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Inorganic ion chemistry of local particulate matter in a populated city of North China at light, medium, and severe pollution levels

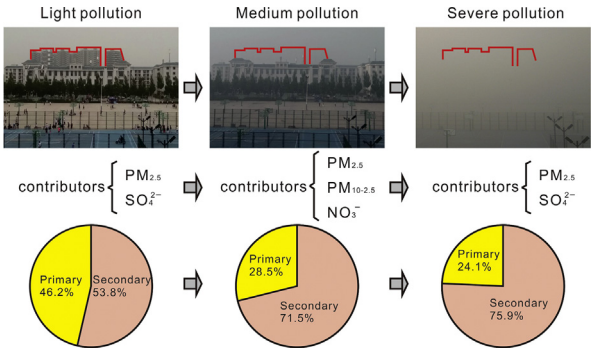
Xiaoyan Song [a], Jinjuan Li [b], Longyi Shao [c], Qiming Zheng [d], Daizhou Zhang [e,*]

[a] College of Geosciences and Engineering, North China University of Water Resources and Electric Power, Zhengzhou, Henan 450046, China
[b] College of Resources and Environmental Engineering, Guizhou University, Guiyang, Guizhou 550025, China
[c] College of Geoscience and Surveying Engineering, China University of Mining & Technology, Beijing 100083, China
[d] School of Resources and Environment Engineering, Henan University of Engineering, Zhengzhou, Henan 451191, China
[e] Faculty of Environmental and Symbiotic Sciences, Prefectural University of Kumamoto, Kumamoto 862-8502, Japan

HIGHLIGHTS

- The particulate pollution at Zhengzhou was divided into three levels: light, medium and severe.
- PM_{10} increase was dominated by $PM_{2.5}$ at the light and severe levels, and by both $PM_{2.5}$ and $PM_{10-2.5}$ at the medium level.
- Secondary aerosol species (inorganic and organic) are major contributors to $PM_{2.5}$ elevation.
- SO_4^{2-} hindered NO_3^- formation in $PM_{2.5}$ when it constituted >20% of $PM_{2.5}$ in mass.

GRAPHICAL ABSTRACT



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ABSTRACT

Twenty-six pairs of $PM_{2.5}$ and PM_{10} samples were collected during haze episodes in Zhengzhou (113°28′ E, 34°37′ N), a highly populated city in North China. The samples were used to examine the inorganic ion chemistry of particulate matter (PM) of local origin at light ($PM_{2.5}$ < 60 μg m^{-3} and PM_{10} < 135 μg m^{-3}), medium ($PM_{2.5}$: 60–170 μg m^{-3} and PM_{10}: 135–325 μg m^{-3}), and severe ($PM_{2.5}$ > 170 μg m^{-3} and PM_{10} > 325 μg m^{-3}) pollution levels. At the light and severe pollution levels, the increase of PM_{10} was accounted for by the increase of $PM_{2.5}$, and the variation of $PM_{10-2.5}$ was small. In contrast, the increase of PM_{10} at the medium pollution level was caused by the increase in both $PM_{2.5}$ and $PM_{10-2.5}$. Sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride in the form of ammonium chloride (Cl^-_S) accounted for 47.8% and 60.3% of the $PM_{2.5}$ mass at the light and severe levels, respectively. These values indicate a large contribution of secondary inorganic species to the $PM_{2.5}$ growth. As the pollution level changed from light to medium, the contribution of SO_4^{2-} to the growth of $PM_{2.5}$ decreased from 49.0% to 15.1%, while those of NO_3^- and Cl^-_S increased from 25.1% and 0.6% to 32.5% and 2.8%, respectively, indicating the substantial production of nitrate and chloride. At the severe level, the contribution of SO_4^{2-} was 30.1%, while those of NO_3^- and Cl^-_S were 5.9% and 0.5%, respectively, suggesting a hindering effect of sulfate on the production of nitrate and chloride. These results indicate that the production of secondary species with the increase of $PM_{2.5}$ was dominated by sulfate-associated conversions at the light and severe pollution levels and was substantially influenced by nitrate- and chloride-associated conversions at the medium pollution level. The estimation of carbonate presence in the PM indicates that part of the carbonate in coarse particles ($PM_{10-2.5}$) of crustal origin enhanced sulfate production via heterogeneous surface reactions.

* Corresponding author.
E-mail address: dzzhang@pu-kumamoto.ac.jp (D. Zhang).

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Quantification of the contribution of primary and secondary species to $PM_{2.5}$ showed that it was dominated by both primary and secondary particles at the light pollution level, and it was mainly composed of secondary species at the severe pollution level.

1. Introduction

Due to its complex composition, airborne particulate matter (PM) has significant effects on regional climate, public health, water body acidification, ecosystems and visibility (Zhang et al., 2012; Zhang et al., 2013; M. Qin et al., 2015; Bari and Kindzierski, 2016). Soluble ions, such as sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), have substantial anthropogenic sources and are major contributors to PM load, especially for fine particles ($PM_{2.5}$) (Y. Pan et al., 2016; Tian et al., 2016).

