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Oxidative potential of ambient $PM_{2.5}$ in the coastal cities of the Bohai Sea, northern China: Seasonal variation and source apportionment ☆

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ABSTRACT

Emissions of air pollutants from primary and secondary sources in China are considerably higher than those in developed countries, and exposure to air pollution is main risk of public health. Identifying specific particulate matter (PM) compositions and sources are essential for policy makers to propose effective control measures for pollutant emissions. Ambient $PM_{2.5}$ samples covered a whole year were collected from three coastal cities of the Bohai Sea. Oxidative potential (OP) was selected as the indicator to characterize associated PM compositions and sources most responsible for adverse impacts on human health. Positive matrix factorization (PMF) and multiple linear regression (MLR) were employed to estimate correlations of $PM_{2.5}$ sources with OP. The volume- and mass-based dithiothreitol (DTT_v and DTT_m) activities of $PM_{2.5}$ were significantly higher in local winter or autumn ($p < 0.01$). Spatial and seasonal variations in DTT_v and DTT_m were much larger than mass concentrations of $PM_{2.5}$, indicated specific chemical components are responsible for $PM_{2.5}$ derived OP. Strong correlations ($r > 0.700$, $p < 0.01$) were found between DTT activity and water-soluble organic carbon (WSOC) and some transition metals. Using PMF, source fractions of $PM_{2.5}$ were resolved as secondary source, traffic source, biomass burning, sea spray and urban dust, industry, coal combustion, and mineral dust. Further quantified by MLR, coal combustion, biomass burning, secondary sources, industry, and traffic source were dominant contributors to the water-soluble DTT_v activity. Our results also suggested large differences in seasonal contributions of different sources to DTT_v variability. A higher contribution of DTT_v was derived from coal combustion during the local heating period. Secondary sources exhibited a greater fraction of DTT_v in summer, when there was stronger solar radiation. Traffic sources exhibited a prevailing contribution in summer, and industry contributed larger proportions in spring and winter. Future abatement priority of air pollution should reduce the sources contributing to OP of $PM_{2.5}$.

1. Introduction

Fine particulate matter (*i.e.*, $PM_{2.5}$, particles with aerodynamic diameters <2.5 μm), exert some significant negative effects on human health, atmospheric visibility, and climate change (Tao et al., 2009; Chen et al., 2013; Apte et al., 2015). Due to rapid economic development and urbanization in recent decades, energy consumption (especially fossil fuel and biomass energies, represented by coal, firewood, and straw) and car ownership increased rapidly in China, and resulted in severe air pollution across China (Chan and Yao, 2008). Exposure to ambient $PM_{2.5}$ pollution exceeding the Air Quality Guidelines by World Organization Health (WHO) may lead over 1.3 billion Chinese population at higher health risk (Song et al., 2017). Therefore, $PM_{2.5}$ pollution is a nationwide problem and public concern in China, and the government (policy makers) urgently need the relevant information to control and abate the source emissions of $PM_{2.5}$ (Fang et al., 2009).

To date, numerous epidemiological studies have linked long-term exposure to $PM_{2.5}$ to adverse impacts on human health, such as increased morbidity and/or mortality from

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cardiopulmonary diseases (Pope et al., 2011; Apte et al., 2015; Madaniyazi et al., 2015), asthma occurrences (Breton et al., 2012), chronic obstructive pulmonary disease (COPD, Ni et al., 2015), and lung cancer (Zhou et al., 2016). A number of studies have proposed the credible pathological mechanisms for explaining the health effects of $PM_{2.5}$ that the redox chemical components of $PM_{2.5}$ could simulate cellular generation of excessive reactive oxygen species (ROS) and systemic inflammation (Donaldson et al., 2001; Li et al., 2003; Nel, 2005). Increasing evidence suggested that the health effects of $PM_{2.5}$ were not determined by the levels of $PM_{2.5}$ mass but chemical components and sources. Studies performed in Los Angeles found the trace levels of chemical components in $PM_{2.5}$ including polycyclic aromatic hydrocarbons (PAHs) and hopanes from the combustion sources induced health risk of systemic inflammation in older adults but bulk chemical components in $PM_{2.5}$ from natural sources not (Delfino et al., 2010). Consequently, current regulations only restriction on PM mass concentrations could not control the specific emission sources of $PM_{2.5}$ contributing to harmful health effects, especially in China, where PM concentrations were considerably high and ROS activity was underexamined.

