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# Element composition and source apportionment of atmospheric aerosols over the China Sea

**Ruojie Zhao [1], Bin Han [2], Bing Lu [3], Nan Zhang [1], Lin Zhu [1], Zhipeng Bai [2]**

[1] *College of Environmental Science and Engineering, Nankai University, Tianjin 300071, People's Republic of China*
[2] *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, People's Republic of China*
[3] *Yunnan Kaisen Environmental Protection Technology Co., Ltd, Kunming 650105, People's Republic of China*

## ABSTRACT

Four categories of different size marine aerosols ($PM_{1.0}$, $PM_{1.0–2.5}$, $PM_{2.5–10}$ and $PM_{10–100}$) were collected from the Yellow Sea and East China Sea in the spring of 2011 and analyzed for 22 elements by inductively coupled plasma–mass spectrometry (ICP–MS). The enrichment factors and air mass backward trajectory analysis were used to identify the potential sources. During the sampling periods, two sampling areas were influenced by Asian Dust on the basis of Al concentrations (an indicator of mineral dust). Average mass concentrations of particles showed relatively higher values in the Yellow Sea except $PM_{2.5–10}$. Al, Ba, Ca, Fe, Mg, Ti, Na, K, Pb, Zn, Cr, P and Zr were abundant elements and they accounted for more than 96% of the total concentrations of elements in all samples of the two areas. High levels of trace elements were associated with the airflow from Asia as the air passed over heavily populated and industrialized regions before reaching the northwest Pacific Ocean. For the crustal elements, there were higher levels in the East China Sea, while the anthropogenic elements showed higher levels in the Yellow Sea. These results indicated that Asian Dust Storm had more effects on East China Sea during the sampling periods, and Yellow Sea suffered from more influence by human activities. Size distribution analysis revealed that elements derived from crust and anthropogenic sources tend to reside in fine particles and owing to the long distance away from the land, the concentrations of anthropogenic elements in $PM_{2.5}$ were slightly higher in the East China Sea than those in the Yellow Sea. The results also suggested that the impact of Asian Dust presented a downward trend from west to east and from north to south in general.

***Keywords:*** *Yellow Sea, East China Sea, marine aerosols, trace elements, size distribution*

***Corresponding Author:***
*Lin Zhu*
☎ : *+86-22-23504379*
🖷 : *+86-22-23508807*
✉ : *zhulin@nankai.edu.cn*

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## 1. Introduction

In the context of rapid economic development and industrial growth, and the lack of waste control measures in Northeastern Asia, particularly in China, anthropogenic emissions into the atmosphere have had a drastical increase in recent years. Asian Dust Transport (ADT) (Gao et al., 1992a), a long–range transport process of dust advected off the Asian continent in the springtime, delivers soil dust originating from the loess and desert regions, and a variety of atmospheric substances to the adjacent sea and remote wide areas of the North Pacific (Duce et al., 1980; Uematsu et al., 1983; Zhang et al., 2001; Park et al., 2004; Nakamura et al., 2005; Han et al., 2008). Atmospheric pathway has been recognized as an important source for many oceanic chemicals, including Fe (Duce and Tindale, 1991; Gao et al., 2001), Al (Kang et al., 2009), Cu (Kocak et al., 2005), Zn (Spokes et al., 2001; Kang et al., 2009), and Pb (Lin et al., 2000; Kocak et al., 2005; Kang et al., 2009). Recently, scientists have documented that the concentrations of crustal–originated metals in the atmosphere decreased exponentially from the source to downwind regions during the long–range transport (Gao et al., 1992a; Spokes et al., 2001; Han et al., 2008). However, it is still estimated that $6–12\times10^6$ tons of Asian crustal materials are transferred to the central North Pacific annually (Uematsu et al., 1983). Some nutrients in the atmosphere have also been found to affect marine ecosystems when aerosol particles are deposited and dissolved in the ocean (Duce et al., 1991). Aeolian iron Fe fluxes in the dust aerosol can enrich the ocean and influence the photosynthetic rate of marine phytoplankton (Fung et al., 2000; Gao et al., 2001).

