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One year online measurements of water-soluble ions at the industrially polluted town of Nanjing, China: Sources, seasonal and diurnal variations

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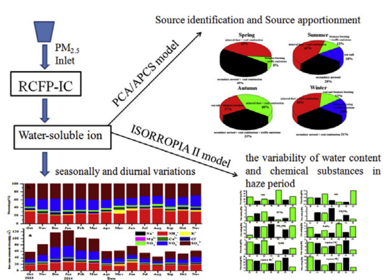
HIGHLIGHTS

- Clear seasonal and diurnal variations were elucidated.
- Sources of WSIs were apportioned by a PCA/APCS receptor model.
- NO_3^- in winter significantly increased during haze episode, while SO_4^{2-} and NH_4^+ were enhanced significantly in summer.
- Haze caused by biomass burning in summer in Nanjing.

GRAPHICAL ABSTRACT



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ABSTRACT

Half-hourly mass concentrations water-soluble ions (WSIs) and $PM_{2.5}$ were measured online a Rapid Collector of Fine Particles and Ion Chromatography system (RCFP-IC) and FH62C14 Continuous Particulate Monitor in Nanjing from October 18, 2013 to November 17, 2014. The WSIs concentration ranged from 7.07 to 333.42 μg m^{-3} with an annual mean of 76.32 μg m^{-3}. The WSIs ranked in the order of $SO_4^{2-} > NH_4^+ > NO_3^- > Cl^- > NO_2^- > K^+ > Ca^{2+} > Na^+ > Mg^{2+}$. The $PM_{2.5}$ concentration ranged from 4.00 to 400 μg m^{-3} with an annual mean of 83.58 μg m^{-3}. The concentrations of WSIs varied in the order of winter (115.77 μg m^{-3}) > spring (76.10 μg m^{-3}) > autumn (63.72 μg m^{-3}) > summer (59.75 μg m^{-3}), with the highest level in January (123.99 μg m^{-3}) and lowest level in August (43.73 μg m^{-3}). Different WSIs had distinct diurnal variations. The source analysis of the WSIs in the PCA/APCS mode illustrated that the sources consisted of secondary aerosol, coal combustion, mineral dust, biomass burning, traffic emissions and sea salt. In addition, there were seasonal variations amongst the various sources. The haze formation mechanism was different in summer and winter. The winter was dominated by NH_4NO_3 (18.56%), $(NH_4)_2SO_4$ (28.63%), NH_4^+ (11.27%), SO_4^{2-} (18.35%) and NO_3^- (13.13%), and by NH_3 (25.93%), $(NH_4)_2SO_4$ (13.37%), SO_4^{2-} (15.74%) and NO_3^- (9.97%) in summer. Consequently, the proportions of HCl, HNO_3, NH_4^+,

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SO_4^{2-} and NO_3^- were much larger during haze episodes in winter, while it was dominated by NH_4NO_3, NH_4^+, $(NH_4)_2SO_4$, SO_4^{2-} and NO_3^- during summer haze episodes.

1. Introduction

Over the past several decades, the rapid industrialization and urbanization have caused a sharp enhancement of $PM_{2.5}$ level in most megacities in China (Chan and Yao, 2008; Qian et al., 2000). $PM_{2.5}$ can be directly emitted into the air (primary PM from coal combustion, automobile exhaust and mineral dust, etc.) or generated in the atmosphere from precursor gasses (secondary PM from gas condensation, heterogeneous reactions on aerosol surfaces or in aerosol droplets and in-cloud processes, etc.) (Chan and Yao, 2008; Chen et al., 2004; Matsuki et al., 2005; Shi et al., 2014; Sun et al., 2006). It's reported that $PM_{2.5}$ causes significant visibility reduction and health problems in urban areas (Larson et al., 1989; Seaton et al., 1995; Tie et al., 2009; Zhang et al., 2015). Water-soluble ions are the major components of $PM_{2.5}$ (Chan and Yao, 2008; Lin et al., 2014; Zhang et al., 2015), and the major ionic species, such as sulfate, nitrate and ammonium, have great influences on the hydroscopic nature and acidity of aerosols (Ocskay et al., 2006; Zhou et al., 2009), while their characteristics vary significantly with season and geographic location.

