 2010). Cluster analysis was used to group the trajectories into several different paths. The aim of the clustering technique is to maximize the homogeneity of the trajectories within the clusters and to maximize the heterogeneity among the clusters (NOAA’s ARL, 2009; Makra et al., 2011).

3. Results and discussion

3.1. Overview of the TSP samples

The seasonally averaged concentrations of chemical species during the four seasons are summarized in Table 3. The concentration of TSP varied from 41.15 to 256.40 $\mu g\ m^{-3}$ with the average value of 123.22 $\mu g\ m^{-3}$. The TSP averaged concentrations in four seasons ranked as spring $>$ winter $>$ autumn $>$ summer. The average of TSP in spring was approximately 2.6 times of that in summer.

Metal elements accounted for 2.34% of the mass concentration of TSP. Al was the dominant trace metal with a concentration in the range of 299.5–1791 ng m^{-3}. Fe was the second-most abundant trace metal, with a concentration ranging from 326.5 to 2111 ng m^{-3}. The concentrations of other trace elements in the marine TSP samples ranked as Zn (65.1–291.8 ng m^{-3}) $>$ Pd (42.3–148.7 ng m^{-3}) $>$ Cu (8.7–22.5 ng m^{-3}) $>$ V (4.0–11.2 ng m^{-3}) $>$ Cd (0.04–5.11 ng m^{-3}).