Studies on elemental compositions, inorganic ions and carbonaceous concentrations of aerosols have been conducted on remote islands in China Sea (Liu et al., 1998; Kaneyasu and Takada, 2004; Feng et al., 2007), Ulleung Island in the East/Japan Sea (Kang et al., 2011), Jeju Island near South Korea in the Yellow Sea (Chen et al., 1997; Kim et al., 1998; Park et al., 2004; Topping et al., 2004), by shipboard measurements in the Japan/East Sea (Kang et al., 2009) and China Sea (Gao et al., 1996; Gao et al., 1997; Liu and Zhou, 1999; Nakamura et al., 2005; Sheng et al., 2005; Zhang et al., 2007; Kim et al., 2009) to evaluate the relative importance of source intensities to marine aerosols. These studies have generally defined specific variation trends of aerosol loadings and characteristics that are largely dependent on continental sources and the air mass history. However, there is relatively little information on overall features of marine aerosols in the China Sea.

The China Sea, surrounded by China, Korean peninsula, and Japanese islands, is in the transport path of the continental pollutants and Asian Dust to the Pacific when northwestern winds prevail. In the past decades environmental deterioration in China made the China Sea extremely sensitive to external ecosystem changes. The atmospheric input has exposed great impact on the environment of this area. It is, therefore, essential to collect aerosols in the China Sea in order to have a comprehensive understanding about the interaction of land and sea.

Liu et al. (1994) once investigated the size distribution of marine atmospheric particles at Near–China Ocean, however, most of the previous researchers focused their investigations on the continent (Wang et al., 2005; Wang et al., 2009; Song and Gao, 2011; Pan et al., 2013). Thus in this study we carried out intensive ship sampling over the Yellow Sea and East China Sea, and collected four categories of different size particles: $PM_{1.0}$, $PM_{1.0–2.5}$, $PM_{2.5–10}$ and $PM_{10–100}$, which provided important data to evaluate the size distribution of the elements. The major objective of this study is to investigate the nature and sources of aerosols through the analyses of their chemical properties, size distribution and transport path, and to provide important data to evaluate the role of atmospheric pathways of terrigenous materials in the marine biogeochemical cycles.

## 2. Methodology

### 2.1. Sample collection

Atmospheric PM samples were collected using a low volume sampler (LVS3, Germany) over the China Sea during March and April, 2011. The active volumetric flow control system maintained a constant volumetric flow at a rate of 2.3 $m^3$/h. The impactor (Cascade Preseparator, Kalman System Ltd.) allowed aerosol collection onto three stages equipped with substrates, and onto a quartz fiber filter (QFF). The cut–offs for each stage were: <1 µm (base filter), 1–2.5 µm (Stage 1), 2.5–10 µm (Stage 2), 10–100 µm (Stage 3). The samplers were installed on the top roof of the "Dong Fang Hong–2" research vessel. To reduce the possibility of sample contamination, the sampler was turned off when the ship anchored for other research activities. Detailed sampling information was summarized in Table S2 (see the Supporting Material, SM), along with the ship tracks shown in Figure S1.

Prior to sampling, quartz fiber filters were kept at 650 °C for 5 h to remove any organic compounds that may be present. Filters were weighted by a sensitive microbalance (Mettler Toledo, MX5) with a sensitivity of ±0.010 mg. Prior to weighing, the filters were equilibrated in a desiccator at room temperature over 48 h. After sampling, the filters were removed from the inlet and put in the plastic sylphon. After weighing, the filters were stored in a freezer (at −4 °C) until chemical analysis.

### 2.2. Chemical analyses

The samples were subdivided into two groups according to the sampling area: Yellow Sea and East China Sea (see the SM, Figure S1). Concentrations of $PM_{1.0}$, $PM_{1–2.5}$, $PM_{2.5–10}$ and $PM_{10–100}$ were obtained by standard gravimetric methods. Half of each quartz fiber filter was cut into portions for individual analysis for 22 elements (Al, Ba, Ca, Fe, Mg, Zr, Sr, Ti, Na, P, K, V, Cr, Mn, Ni, Cu, Zn, As, Y, Mo, Sn, and Pb). Elements were extracted into acid solution using a hot plate in the following sequence: after broken into pieces, filter samples were placed in a vessel of solution container and treated initially by concentrated acid solutions (0.5 mL $HNO_3$ and 1 mL HF). After placed into a stainless steel vessel and covered, they were then put into an oven for 24 h at 190 °C (total digestion). Cooling it after taken out, the vessel was boiled to dryness on a hot plate (190 °C). This was repeated for another time. Five mL $HNO_3$ was added into the vessel, and then it was kept at 130 °C for 3 h. The solution was cooled and transferred into a clean plastic bottle. Three mL of extracted solution was transferred into a Teflon vial and finally it was diluted to 50 mL using distilled water. The extracts were then analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) (IRIS Intrepid II, Thermo Electron).

