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Impacts of meteorological condition and aerosol chemical compositions on visibility impairment in Nanjing, China

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ABSTRACT

With rapid industrialization and urbanization, air pollution and corresponding visibility problems in Nanjing were increasingly severe during the last few years. To better understand the potential causes of impaired visibility, particulate matter (PM) mass and chemical composition were measured from May 2013 to May 2014 in Nanjing. During the period, major water soluble ions and organic carbon exhibited obvious seasonal variations with the highest level in winter. On average, the water-soluble ions ranked in the order of $SO_4^{2-} > NO_3^- > NH_4^+ > Cl^- > Na^+ > Ca^{2+} > K^+ > F^- > Mg^{2+}$. The NO_3^-/SO_4^{2-} average ratios were over 1.0 in the fall and winter due to the low temperature favored a shift from the gas phase as nitric acid to the particle phase as ammonium nitrate. The averaged mass concentrations of organic carbon (OC) and elemental carbon (EC) were 18.96 and 2.60 μg m^{-3} respectively. The daily average visibility in Nanjing over study period ranged from 1.2 km to 18.4 km. High aerosol concentration and relative humidity were two important factors that cause low visibility events in Nanjing. The correlation between $PM_{2.5}$ concentration and visibility under different relative humidity values showed that visibility was exponentially decreased with the increased $PM_{2.5}$ concentrations when relative humidity less than 80%. However, the relationship was no longer to follow the exponentially decreasing trend when relative humidity >80%, and the visibility maintained in very low values, even with low $PM_{2.5}$ concentrations. This indicated the hygroscopic growth of particles played more important roles for reduction of visibility. The annual average chemical extinction coefficient based on the revised IMPROVE (Interagency Monitoring of Protected Visual Environments) equation was 267.69 ± 139.24 Mm^{-1} in Nanjing. On average, organic matter was found to be the largest contributor accounting for 35.69% of chemical extinction coefficient. The contributions of ammonium sulfate and ammonium nitrate were also important with the annual average of 28.80% and 24.08%, respectively. For visibility >10 km, organic matter was the largest contributor to extinction coefficient, while organic matter and ammonium sulfate were the main contributors for visibility <5 km. The results showed that the most influential factors affecting visibility in Nanjing were organic matter and sulfate. The reduction of carbonaceous species and sulfate could effectively improve the visibility of Nanjing. The paper aims to help environmental scientists and policy makers understand air pollution in Nanjing and air pollution control strategies taken by government.

1. Introduction

Visibility is a visual indicator of air quality reflecting the atmospheric turbidity. However, visibility degradation is a pervasive

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environmental problem in China due to rapidly expanding economic and industrial developments (Anderson et al., 2003; Quinn and Bates, 2003; Che et al., 2007). Meanwhile, visibility degradation has also become a problem of public concern in most metropolitan areas in recent years. For example, the average visibility varied in range of 8.6–16.5 km in megacities Chengdu, Beijing, Shanghai, Guangzhou, Hangzhou and Nanjing, China on basis of long term database (Chang et al., 2009; Gao et al., 2011; Deng et al., 2013). Wu et al. (2006) found that the number of hazy days in Guangzhou increased from 65 days in 2001 to 144 days in 2004.

Previous studies have demonstrated that the size distribution, the chemical composition and concentration of aerosol heavily influence visibility (Malm et al., 1996; Chung et al., 1999; Kim et al., 2007). For example, nanoparticles are important precursors for the formation of coarser particles that are known to strongly influence urban visibility, global climate and public health (Horvath, 1994; Albuquerque et al., 2012; Strawa et al., 2010; IPCC, 2013). Due to the different abundance of various chemical constituents and different mass extinction efficiency, percentage contributions of chemical composition to extinction coefficient (b_{ext}) vary by location. Ammonium sulfate is the dominant components responsible for visibility impairing (Chan et al., 1999; Yang et al., 2007; Jung et al., 2009; Zhang et al., 2012b), while organic matter (OM) is also the dominant contributor at other locations (Malm and Day, 2000; Zhang et al., 2012a; Huang et al., 2015). Occasionally, elemental carbon (EC) became the most important contributor due to the severe impact of local emissions, accounting for around 40% of the total extinction (Cheng et al., 2008). In Australia, due to low level of total b_{ext}, the contribution of EC (44%) becomes the most important contributor (Chan et al., 1999). Additionally, relative humidity (RH) is also a key parameter influencing atmospheric visibility. As RH increases, hygroscopic species significantly enlarge particle size, thus increasing the scattering cross section and proportionately reducing visibility (Malm and Day, 2001; Ghim et al., 2005; Deng et al., 2011).