The Yangtze River Delta (YRD) is the largest estuary delta and the fastest-growing economic region in China. During the past decades, large quantities of pollutants have been unavoidably emitted into the atmosphere with the increasing economic expansion in eastern China (Tie et al., 2006; Xu et al., 2008). Previous studies have pointed out high concentrations of particulate matter and WSIs in the YRD region (Cao et al., 2009; Chan and Yao, 2008; Cheng et al., 2012; Du et al., 2011; Fu et al., 2008; Kong et al., 2014; Shi et al., 2014; Wang et al., 2003, 2012; Xiu et al., 2004). The aerosol mass concentrations (Wang et al., 2003; Xiu et al., 2004), spatial and seasonal variability (Cao et al., 2009; Cheng et al., 2012), chemical composition and sources (Cao et al., 2009; Du et al., 2011; Kong et al., 2014), aerosol impacts on visibility (Shi et al., 2014; Wang et al., 2012) and haze formation mechanism (Du et al., 2011; Fu et al., 2008; Lin et al., 2014) have been studied in YRD. Fu et al. (2008) indicated that WSIs account for 41–61% of $PM_{2.5}$. Wang et al. (2003) observed that ions of NO_3^-, SO_4^{2-}, NH_x (ammonia and ammonium), Ca^{2+}, K^+ and Na^+ are abundant in PM_{10} and $PM_{2.5}$ aerosols. Cao et al. (2009) found that NH_4NO_3 dominated in spring, autumn, and winter, and $(NH_4)_2SO_4$ dominated in summer. Lin et al. (2014) discovered that the gradual replacement of $CaSO_4$ and $Ca(NO_3)_2$ by $(NH_4)_2SO_4$ and NH_4NO_3 was the major cause of no improvement in the visibility impairment in Shanghai during recent years. The previous studies on determining the chemical properties of aerosols usually used filter sampling and subsequent off-line chemical analysis (e.g., 12–24 h or more) (Schaap et al., 2011). However, sampling with such long measurement times cannot allow for catching rapid spatial and temporal changes in both aerosol properties and associated processes in the atmosphere.

Nanjing is one of the largest cities in the YRD and also one of the most massively industrialized and urbanized regions in South China. High level of ambient particulate loadings has been a persistent and the most serious air pollution problem in the region (Wang et al., 2003, 2012). In order to better understand the secondary aerosol pollution and potential source regions in Nanjing, half-hourly mass concentrations of WSIs in $PM_{2.5}$ were measured online with a RCFP-IC from October 18, 2013 to November 17, 2014. In this study, we illustrated the seasonal and diurnal variations of major WSIs. The principal component analysis (PCA), absolute principal component scores (APCS) receptor model is used to acquire source profiles and source apportionments of the WSIs pollution in Nanjing. Meanwhile, the haze formation was discussed by analyzing the characteristics of WSIs in different type haze events in winter and summer. In addition, the chemical compositions and water content of aerosol on haze days and clean days were investigated on the basis of the ISORROPIA II model results. To our knowledge, these are the only long term online measurements of water-soluble ions in YRD region, China. The unique datasets may improve our knowledge of aerosol properties in YRD region and there by provide baseline information for future measurements and modeling studies.

2. Experimental methods

2.1. Sampling

The observation site was located on the meteorology building (32.21°N, 118.72°E) of the Nanjing University of Information Science & Technology campus, which is 40 m above the ground. The information of the station and its' surroundings is shown in Fig. 1. The Nanjing Chemical Industry Park (NCIP) is located at approximately 3 km southeast of the measurement site. In addition, there are some iron and steel plants and cogeneration power plants in the range of 1 km from the site. This region represents a combination of traffic, urban, industry and croplands sources.

2.2. Instrument descriptions

A Rapid Collector of Fine Particles and Ion Chromatography system (RCFP-IC) an on-line analyzer with a $PM_{2.5}$ sampling inlet was equipped to conduct an intensive measurement from Oct. 18, 2013 to Nov. 17, 2014. It provided half-hourly mass concentrations of Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Li^+, Cl^-, NO_2^-, NO_3^- and SO_4^{2-} (Li^+ was used as an internal standard). The IC system was produced by the Dionex Corporation with a model of ICS-90. An IonPac AS14 column (4 × 250 mm) was used for the anion analysis using an eluent of 3.5 mmol L^{-1} $NaHCO_3$, and an IonPac CS12A column (4 × 250 mm) was used for the cation analysis using an eluent of 20 mmol L^{-1} methanesulfonic acid. The detailed principles of RCFP-IC can be found elsewhere (Chang et al., 2007; Cheng et al., 2014; Wen et al., 2006; Zhang et al., 2007). The detection limits for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_2^-, NO_3^- and SO_4^{2-} were 0.11, 0.13, 0.11, 0.14, 0.22, 0.16, 0.26, 0.22 and 0.11 μg m^{-3}, respectively. A denuder, which can remove acidic (mainly HNO_3, HCl, SO_2 and H_2SO_4) and alkaline gases (mainly NH_3) from the air, was not installed in the front of injection tube in the RCFP-IC system. Hence, the sampling gases, such as NH_3, HNO_3 and H_2SO_4 were directly dissolved in deionized water during the measurements. The concentrations of NO_3^-, SO_4^{2-} and NH_4^+ in our study were the sum of gas-dissolved ions and ions in aerosol, whose proportions were higher than those in the aerosol only. Based on local meteorological characteristics, the period from March to May was designated as spring, the period from June to August was designated as summer, the period from September to