### 2.3. Atmospheric circulation overview

Based on NCEP FNL analysis data (1°x1°), average atmospheric circulation near the ground was analyzed during the observation periods of two areas (see the SM, Figure S2). During the sampling period over the Yellow Sea, atmospheric circulation changed quickly and the source routes of air masses were very complicated. A cold high pressure system could be found in Shandong Peninsula and Yellow Sea was located in advance of the cold front and controlled by northeasterly wind. However, weather was relatively stable and the northerly winds prevailed during the sampling period over the East China Sea. Air masses arriving in this region mainly came from Inner Mongolia and North China Plain.

### 2.4. Quality assurance and quality control

Each filter was weighted 3 times before and after sampling and the average value was used. All the glassware and filters assembly were acid washed and oven dried to avoid contamination among samples.

For elements analysis, calibration was achieved using multi–element standards prepared from stock solution in 2% $HNO_3$. The quality assurance and quality control of analyses were validated by analyzing two types of standard reference materials (Soil Standard Series: GBW 07408 for ocher and GBW 07404 for calcareousness, produced by National Research Center for Certified Reference Materials, China). The recovered values for all the target elements fell into the range or within 5% of the certified values. Indium was added to the cooled extracts as an internal standard to monitor analytical drift. Three different concentrations (100 ppm, 50 ppm, and 1 ppm) of V, Fe, Cu, Zn, Cd, Pb and Al were used to protract the standard curves. To check the accuracy of the analysis of the acidic digestions, standard soil materials were pre–treated and analyzed with the same procedure. For most elements, relative analytical errors were less than 10%. Two random filters were chosen and cut into two pieces with about the same area. Pre–treatment and analysis were simultaneously conducted for parallel analysis. 2 mL $HNO_3$ and 10 mL HCl were added into a 100 mL bottle, diluted to scale line, to avoid the error of the equipment during analyzing.

## 3. Results and Discussions

### 3.1. Overall mass concentrations

Comparison of the total average mass concentrations of four size fractions between the two sampling areas was shown in Figure 1. Results indicate that the mass concentrations of aerosols over the Yellow Sea were higher compared to those over the East China Sea except $PM_{2.5–10}$. Yellow Sea is surrounded by Chinese mainland and Korean peninsula, and much closer to the land than East China Sea which is a relatively open sea. To a great extent, the aerosols in the oceans are controlled by inputs from the continental atmosphere, especially for coastal waters. Thus, the geographic position may explain the higher mass concentrations over the Yellow Sea.

We used the sum of $PM_{1.0}$ and $PM_{1.0–2.5}$ to represent the mass concentration of $PM_{2.5}$. Similarly, $PM_{10}$ is the sum of $PM_{1.0}$, $PM_{1.0–2.5}$ and $PM_{2.5–10}$. The fine/coarse ratio has commonly been used as a first step in attempting to identify natural and anthropogenic sources of particles. In the present study, this ratio was 70% in the Yellow Sea and 51% in the East China Sea, respectively. In the previous research which was carried out in Bohai Sea in the spring of 2007, Ji et al. (2011) observed that 57% of $PM_{10}$ was associated with $PM_{2.5}$. Coal combustion, mobile vehicles and secondary pollutants (Zhang et al., 2007) are mainly found in fine particles. According to the relevant data from Chinese Statistical Yearbook of 2007 and 2011, the possession of civil vehicles, industrial waste gas emissions and coal combustion in China had increased by 42 million (from 36 to 78), 18 818 billion standard cubic meters (from 33 099 to 51 917), and 370 million tons (from 1 839 to 2 209) in four years, respectively. Therefore, the ratio of $PM_{2.5}/PM_{10}$ was greater in the Yellow Sea than that in Bohai Sea.