In China, studies of particulate matter (PM) mainly focus on concentration levels and chemical characteristics for different cities and pollution events (Tan et al., 2009; An et al., 2015; Ma et al., 2016; Wang et al., 2016a). Due to frequent haze events in China, visibility is often seriously impaired (Wu et al., 2006), exerting hazardous influences on both road traffic and air transport. However, studies on visibility and its relationship with aerosol chemical compositions are still rather limited, and mainly concentrated on Pearl River Delta, Beijing and Shanxi Province (Cheung et al., 2005; Yang et al., 2007; Tao et al., 2009; Cao et al., 2012). The Yangtze River Delta is regarded as one of major haze regions in China, and experiences with high concentration of fine particulate matter and low visual range (Che et al., 2007; Gao et al., 2011; Shen et al., 2015a). However, knowledge on influence of meteorological condition and aerosol chemical composition on visibility impairment over Yangtze River Delta are still insufficient (Shen et al., 2014). In this study, water soluble inorganic ions and carbonaceous fractions (OC and EC) in $PM_{2.1}$ were determined from May 2013 to May 2014 in northern suburb Nanjing. The objectives of this paper are (1) to present the characteristics of water soluble inorganic ions and carbonaceous fractions in $PM_{2.1}$; (2) to examine the seasonal variations of light extinction by IMPROVE algorithm; (3) to investigate the relationships between light extinction coefficients and chemical compositions of $PM_{2.1}$ in Nanjing.

2. Sampling and analysis

2.1. Site and sampling

The sampling site is located on the roof of meteorological building at the Nanjing University of Information Science and Technology (32° 207′ N, 118° 717′ E; altitude 62 m). The location of the sampling site is shown in Fig. 1. Traffic congestion of vehicles is quite common at the study site because the Ningliu highway is located near the site, approximately 500 m to the east. Furthermore, Yangzi Petrochemical, Nanjing Chemical Industry and Nanjing Iron and Steel Group are located in the study region. These industries can produce exhaust with large amounts of aerosol particles. Therefore, this research has important significance for the improvement of air quality in the northern suburb of Nanjing.

Aerosol samples were collected with nine-stage impact sampler (Anderson, USA), with the flow rate at 28.3 L min^{-1}. The size diameters of the nine stages are ≤0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and 9.0–10.0 μm. In this study, the samples of $D_p < 2.1$ μm were analyzed to investigate the extinction contribution of fine particle. Every sample was collected continuously for 23 h and then kept in a refrigerator before analyzing. We used cellulose filters for ionic species and metallic elements and quartz filters for EC and OC. Before use, quartz filters were fired for 5 h at 800 °C to lower the blank levels for EC and OC. All of these filters were kept in a refrigerator for cryopreservation. Samplings were collected from May 18 to July 17 (June 16 to June 18 are missing) of 2013, October 15 to November 13 of 2013, January 1 to January 31 of 2014 and April 1 to May 31 of 2014 once per day. The four seasons in Nanjing were designated as December and February for winter, March to May for spring, June–August for summer, and September–November for autumn.

2.2. Gas and meteorological factor

Nitrogen Dioxide (NO_2) was measured by Model 42CTL High Precision Chemiluminescence NO–NO_2–NO_x Analyzer produced by USA Thermo Electron. $PM_{2.5}$ was measured by β-ray particulate continuous monitor with the time resolution 30 min. These instruments were also placed on the roof of meteorological building.

Visibility and meteorological factors were observed with Model CJY-1 Visibility Monitor and Model CAWSD600 Automatic Weather Station, which were also installed on campus with time resolutions were 1 h and 5 min, respectively.

2.3. Chemical analysis

A quarter of the cellulose filters were poured into Polyethylene Glycol Terephthalate (PET) bottles with 50 ml deionized water and kept still after ultrasonic shaking for 30 min. Extracts were filtered using a syringe filter (0.22 μm, Xiboshi), and then put into an automatic sampler to analyze the water solution ions by using an ion chromatograph (IC, Dionnex, ICS-90). The five cations, viz., sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and five anions, viz., fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) were analyzed. In order to achieve the quality control of the analyzed samples, two blank samples were routinely run after every nine samples.

The DRI Model 2001 thermal/optical carbon analyzer was used to analyze a quarter of quartz filters to measure concentrations of EC and OC. The samples were heated to 140, 280, 480, and 580 °C in pure He to determine OC1, OC2, OC3, and OC4. Then, the samples were heated to 580, 740, and 840 °C in 2% O_2/98% He to determine EC1, EC2, and EC3. Volatilized compounds were converted to carbon dioxide (CO_2) through an oxidizer (heated manganese dioxide, MnO_2). CO_2 was reduced to methane (CH_4) through a methanator. Finally, CH_4 equivalents were quantified with a flame ionization detector (FID). The charring effect can make part of organic carbon into pyrolysis carbon in anaerobic heating. Hence, the correction for pyrolysis was made by continuously monitoring the filter through a