Atmospheric Environment 127 (2016) 22–33

Contents lists available at ScienceDirect

Atmospheric Environment

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

The contribution of anthropogenic sources to the aerosols over East China Sea

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HIGHLIGHTS

- Six main contributors to aerosols over coastal ECS are identified.
- Over 50% of resolved aerosol mass is contributed by anthropogenic sources.
- Anthropogenic emissions are mainly from Shandong and Yangtze River Delta.
- Ship emission is a significant source of aerosols over coastal ECS in summer.

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form
26 November 2015
Accepted 1 December 2015
Available online 9 December 2015

Keywords:
Aerosols
Source apportionment
Anthropogenic contribution
East China Sea

ABSTRACT

Total suspended particulate (TSP) samples were collected at a pristine island (Huaniao) in northern East China Sea (ECS) between Mar. 2011 and Jan. 2013 and analyzed for the concentrations of major ions and trace elements. Aerosol sources and the distribution of source regions are identified using positive matrix factorization (PMF) and potential source contribution function (PSCF) methods. It is found that aerosols over Huaniao Island are contributed by six main factors including primary industrial emissions (11.3%), secondary aerosol (22%), oxalate-associated aerosol (15.7%), sea salt (36.7%), ship emission (6.3%) and mineral dust (8.1%). Anthropogenic source contribution to the resolved aerosol mass reached the highest (76.6%) and lowest (18%) values in January 2013 and August 2012 respectively, strongly influenced by the prevailing winds of East Asian monsoon. The main source regions of secondary aerosol are southeastern Hebei and Shandong, which is consistent with the most intensive distribution of coal-fired power plants and the largest emission of precursors in this area. Oxalate-associated aerosol is produced primarily along the coastal line. Primary industrial emissions mainly originate from southwestern Shandong and Yangtze River Delta.

1. Introduction

Atmospheric aerosols not only execute adverse impacts on human health, visibility and acid deposition, but also influence the Earth's radiation budget. Sulfate and organic aerosols can affect cloud properties by providing additional cloud condensation nuclei (CCN) (Ramanathan et al., 2001), and black carbon (BC) absorbs solar radiation (Ramanathan and Carmichael, 2008). Aerosols may change the precipitation pattern and regional atmospheric stability, which leads to an unstable large-scale convection and the change of monsoonal circulation and hydrologic cycle (Huang et al., 2007). Atmospheric deposition of nutrients and pollutants can also affect land and ocean biogeochemical cycles (Mahowald, 2011).

Large quantities of anthropogenic aerosols were produced over East Asia, especially in China, during the past three decades due to rapid industrialization, urbanization and the increase of traffic flow. Anthropogenic aerosols in this region comprise a mixture of sulfates, nitrates, ammonium, organic carbon, black carbon, heavy metals and arsenic (As) (Duan and Tan, 2013; Zhao et al., 2013). Aerosols derived from anthropogenic emissions are typically in a fine mode with the aerodynamic diameter less than 1 μm (Han et al., 2006), which may undergo a long-range transport to eastern China seas and further region (Moreno et al., 2012; Uematsu et al., 2010). Anthropogenic SO_x (SO_2 and sulfate) produced primarily by burning of fossil fuel in East Asia may change

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http://dx.doi.org/10.1016/j.atmosenv.2015.12.002
1352-2310/

sulfate aerosol concentration over the North Pacific during the late winter and early spring (Tan et al., 2002). Nitrogen oxides (as precursors of HNO_3) and NH_3 emitted mainly from industrial and agricultural activities respectively can combine together to form NH_4NO_3 (Pathak et al., 2004), which may significantly influence the aerosol optical properties and direct radiative forcing (Park et al., 2014). In eastern China, insoluble organic carbon (OC) of $PM_{2.5}$ is contributed mostly by biomass burning and biogenic sources (contribution: 59%), whereas refractory elemental carbon (EC) is derived mainly from burning of fossil fuel (contribution: 78%) (Liu et al., 2013). Vehicle emission, fossil fuel combustion and industrial metallurgical processes are important sources for aerosol heavy metals and As in China (Duan and Tan, 2013; Tian et al., 2015).

Positive matrix factorization (PMF) has been used widely in aerosol source apportionment (Choi et al., 2013; Han et al., 2006; Moon et al., 2008; Polissar et al., 2001; Viana et al., 2008). The source area and emission probability can be mapped using potential source contribution function (PSCF) model based on the source categories identified by PMF. Previous studies have demonstrated the potential source regions for soil dust, fresh and aged sea salt, coal and fuel oil combustion, biomass burning, industry pollution and secondary aerosols in East Asia (Choi et al., 2013; Han et al., 2006; Moon et al., 2008). Nonetheless, most of the studies focused on the composition and sources of aerosols in urban area, and very few research sites were located in the downwind oceanic region. Thus the understanding of anthropogenic sources that contribute to the aerosols over ECS is still very limited.

