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Investigating the contribution of shipping emissions to atmospheric $PM_{2.5}$ using a combined source apportionment approach☆

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ABSTRACT

Many studies have been conducted focusing on the contribution of land emission sources to $PM_{2.5}$ in China; however, little attention had been paid to other contributions, especially the secondary contributions from shipping emissions to atmospheric $PM_{2.5}$. In this study, a combined source apportionment approach, including principle component analysis (PCA) and WRF-CMAQ simulation, was applied to identify both primary and secondary contributions from ships to atmospheric $PM_{2.5}$. An intensive $PM_{2.5}$ observation was conducted from April 2014 to January 2015 in Qinhuangdao, which was close to the largest energy output port of China. The chemical components analysis results showed that the primary component was the major contributor to $PM_{2.5}$, with proportions of 48.3%, 48.9%, 55.1% and 55.4% in spring, summer, autumn and winter, respectively. The secondary component contributed higher fractions in summer (48.2%) and winter (36.8%), but had lower percentages in spring (30.1%) and autumn (32.7%). The hybrid source apportionment results indicated that the secondary contribution (SC) of shipping emissions to $PM_{2.5}$ could not be ignored. The annual average SC was 2.7%, which was comparable to the primary contribution (2.9%). The SC was higher in summer (5.3%), but lower in winter (1.1%). The primary contributions to atmospheric $PM_{2.5}$ were 3.0%, 2.5%, 3.4% and 2.7% in spring, summer, autumn and winter, respectively. As for the detailed chemical components, the contributions of shipping emissions were 2.3%, 0.5%, 0.1%, 1.0%, 1.7% and 0.1% to elements & sea salt, primary organic aerosol (POA), element carbon (EC), nitrate, sulfate and secondary organic carbon (SOA), respectively. The results of this study will further the understanding of the implications of shipping emissions in $PM_{2.5}$ pollution.

1. Introduction

$PM_{2.5}$ (i.e., fine particles with an aerodynamic diameter smaller than 2.5 μm) is the major air pollutant in most areas of China. It has a significant influence on human health (Kollanus et al., 2017; Qi et al., 2017) and visibility degradation (Zhou et al., 2015a). It is necessary to effectively reduce the atmospheric $PM_{2.5}$ concentration to mitigate those adverse effects. Understanding the contributions of different emission sources to $PM_{2.5}$ is an important basis for making effective $PM_{2.5}$ pollution mitigation measures. During the past decade, many studies have been conducted to investigate the contributions from sources on land, such as motor vehicles (Abu-Allaban et al., 2007), industry (Bari and Kindzierski, 2016) and biomass burning (Li et al., 2014; Long et al., 2016). However, the influence of emissions from ships, which are considered as “mobile power plants”, received little attention.

Receptor models were useful methods to identify the contributions of emission sources to atmospheric $PM_{2.5}$ (Hua et al., 2015; Song et al., 2006; Zhang et al., 2014b). Some studies have been conducted to obtain the contribution of shipping emissions using various apportionment approaches. For example, Tao et al. (2017) identified the contribution sources for $PM_{2.5}$ in Guangzhou and Zhuhai based on a positive matrix factorization (PMF) analysis, indicating that the primary contribution of shipping emissions to atmospheric $PM_{2.5}$ was >17% in the two cities. Wang et al. (2016) found that shipping emissions contributed 6.3% (primary contribution) of the atmospheric PM in the northern East China Sea, also

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based on a PMF analysis. The study of Yau et al. (2013) showed that 25% (primary contribution) of the $PM_{2.5}$ in Hong Kong was attributed to shipping emissions based on PCA analysis. It can be found that most of the previous studies focused on the contribution of shipping emissions to primary $PM_{2.5}$ due to the limitations of the source apportionment methods used (Lang et al., 2017). The secondary contribution of shipping emissions to $PM_{2.5}$ is still unclear. However, ships could emit large amounts of $PM_{2.5}$ precursors (e.g., SO_2 and NO_2) from heavy fuel oil combustion, and these substances could transform into secondary $PM_{2.5}$ (e.g., sulfate and nitrate) through complex homogeneous/heterogeneous chemical reactions (George et al., 2015; Liu et al., 2017). As a result, the contribution of shipping emissions to secondary $PM_{2.5}$ cannot be ignored. It is necessary to further investigate the comprehensive implications of ship emissions on $PM_{2.5}$, especially on the secondary aerosols.

Qinhuangdao is a coastal city, located in the Beijing-Tianjin-Hebei (BTH) region, which is being faced with the most serious $PM_{2.5}$ pollution in China. The Port of Qinhuangdao is the largest energy output port of China. The coal output accounts for more than 35% of the total shipping transportation amount (CPHA, 2015). As a result, Qinhuangdao could be a typical case study area for studying the contribution of shipping emissions to atmospheric $PM_{2.5}$.

The aim of this study was to investigate the comprehensive (both primary and secondary) contributions of shipping emissions to atmospheric $PM_{2.5}$ in Qinhuangdao. (1) A combined source apportionment approach, including observation, principal component analysis (PCA) and chemical transport model simulation, was firstly applied to comprehensively estimate the contribution of shipping emissions to both the primary and secondary components in $PM_{2.5}$. (2) An intensive $PM_{2.5}$ observation was conducted from April 2014 to January 2015, and detailed $PM_{2.5}$ chemical components in different seasons (spring, summer, autumn and winter) were obtained. (3) The PCA was used to identify the contribution of shipping emissions to elements and sea salt in $PM_{2.5}$. (4) The WRF-CMAQ was applied to simulate the contribution of shipping emissions to $PM_{2.5}$ precursors (e.g., SO_2, NO_2 and VOCs), POA and EC based on estimated shipping emissions. (5) Then, the contribution of shipping emissions to $PM_{2.5}$ was further estimated. (6) In addition, the estimated contribution of shipping emissions was compared with other studies, and the uncertainty of the calculation results was also analyzed.

2. Methodology

2.1. Shipping emission contribution estimation framework

The contribution of shipping emissions to $PM_{2.5}$ was a sum of the contributions to primary and secondary components. For the contribution to primary species (elements & sea salt, POA and EC), it could be estimated by PCA or WRF-CMAQ. As for the contribution to secondary components (SO_4^{2-}, NO_3^- and SOA), it was assumed to be equal to that of the corresponding precursors (SO_2, NO_2 and VOCs) (Cheng et al., 2013; Lang et al., 2017). As a result, the contribution of shipping emissions could be estimated by the following equation (1):

$$CR_{SE} = CR_{SE,primary} + CR_{SE,secondary} \quad (1)$$

$$CR_{SE,primary} = P_{elements} \times CR_{SE,elements} + P_{POA} \times CR_{SE,POA} + P_{EC} \times CR_{SE,EC} \quad (2)$$

$$CR_{SE,secondary} = P_{SO_4^{2-}} \times CR_{SE,SO_2} + P_{NO_3^-} \times CR_{SE,NO_2} + P_{SOA} \times CR_{SE,VOCs} \quad (3)$$

where CR_{SE}, $CR_{SE,primary}$ and $CR_{SE,secondary}$ are the contributions of shipping emissions (SE) to the total, primary and secondary $PM_{2.5}$, respectively; $CR_{SE,elements}$, $CR_{SE,POA}$ and $CR_{SE,EC}$ represent the SE contribution to the elements, POA and EC of $PM_{2.5}$, respectively; $CR_{SE,SO2}$, $CR_{SE,NO2}$ and $CR_{SE,VOCs}$ indicate the SE contribution to different $PM_{2.5}$ precursors − SO_2, NO_2 and VOCs, respectively; and $P_{elements}$, P_{POA}, P_{EC}, P_{SO42-}, P_{NO3-} and P_{SOA} are the mass fractions in the $PM_{2.5}$ for elements, POA, EC, SO_4^{2-}, NO_3^- and SOA, respectively. The mass fractions of detailed components in $PM_{2.5}$ were obtained based on $PM_{2.5}$ sampling and analysis. The SE contribution on elements ($CR_{SE,elements}$) was obtained based on principal components analysis. The SE contributions on POA, EC, SO_2, NO_2 and VOCs were simulated by the WRF-CMAQ modeling system. The straightforward diagram of the combined approach can be found in Fig. 1.

2.2. $PM_{2.5}$ sampling and chemical components analysis

To obtain the atmospheric $PM_{2.5}$ components, an intensive $PM_{2.5}$ observation was conducted in Qinhuangdao. The sampling site was located in a building roof, roughly 10 m off the ground. It was approximately 1.7 km from the city center and 1.3 km from the Port of Qinhuangdao (Fig. 2), and there were no large air pollutant emission sources in the surrounding areas. As a result, the site could well represent the atmospheric environment of the urban area of Qinhuangdao. The $PM_{2.5}$ sampling was conducted in four representative months - April, August, and October 2014 and January 2015 for spring, summer, autumn and winter, respectively. Sixty samples were obtained in the four seasons. The sampling was on a 24-h basis. The $PM_{2.5}$ samples were simultaneously collected on quartz filters (Whatman, Inc., Maidstone, UK) and Whatman 41 filters (Whatman, Inc., Maidstone, UK) for OC/EC and elements/ions analysis, respectively. Ions including SO_4^{2-}, NO_3^-, NH_4^+, Mg^{2+}, Ca^{2+}, K^+, Na^+, PO_4^{3-}, F^- and Cl^- were analyzed by ion chromatography (IC, Metrohm 861 Advanced Compact IC). Twenty-three elements were measured based on ICP-MS (7500a, Thermo) (for Na, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, Ce, Eu, and Pb) and ICP-AES (Ulttma, Jobin Yvon Co., Ltd., France) (for S), respectively. The OC/EC were measured using a Thermal/Optical Carbon Analyzer (DRI, Model, 2001). The details for chemical components analysis and QA/QC can be found in Lang et al. (2017) and Wang et al. (2015). The primary organic aerosol (POA) and secondary organic aerosol (SOA) were further estimated by the minimum ratio of the OC/EC method (Wang et al., 2015). The obtained chemical compositions were then used to estimate the contribution of shipping emissions to the $PM_{2.5}$.

2.3. Shipping emissions

Shipping emissions were needed to simulate their contribution to $PM_{2.5}$ precursors (i.e., POA, EC, SO_2, NO_2 and VOCs). As a result, a high temporal-spatial resolution shipping emission inventory around the Port of Qinhuangdao was estimated. The emissions were calculated for each ship based on the Automatic Identification System (AIS) data, including ship name, ship type, shipping speed over the ground, navigational status (operating mode), heading, rate of turn, position, etc. A detailed method description could be found in Chen et al. (2016). The annual CO, SO_2, NOx, VOCs, PM_{10}, $PM_{2.5}$, OC and EC shipping emissions were 1.59, 11.78, 17.69, 0.80, 1.69, 1.56, 0.31 and 0.10 Mg, respectively. It was found that SO_2 and NOx were the dominant pollutants in shipping emissions,