Considering that the significance of ROS generation mediated the long-term health impacts of $PM_{2.5}$, various kinds of cellular and non-cellular methods have been developed to measure ROS formation in $PM_{2.5}$. The dithiothreitol (DTT) assay has been proven worldwide to be an effective *in vitro* method to measure the oxidative potential (OP) for PM to generate ROS (Kumagai et al., 2002; Cho et al., 2005). Extensive studies were carried out in developed countries to investigate specific PM components and their sources responsible for the variations in OP induced by $PM_{2.5}$ (Ghio et al., 2012; Verma et al., 2014; Charrier et al., 2015; Fang et al., 2016). For example, organic aerosols from biomass burning exhibited high intrinsic generation of ROS, while biogenic secondary organic aerosol were very low in Atlanta (Verma et al., 2015). Transition metals emitted from traffic (vehicular emission) and fly ash by residual oil burning were strongly linked to OP levels of PM (Antonini et al., 2004; Hoffmann et al., 2007; Gasser et al., 2009). Although there were some common components in $PM_{2.5}$ present in developed countries and developing ones, the relative fractions of components from different sources contributing to the $PM_{2.5}$ mixture were dissimilar. Therefore, there is an urgent need to illustrate the main components and calculate the source contributions of OP in developing countries, *e.g.*, China. In recent years, positive matrix factorization (PMF) has been applied to quantifying the source contributions to mass concentrations of $PM_{2.5}$ in some regions of Northern China, where $PM_{2.5}$ was mainly emitted from coal combustion, biomass burning, secondary sources, automobile sources, and dust (Zhang et al., 2013; Zong et al., 2016). However, the differences in DTT activities of the contributing PM sources are not well documented, though a previous study implemented in Beijing demonstrated that DTT activity was associated with six sources or factors: a zinc factor, an aluminum factor, a lead point factor, a secondary source, an iron source and a soil dust source, in which the secondary source explained the greatest fraction of the ROS variability measured (Liu et al., 2014).

This study examined the littoral zone of the Bohai Sea, an economically developed and densely populated region in China, where the specific energy uses are featured by huge consumption of coal combustion and domestic biomass burning (NBSC, 2016). Numerous anthropogenic sources with different scales in the eastern coastal region in China have resulted in massive emissions of various pollutants. For instance, the region generated the highest-intensity emissions from iron and steel smelting-derived air pollutants in China, including persistent organic pollutants (POPs) and heavy metals (Wang et al., 2016). Satellite and ground monitoring from the China National Environmental Monitoring Center explicitly demonstrated that the coastal region of the Bohai Sea was the core area for severe $PM_{2.5}$ pollution in China, characterized by extreme air pollution and frequent haze events (Boynard et al., 2014; Wang and Fang, 2016; Zhang et al., 2016).

The current study aimed to identify the main $PM_{2.5}$ emission sources contributing to OP in the coastal cities of the Bohai Sea by utilizing the DTT assay. Annual $PM_{2.5}$ samples were collected from three representative cities located in the littoral zone of the Bohai Sea: Jinzhou (JZ), in Liaoning Province; Tianjin (TJ), a centrally administered municipality; and Yantai (YT), in Shandong Province. Of the total $PM_{2.5}$ samples collected ($n = 417$), we determined the seasonal profiles of chemical components and the DTT activities of ambient $PM_{2.5}$ in randomly-selected samples ($n = 300$), considering the heavy workload of chemical composition and DTT activity measurements. $PM_{2.5}$ sources were apportioned using the PMF mode, and DTT activities were attributed to the corresponding sources with multiple linear regression (MLR). This work provided an essential information for the local policy makers to control emissions of OP linked to the resolved $PM_{2.5}$ sources for protecting the public health in the studied coastal cities of the Bohai Sea, where the DTT activity has never been assessed.

2. Materials and methods

2.1. Sampling site

A sampling campaign was conducted at three urban sites in JZ, TJ, and YT. Selected site locations include the Environmental Monitoring Center in JZ (121.13°E, 41.13°N), Nankai University in TJ (117.16°E, 39.11°N), and the Parkson Shopping Center in YT (121.38°E, 37.54°N), all of which are located in educational, commercial, and residential districts, respectively. The region of study experiences four distinctive seasons: spring (March, April, May), summer (June, July, August), autumn (September, October, November) and winter (December, January, February). The spring season has high-speed winds; summer has high temperatures and frequent rainfall; and winter shows cold air and low rainfall. The monthly mean temperature, precipitation, and wind speed of each city are listed in Table S1 in the Supplementary Data. All of the studied cities require heating during the cold period, generally lasting for 4 months, namely from mid-November to mid-March (NBSC, 2016).

2.2. Sample collection

The 24-hr ambient $PM_{2.5}$ was sampled over a whole year from May 2015 to April 2016. Air impact samplers with a flow rate of $100\ L \cdot min^{-1}$ (Type 2034, Qingdao Laoying, China) were used to collect ambient $PM_{2.5}$ onto 90-mm quartz microfiber filter (QAT-UP, Pall, USA), as recommended by the China Standard Method of $PM_{2.5}$ (HJ93-2013). The detailed sampling procedure was assigned as follows: (1) continuous 24-hr sampling (once per day) in one typical month selected from each season (namely high-frequency sampling); and (2) 24-hr sampling once every 7 days on average for the other time intervals. The dates of high-frequency sampling in each city were listed in Table S2. To investigate the diurnal variation, the daytime (from 7:00 a.m. to 6:55 p.m.) and nighttime (from 7:00 p.m. to 6:55 a.m.) samples were collected during the high-frequency sampling months in summer and in winter, separately. Each daytime or nighttime sample was collected in two consecutive days for adequate mass loadings. Accordingly, after the exclusion of lost or damaged samples, 145, 129 and 143 available samples were obtained for JZ, TJ, and YT, respectively. Considering heavy workloads of DTT activity and chemical constitution