Our sampling site, Huaniao Island, is located approximately 100 km to the Yangtze River estuary in northern ECS and will be first struck by the air pollutants transported from Yangtze River Delta (YRD) and northern China to ECS. It is also under the impact of ship emissions from Yangshan Port, one of the largest container ship ports in the world. The long-term observation at this site is very helpful for understanding the anthropogenic contribution to the aerosols over ECS. In this study, the source contributions to aerosols and their variation with the season are identified by PMF based on the two-year observatory data, and spatial distributions of apportioned anthropogenic sources are analyzed by PSCF model.

2. Methodology

2.1. Aerosol sampling

The sampling site (122.67°E, 30.86°N) is on Huaniao Island in northern ECS (Fig. 1). The local emissions are negligible since only about 200 fishermen households live there. This site stands for the frontline of ECS influenced by the aerosols transported from eastern China. Total suspended particulate (TSP) samples were collected using a high volume sampler (1130 L min^{-1}, Thermo Scientific). Aerosols were collected on an acid-cleaned Whatman® Grade 41 cellulose filter (20.3 × 25.4 cm) and the duration was 24 h. The total aerosol mass was obtained through weighing the filters before and after aerosol collection by a balance with a reading precision of 10 μg (Sartorius 2004 MP®). The filters were kept at a constant temperature (20 ± 1 °C) and relative humidity (40 ± 1%) for 24 h before weighing. The numbers of samples and field blanks collected in each sampling period are listed below:

2.2. Chemical analysis

One-thirty-second (1/32) of each TSP sample or operational blank was cut and extracted ultrasonically by 20 mL of milli-Q water (18.25 MΩ cm^{-1}). Thirteen ions were analyzed by Ion Chromatography (ICS 3000, Dionex) including SO_4^{2-}, NO_3^-, F^-, Cl^-, NO_2^-, PO_4^{3-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, acetate (Ac^-) and oxalate ($C_2O_4^{2-}$). One-sixteenth (1/16) sub-sample was digested with 8 mL of ultrapure HNO_3 and 0.6 mL of ultrapure HF (purified from GR HNO_3 and HF by sub-boiling distillation) in MARS Xpress microwave digestion system, and a total of 22 elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Ti, V and Zn) were determined using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; SPECTRO, Germany). Detailed procedures for analysis of ions and trace elements were given in previous studies (Guo et al., 2014; Zhu et al., 2013).

The average repeatability for soluble ions analyzed by ICS-3000 is less than 5%. The average repeatability for elements determined by ICP-OES is about 5.7%, and the digestion recoveries for all of the certified elements range from 80% to 120%. The detection limits (DLs) are calculated as three times the standard deviation of the blank filters and converted to ng m^{-3} using the volume of the extraction solution and sampling duration and flow rate. The DLs for soluble ions of SO_4^{2-}, NO_3^-, F^-, Cl^-, NO_2^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, acetate and oxalate in aerosols are 2.4, 7.2, 3.6, 2.4, 2.4, 26, 11, 29, 6.4, 4.3, 8.1 and 5.7 ng m^{-3}, respectively. For the total digestion of the aerosol samples, the DLs are 8.0–34 ng m^{-3} for Al, Ca, Fe, Na, P and S, 1.4–5.7 ng m^{-3} for Cu, K, Mg, Mn and Zn, and 0.1–0.9 ng m^{-3} for As, Ba, Cd, Ce, Co, Cr, Mo, Ni, Pb, Ti and V. Field blanks are subtracted from the sample results.

2.3. Positive matrix factorization

The updated version PMF 3.0 (USEPA, 2008) is used, which decomposes a matrix of speciated sample data **x** into a source contribution matrix **g** and a source strength matrix **f** (Paatero, 1997).

$$\mathbf{x}_{ij} = \sum_{k=1}^{p} \mathbf{g}_{ik}\mathbf{f}_{kj} + e_{ij} \quad (1)$$

Where x_{ij} is the atmospheric concentration of each species j in each sample i collected at the receptor site; g_{ik} is the contribution of each source k (or source score) to each sample i; p is the number of source factors; f_{kj} is the mass fraction (or source loading) of each species j in each source k; e_{ij} is the residual or error for each sample (Norris et al., 2008).

The results are constrained as no negative contribution from a source to a sample and therefore the ambiguity caused by rotating factors is minimized. In addition, each data point is individually weighed. The missing value is replaced by median of the data set accompanied with a large uncertainty in order that the missing data will not significantly weigh the results (Norris et al., 2008). The PMF solution minimizes the object function Q based upon the uncertainties (u).

$$\mathbf{Q} = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{\mathbf{x}_{ij} - \sum_{k=1}^{p}\mathbf{g}_{ik}\mathbf{f}_{kj}}{u_{ij}}\right)^2 \quad (2)$$

Positive matrix factorization method requires an estimate of uncertainty for each data point (Norris et al., 2008). When the concentration is greater than minimum detection limit (MDL), the uncertainty can be calculated as:

$$Unc = \sqrt{(ErrorFraction \times concentration)^2 + (MDL)^2}. \quad (3)$$

If the concentration is less than or equal to MDL, the uncertainty is calculated using the following equation: