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Spatial and temporal characteristics of $PM_{2.5}$ acidity during autumn in marine and coastal area of Bohai Sea, China, based on two-site contrast

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ABSTRACT

In-situ pH of atmospheric particulate, defined as the pH value of aqueous phase in ambient aerosol, has been reported to have significant influence on the formation progress of secondary aerosol, especially through the heterogeneous pathway. In this study, $PM_{2.5}$ samples were collected in the marine and costal area of Bohai Sea from September 8th to October 8th in 2013, with daytime and nighttime separated. Eight water-soluble ions including SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{2+}, Na^+ and Mg^{2+} were analyzed by ion chromatography. The in-situ pH of $PM_{2.5}$ was estimated using Aerosol Inorganics Model II, with meteorological parameters (temperature and relative humidity) and basic chemical composition data (concentrations of water-soluble ions) serving as input. Five indicators were conjunctively applied to describe the spatial and temporal characteristics of $PM_{2.5}$ acidity over Bohai Sea during autumn. As a result, strong acidity was found in both marine and coastal area. Marine area had a stronger acidity under a more NH_4^+-deficiency and humid condition. And the difference of $PM_{2.5}$ acidity between daytime and nighttime was more obvious in coastal area than that in marine area, with stronger acidity observed during the daytime. Local SO_2 emission was identified as an important factor influencing the diurnal variation of aerosol acidity. Meanwhile, sulfurous species were identified as a mixture of NH_4HSO_4 and H_2SO_4 in marine area while a mixture of NH_4HSO_4 and $(NH_4)_2SO_4$ in the coastal area. Analysis in the impact of aerosol acidity on nitrate formation has indicated that heterogeneous pathways were important in nitrate formation in coastal area of Bohai Sea as well as the homogeneous pathways.

Capsule abstract: $PM_{2.5}$ was highly acidic around Bohai Sea, and the acidity of $PM_{2.5}$ was stronger in marine area than coastal area during autumn.

1. Introduction

Ambient aerosol appears to be acidic because acidic ions such as SO_4^{2-} and NO_3^- cannot be fully neutralized by alkaline ions, such as Ca^{2+} and NH_4^+ (Pathak et al., 2011; Xue et al., 2011; Yao et al., 2011; Rengarajan et al., 2011; Huang et al., 2011). Recently, acidic aerosol has been reported to ubiquitously exist worldwide. Except for the direct inhalation, acidic aerosol can expose human health to a high risk by activating the hazardous components in particulates as well (He et al., 2012; Zhang et al., 2007; Amdur and Chen, 1989; Utell and Looney, 1995). Meanwhile, acidic aerosol can do harm to ecosystem through wet/dry deposition (He et al., 2012; Larssen et al., 2006; Likens et al., 1996). And the larger hygroscopicity of acidic aerosol can result in degradation of atmospheric visibility and disturbance in radiative balance of atmosphere because particulates' ability to scatter light and to nucleate cloud droplets can be enhanced by larger hygroscopicity (Zhang et al., 2007; Watson, 2002; Boucher and Anderson, 1995; Crumeyrolle et al., 2008).

The formation of secondary aerosol (SA) is closely interrelated to aerosol acidity, especially in the heterogeneous reactions. For the secondary inorganic aerosol (SIA), recent research has found that aerosol acidity can tip the scale in the pathway of sulfate formation. The large unidentified source of sulfate during the heavy-haze days in Beijing was explained by the oxidation from NO_2 in aerosol water content. Changes occurred in pH played a critical role in the transition to an NO_2-dominated process of aqueous sulfate production under haze days from an H_2O_2-dominated process of aqueous sulfate production in cloud droplets (Cheng et al., 2016). And for the secondary organic aerosol

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(SOA), it is reported that the catalytic action of acid in heterogeneous reactions might play a significant role in enhancing the SOA production in the atmosphere (Jang et al., 2002; Edney et al., 2005; Gao et al., 2004b; Iinuma et al., 2005). Therefore, aerosol acidity deserves to be lucubrated in the field of atmospheric physics and chemistry.

Generally, the actual aerosol acidity can't be measured directly because of low water content in particles. Thus thermodynamic models have been developed to estimate the in-situ pH in deliquesced aerosol. Thermodynamic equilibrium models such as SCAPE2 (Meng et al., 1995), ISORROPIA (Nenes et al., 1998) and EQUISOLV II (Jacobson, 1999) can extrapolate in-situ aerosol pH through measuring the pH of aerosol extracts and estimating liquid water content based on the information of ionic species, temperature and relative humidity during sampling (Yao et al., 2006). Another thermodynamic equilibrium model named AIM II (Aerosol Inorganics Model II, Clegg et al., 1998) is also widely utilized to estimate the in-situ pH of aerosol using measured strong acidity, concentrations of ionic species, average temperature and relative humidity as the input. And by comparison, Model II is more suitable to estimate in-situ aerosol pH in the atmosphere than SCAPE2 and ISORROPIA (Yao et al., 2006).

Same with other maritime countries, coastal regions own the largest population density and the most developed technology and economy in China. Circum-Bohai Sea Region, together with Yangtze River delta and Pearl River Delta has the fastest economic growth in China. Bohai Sea is semi-enclosed with an area about 78 km^2 and about one third of China's water transport vessels and fishing boats were navigated over the Bohai Sea by 2013 (China Statistical Yearbook, 2013; Chinese Fishery Statistical Yearbook, 2013). Bohai Bay, a shallow bay located in the west of Bohai Sea, is adjacent to Beijing-Tianjin-Hebei Region (the political center of China) and surrounded by Shandong province, Hebei province and Tianjin municipality. Located at the downwind area of North China Plain, Bohai Bay is inevitably impacted by regional transport of air pollution and the local emission from ships in recent years (Zhang et al., 2016).

Numbered previous studies about air pollution around Bohai Sea were focused on the characteristics of particle concentration and compositions (Gu et al., 2011; Zhang et al., 2014; Ni et al., 2013; Xu et al., 2015). However, there is rare published literature studying the characteristics of $PM_{2.5}$ acidity over the Bohai area. In this study, the experiment was designed to explore the spatial and temporal variation of $PM_{2.5}$ acidity in Bohai area during autumn. Thus, a coastal and a marine sampling site were chosen and sampling time was divided to daytime and nighttime. The $PM_{2.5}$ pollution characteristics were analyzed and five indicators were applied to discuss the characteristics of $PM_{2.5}$ acidity. Meanwhile, the impact of aerosol acidity on nitrate formation was discussed as well.

2. Experimental methods

2.1. Sampling sites

Aiming at studying the characteristics of $PM_{2.5}$ acidity in the region of Bohai Sea, the $PM_{2.5}$ samples were collected at two chosen sites noted on Fig. 1. One monitoring station was located in Tanggu district of Tianjin municipality which represents the coastal area. And the other station in Bohai Sea was also set up to compare the differences between the coast and sea.

The Tanggu (TG) sampling site (117°43′E,39°3′N) was located in Binhai meteorological warning center, approximately 4 km southwest, 8 km west and 9 km northeast from the coastline, which can represent the west coastal region of Bohai Sea. Tanggu district, located in the east of Tianjin, is the central area of Bohai Sea Economic Circle. It has the largest comprehensive trading port of northern China, Tianjin Port. Tianjin Port has an annual throughput of 250 million tons and maintains trading with over 180 countries and regions, which means that this site is inevitably affected by local emissions due to the industrialization as well as pollution transporting from Beijing-Tianjin-Hebei district.

The Bohai Sea (BS) sampling site (118°25′E,38°27′N)was located at an offshore oil drilling platform which lied in Bohai Sea and ~70 km away from the northern coast of Bohai Sea Gulf and ~40 km from the southern, as it is shown in Fig. 1. Detailed introduction about the oil drilling platform is available in Text S1. Bohai Sea, surrounded by mainland from three sides, is the only inland sea of China. So it seems that atmospheric pollutants generated from adjacent area, such as Liaotung Peninsula in the north and the whole Beijing-Tianjin-Hebei region in the west, could transport to this sampling site and play an important role due to the open marine environment.

The sampler at Tanggu sampling site was approximately 10 m above the ground and that at Bohai Sea sampling site was 30 m over the sea level. All of the $PM_{2.5}$ samples were collected from September 8th to October 8th in 2013 using medium-volume samplers (TH-150, Wuhan Tianhong Intelligence Instrumental Facility, Wuhan, China) with flow rates of 100 L min^{-1}. Considering the difference of pollutants emission and meteorological conditions between daytime and nighttime, the sampling time was divided into two 11-hour periods, 8:00–19:00 for the daytime and 20:00–7:00 (the next day) for the nighttime. Field blanks were used to determine any possible contamination. Concentration of gaseous pollutants in Tanggu was downloaded from an official website (http://106.37.208.233:20,035/) while the information of gaseous pollutants was not available in Bohai Sea. Meanwhile, hourly meteorological information including wind speed (WS, m s^{-1}), temperature (T, °C) and relative humidity (RH, %) was obtained from auto-monitoring station set at Tanggu and Bohai Sea.

2.2. Gravimetric and chemical composition analysis

Particles were collected on quartz fiber filters for subsequent gravimetric and chemical composition analysis. Each quartz filter was pre-baked in a muffle furnace for 4 h at 900 °C to reduce residual carbon level before sampling. All the filters were weighted twice on a Mettler Toledo microbalance (resolution 1 μg) before and after sampling. It is important to emphasize that filters were conditioned for 48 h in a balance room under controlled relative humidity (RH, 50 ± 5%) and temperature (T, 20 ± 1 °C) before weighting. In addition, all the quartz filters were stored in a freezer (4 °C) before subsequent composition analysis to improve the accuracy of experimental results.

The quartz fiber filters were used to analyze water-soluble ions, including SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{2+}, Na^+ and Mg^{2+}, by Ion chromatography (DX-120 IC). The method detection limits (MDLs) were within the range of 0.01 to 0.04 μg m^{-3} for cations and 0.03 to 0.07 μg m^{-3} for anions (Hsu et al., 2007; Liu et al., 2016b). A quarter of each quartz fiber filter was placed into the glass tube and deionized water was applied to extract. To ensure the water-soluble ions in samples were extracted completely into the solution, the extraction procedure was carried out for at least three times. All the extract solutions were stored under 4 °C until the moment for detection by ion chromatography. Prior to the ions detection, standard solutions were prepared and detected for over three times and low relative standard deviations (RSD) were obtained. Analytical quantification was carried out by using calibration curves made from standard solutions prepared in a concentration range of 1 to 120 mg L^{-1} (vary with each ion). Expect for ionic species, carbonaceous species and elements had been analyzed as well and the analytical methods are introduced in Text S2.

The background contamination was observed regularly by using blank tests, which were applied to validate and correct data. The analysis of blank and duplicate samples was carried out for approximately 10% of all the samples. For quality assurance and quality control (QA and QC), certified reference materials (CRMs, produced by National Research Center for Certified Reference Materials, China) were pretreated and analyzed with the same procedure which had been described in previous studies (Tian et al., 2014; Liu et al., 2016b; Zhao