SO_4^{2-}, NO_3^- and NH_4^+ (usually called SNA) are the major soluble inorganic components in PM (Sun et al., 2010; Minguillón et al., 2012; B. Pan et al., 2016; Tian et al., 2016). Apart from a small amount of SNA particles directly emitted from industrial activity (e.g., gypsum particles from vitriol plants and ammonium nitrate particles from fertilizer plants), most SNA in aerosol particles are formed via heterogeneous and homogeneous conversions in the air (Tang et al., 2006; J. Wang et al., 2016). Sulfate in SNA is usually in the form of ammonium calcium sulfate (koktaite), calcium sulfate (gypsum and anhydrite), ammonium magnesium sulfate (boussingaultite), or ammonium sulfate (mascagnite) (Mori et al., 1998; Satsangi and Yadav, 2014; Song et al., 2014). Nitrate is mainly in the form of ammonium nitrate or calcium nitrate (Jacob, 2000; Tang et al., 2006). Previous studies have revealed that anions in $PM_{2.5}$ are dominated by SO_4^{2-} and NO_3^-, followed by Cl^-. Cations are dominated by NH_4^+, followed by Ca^{2+}, Mg^{2+}, K^+ and Na^+ (Cuccia et al., 2013; Song et al., 2016; Tian et al., 2016; Q. Wang et al., 2016).

North China has been subject to serious haze pollution in recent years, and there have been frequent alerts corresponding to heavy air pollution in the area. An analysis of $PM_{2.5}$ in urban areas has found that the mechanisms dominating $PM_{2.5}$ differed with the $PM_{2.5}$ level. Ma et al. (2017) studied the increase of $PM_{2.5}$ during winter haze episodes in Beijing and reported that the increase of $PM_{2.5}$ was mainly caused by regional transport from other areas (mostly from the areas to the south of Beijing) in the initial stage of haze episodes ($PM_{2.5}$ < 150 μg m^{-3}) and by local heterogeneous conversions in later stages ($PM_{2.5}$ > 150 μg m^{-3}). There have been many studies showing that regional transport from neighboring industrial areas has always contributed substantial pollutants to severe haze episodes in the megacity areas of Beijing and Tianjin in the North China Plain (S. Qin et al., 2015; L. Wang et al., 2015; Wang et al., 2017). To understand the chemical characteristics of PM during the haze episodes in North China, data on the ionic composition and variation of the PM in the industrial areas are necessary. Although some studies have reported the chemical composition and the source apportionment of $PM_{2.5}$ in some relevant industrial cities (Jia et al., 2018; Meng et al., 2016; Qin et al., 2017; Song et al., 2015; Yang et al., 2018), the available data are limited for an in-depth examination of the evolution of ionic species in PM under various pollution conditions.

In this study, we investigated $PM_{2.5}$ and PM_{10} in Zhengzhou, a city approximately 625 km to the south of Beijing and located in the south of the North China Plain. It has been proven that urban and surrounding areas of cities such as Zhengzhou are major source areas of primary pollutants in the North China Plain (Li et al., 2011; Niu et al., 2011, 2016; Meng et al., 2016; Shen et al., 2016; Qin et al., 2017; Tang et al., 2017; Wu et al., 2017; Yang et al., 2018). The purpose of this study is to investigate the ion chemistry of aerosols originating from local areas at different PM pollution levels when haze occurred in Zhengzhou. The contributions of the ionic species and primary species to the $PM_{2.5}$ and PM_{10} and the production of sulfate, nitrate and chloride, corresponding to the pollution levels were demonstrated.

2. Methods

2.1. Sample collection

The collection site is in Zhengzhou (113°28′ E, 34°37′ N). The city is the capital of Henan Province, China. It is an area of approximately 7446 km^2, and the population is >9.5 million. The weather is under the influence of the middle latitude westerly of the Northern Hemisphere. The annual mean temperature is approximately 15.6 °C, the annual rainfall is approximately 542 mm, and the annual sunshine time is approximately 1870 h. The city is surrounded by small cities (called satellite cities), including Jiaozuo, Hebi, and Xinmi (Fig. 1). The satellite cities are industrial cities with coal-related enterprises, including coal mines, power plants, and coal-powered factories. As Guo (2017) and Wang (2015) reported, the pollutant sources in Zhengzhou, including traffic, coal burning, vegetation burning, dust, secondary particles and other sources, are approximately similar in the four seasons, although the emission amounts are seasonally different.

$PM_{2.5}$ and PM_{10} samples were collected between summer 2015 and spring 2016 on the roof of a five-story building (approximately 16 m above the ground) on the campus of the North China University of Water Resources and Electric Power. The university is in the urban area of Zhengzhou, and it is surrounded by residential buildings. In total, 33 pairs of 24-h $PM_{2.5}$ and PM_{10} samples were collected on quartz fiber filters using a TSP-PM_{10}-$PM_{2.5}$ sampler (Laoshan Electronic Instrument Factory Co. Ltd.). Of these samples, 9 pairs were collected in spring, 7 pairs in summer, 5 pairs in autumn and 12 pairs in winter. After collection, the samples were immediately equilibrated in a climatic chamber for 24 h and then stored in a refrigerator (−15 °C) to avoid possible volatilization, contamination and deliquescence. Meteorological conditions, including temperature, relative humidity (RH), pressure, wind speed, and wind direction, were monitored using a meteorological monitor (NK5919 Kestrel, USA) (Tables 1 and S1).

The samples were categorized and screened according to the meteorological conditions under which they were collected. Twenty-six pairs of $PM_{2.5}$ and PM_{10} samples were collected when the weather was governed by high pressures and the wind speed was smaller than 1.5 m s^{-1}, i.e., when the weather was very stable. Under stable weather conditions, air pollutants were mainly from local areas, including the satellite cities. Contributions from pollutants that had been transported over long distances from other areas were minor because of the weak wind. These samples were used to examine the ionic chemistry of aerosol particles from local areas.

The remaining seven pairs were collected under windy conditions when the wind speed was >3 m s^{-1}. The analysis of backward trajectories of air parcels loading the particles indicated that these samples likely contained particles that had been transported long distances from areas outside Zhengzhou and the surrounding satellite cities. It is difficult to use these samples to examine the ionic chemistry of aerosol particles from either local areas or long-distance areas. In this study, these samples are not considered, and we focus on the ion chemistry