Science of the Total Environment 650 (2019) 2605–2613

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Characterization of water soluble inorganic ions and their evolution processes during $PM_{2.5}$ pollution episodes in a small city in southwest China

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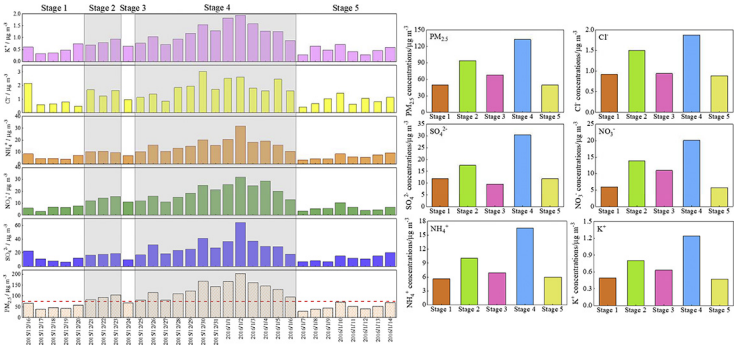
HIGHLIGHTS

- Major WSIIs in $PM_{2.5}$ were measured in a small city in southwest China.
- Seasonal patterns of $PM_{2.5}$ and WSIIs were discussed.
- Impacts of meteorological conditions and WSIIs variations on $PM_{2.5}$ pollution events.
- Extremely enhanced SNA was responsible for heavier $PM_{2.5}$ pollution events.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 July 2018
Received in revised form 12 September 2018
Accepted 28 September 2018
Available online 01 October 2018

Editor: Xinbin Feng

Keywords:
Water soluble inorganic ions
$PM_{2.5}$
Pollution episodes
Sichuan Basin

ABSTRACT

$PM_{2.5}$ samples were collected in four segregate one-month periods, each representing one season, for analyzing their contents of water soluble inorganic ions (WSIIs) in a small city inside Sichuan Basin. Daily $PM_{2.5}$ concentrations ranged from 23.2 to 203.1 μg m^{-3} with an annual mean of 66.9 ± 33.6 μg m^{-3}. Annual mean concentrations of WSIIs was 28.8 ± 20.3 μg m^{-3}, accounting for 43.1% of $PM_{2.5}$. Seasonal mean concentrations of WSIIs ranged from 17.5 ± 9.3 μg m^{-3} in summer to 46.5 ± 27.6 μg m^{-3} in winter. Annual mean mass ratio of NO_3^-/SO_4^{2-} was 0.49, demonstrating predominant stationary sources for secondary inorganic aerosols (SNA, including SO_4^{2-}, NH_4^+ and NO_3^-); whereas annual mean molar ratio of $[NH_4^+]/[NO_3^-]$ was 3.5, suggesting dominant agriculture emissions contributing to the total nitrogen. During a severe and long-lasting (13 days) winter pollution period when mean $PM_{2.5}$ concentration reached to 132.5 μg m^{-3}, $PM_{2.5}$ concentration was enhanced by a factor of 2.6 while that of SNA by a factor of 2.9 compared to those before the pollution event, and the fraction of SNA in $PM_{2.5}$ only increased slightly (from 46.7% to 50.6%). Thus, local accumulation of pollutants under poor diffusion

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https://doi.org/10.1016/j.scitotenv.2018.09.376

conditions played a major role causing the extremely high $PM_{2.5}$ concentration, besides the contributions from the enhanced SNA formation under specific weather conditions.

1. Introduction

Atmospheric particulate matter, especially fine particles ($PM_{2.5}$), has been paid extensive attention worldwide due to its adverse effects on human health, air quality, terrestrial and aquatic ecosystems, e.g., causing cardiovascular and respiratory diseases, visibility degradation, soil acidification and eutrophication of water (Bowman et al., 2008; Matson et al., 2002; Tao et al., 2017; Taus et al., 2008; H.B. Wang et al., 2017; Wright et al., 2018). Particulate matter also plays a significant role in global climate by scattering and absorbing radiation (Mahowald, 2011; Mallet et al., 2016). The National Ambient Air Quality Standards of China (NAAQS-China) was promulgated in 2012 by the Chinese government, defining a $PM_{2.5}$ daily mean limit of 75 μg m^{-3} and annual mean limit of 35 μg m^{-3}. However, about two thirds of megacities in China have not met the standard yet (Zhao et al., 2016).

Water soluble inorganic ions (WSIIs), especially secondary inorganic aerosols (SNA, including SO_4^{2-}, NO_3^- and NH_4^+), were major chemical components of $PM_{2.5}$. Cheng et al. (2016) stated that SNA accounted for 36% of $PM_{2.5}$ mass in the studied 45 global megacities in 2013, and the percentage contributions were higher than 40% if looking separately at several heavy polluted megacities (e.g., Beijing, Nanjing, Chengdu, and Harbin) with annual mean concentrations higher than 75 μg m^{-3}. Tao et al. (2017) conducted a thorough review of the relative contributions of dominant chemical species to $PM_{2.5}$ mass across China, and found that, on an annual basis, SNA contributed 36–39% to $PM_{2.5}$ mass in the Beijing-Tianjin-Hebei region (BTH), 33–38% in the Pearl River Delta region (PRD), and 25–54% in the Yangtze River Delta (YRD) region, depending on the location of sampling sites. J.D. Wang et al. (2017) found similar results with those in Cheng et al. (2016) and Tao et al. (2017) based on at least one year measurement of chemical components of $PM_{2.5}$ in 31 provinces and suggested an average of 34% contribution of SNA to $PM_{2.5}$ across China. All of these studies highlighted the important role of SNA in $PM_{2.5}$ levels in the air.

Generally, the concentrations of $PM_{2.5}$ were the highest in winter and $PM_{2.5}$ pollution events occurred frequently in urban areas in this season regardless of geographical regions in China (Leng et al., 2016; Nie et al., 2017; Quan et al., 2014; Wang et al., 2015). Coal combustion and biomass burning in winter were largely responsible for $PM_{2.5}$ pollution in northern China (Shang et al., 2018; Sun et al., 2013; Wang et al., 2015; Li et al., 2017). Dramatic increase of $PM_{2.5}$ concentrations in relatively short time periods was likely caused by quick heterogenic reactions forming secondary aerosols under high relative humidity conditions (W.Q. Xu et al., 2017; B. Zheng et al., 2015; G.J. Zheng et al., 2015). In addition, the significant role of high relative humidity in secondary aerosol formation was emphasized in recent studies (Cheng et al., 2015; B. Zheng et al., 2015).

Fewer studies on $PM_{2.5}$ pollution were carried out in Sichuan Basin than in other regions like BTH, YRD, and PRD, especially on the evolution of $PM_{2.5}$ pollution events in winter (Chen et al., 2017a; Chen and Xie, 2014; Tao et al., 2014; Tian et al., 2017; Wang et al., 2018a). In the present study we collected and analyzed $PM_{2.5}$ samples in Fuling, a district of Chongqing located in the eastern margin of Sichuan Basin. The region has a subtropical climate characterized by mild winter and extremely hot summer. In addition, high relative humidity and low wind speed are common all year round. Considering the unique meteorological conditions and topography, the seasonal variations of WSIIs and their effects on $PM_{2.5}$ pollution events might be different from the cases in the other regions in China. The main objectives of the present study are to (1) characterize seasonal variations of WSIIs in $PM_{2.5}$, (2) investigate aerosol acidity, chemical associations of $WSII_S$, and source characteristics of SNA, and (3) explore the impacts of meteorological conditions and WSIIs variations on $PM_{2.5}$ pollution events.

2. Methodology

2.1. $PM_{2.5}$ sampling

$PM_{2.5}$ samples were collected on a rooftop of a building 20 m above the ground inside the Yangtze Normal University in Fuling (FL, 229°45′ N, 107°16′ E), a small urban city located about 80 km northeast of the megacity Chongqing (Fig. 1). There are no significant industries near the sampling site. Two highways (Nanfu and Changfu) are located about 1 km west and northeast of the sampling site, respectively.

About 29 daily $PM_{2.5}$ samples (23-h duration) were collected in each of the four seasons: spring (2 to 29 April 2015), summer (2–30 July 2015), autumn (16 October to 13 November 2015), and winter (16 December 2015 to 14 January 2016). Two $PM_{2.5}$ samples were collected in parallel by one sampler (SASS, Met One Inc.) with a flow rate of 6.7 L min^{-1} in each day. One channel was loaded with Teflon filter (Whatman, 47 mm) for $PM_{2.5}$ mass analysis, and another one was loaded with pre-baked quartz filter (Whatman, 47 mm) for WSIIs analysis. In total, 116 Teflon samples, 116 quartz samples, and 8 field blanks were collected during the campaign.

Before and after sample collection, all the Teflon filters were weighted using an microbalance (Sartorius, ME 5-F, Germany) after stabilization for 48 h under controlled conditions (temperature: 20–23 °C, relative humidity: 45–50%). Hourly concentrations of NO_2, SO_2, and O_3 were measured by on-line gas analyzers including Thermo 42i NO_2, 43i SO_2, and 49i O_3 analyzer (Thermo Scientific Corp., USA). Hourly meteorological parameters, including ambient temperature (T), relative humidity (RH), wind speed (WS) and direction, and precipitation were obtained from the network of the China Meteorological Data Service Center (http://data.cma.cn).

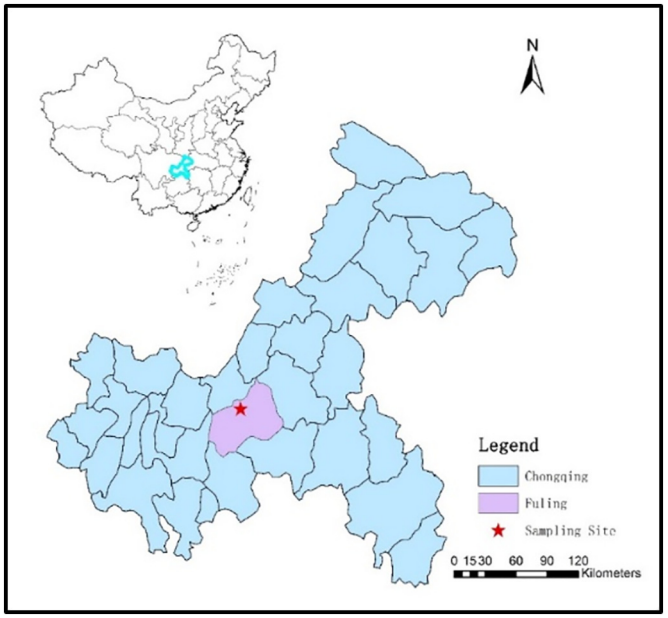

Fig. 1. Location of the sampling site.