Influence of Meteorological Factors and VOCs on PM_{2.5}during Severe Air Pollution Period in Shijiazhuang in Winter

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Abstract. The object of this study was to investigate the chemical compositions of $PM_{2.5}$ and its correlations with the concentration of volatile organic compounds(VOCs) and meteorological parameters during severe air pollution period in Shijiazhuang, a northern city, China in winter. $PM_{2.5}$ samples were collected from November 26, 2015 to December 3, 2015. The results showed that the hourly average concentration of $PM_{2.5}$ was from 239.9µg/m³ to 1062.8µg/m³. The correlation analysisshowed that $PM_{2.5}$ had higher correlations with wind speed (r=-0.78) and relative humidity(r=0.79), and therewas an apparent correlation between $PM_{2.5}$ and the concentrations of VOCs(r=0.88). Moreover, the major compositions of $PM_{2.5}$ comprises carbonaceous fractions, namely organic carbon(OC) and elementalcarbon(EC). During this period, (OC/EC) min was 2.12, by which calculating that the average concentration of secondaryorganic carbon (SOC)was 20 ug/m³, accounting for 50.5% of OC, indicating serious SOC pollution in Shijiazhuang. Since VOCsare the origin of SOC, it is further confirmed that VOCs are one of the main sources of $PM_{2.5}$.

Introduction

Aerosol particles play important role on air quality in rural andurban areas as well as on regional and global climate (IPCC, 2007). Air pollution has become a serious environmental problem in Chinaalong with the rapid economic growth over the past several decades. In particular, severe haze pollution in recent winters hascaused worldwide attention. Particulate Matter (PM), especiallyfine PM (the aerodynamic diameter less than 2.5 μ m, PM_{2.5}), is a critical pollutant in most cities of Chinasuch acute particulate air pollution has resulted in poor visibility and air quality^[1].PM_{2.5} is also known as particulate matter into the lungs, small particle size, easy to adsorption and enrichment of toxic substances in the air, and with the breath may enter the blood circulation and affect people's health^[2].

Carbonaceous particles consist of organic carbon (OC), elemental carbon (EC) and carbonate carbon (CC). In $PM_{2.5}$, CC occupies a very small proportion, thus its content can be ignored^[3]. OC is composed of hundreds of compounds, including primary organic carbon (POC) mainly in direct emissions and the secondary organic carbon(SOC) formed through photochemical reaction pathways. SOC is the precursors of secondary organic aerosol (SOA), which is mainly attributed to scattering of visible light.

PM_{2.5} pollution in Shijiazhuang is very serious, especially, in winter.

From November 27, 2015 to December 1, 2015, serious air pollution incident was endured in Shijiazhuang.During this period, the hourly average concentration of $PM_{2.5}$ is more than $300\mu g/m^3$, causing inconvenience people's lives, work and transportation.

In this study, the chemical compositions of $PM_{2.5}$ and its correlations with the concentration of VOCs and meteorological parameters during severe air pollution period in Shijiazhuang were investigated. According to (OC/EC) _{min}, the average concentration of SOC was also calculated.

Monitoring site and devices

Monitoring site was located in Yuhua District, Shijiazhuang.Air pollution data and meteorological data from Nov 26, 2015 to Dec 3, 2015 were collected from Hebei University of

Science and Technology offers atmospheric monitoring platform, on which there are several devices made in Japan. The first one, PM-712 are used to measure the concentration of $PM_{2.5}$; the second, VOC, VOCs; the third, APC-710, OC and EC; the last, WXT, meteorological parameters.

Results

Concentration levels of PM_{2.5}

Fig. 1 showed the change of average hourly concentrations of $PM_{2.5}$ from November 26, 2015 to December 3, 2015. As shown in Fig. 1, the air pollution from Nov 27 to Dec 1, 2015 is a heavy process. Daily average concentration of $PM_{2.5}$ was 68.8 µg/m³ on Nov 26, which was the second level of good air quality according to the "Ambient Air Quality Standards" (GB 3095-2012). The daily average concentration of $PM_{2.5}$ on Nov 27 and Nov 28 increased to 264.4 µg/m³ and 289.8 µg/m³, respectively. In the morning of Dec 2, along with a surge of cold air flowing into Shijiazhuang, the daily average concentration of $PM_{2.5}$ decreased to 37.6 µg/m³. In the pollution process, $PM_{2.5}$ concentration first increased and then decreased, the maximum $PM_{2.5}$ concentration was achieved on Nov 29. As shown in Fig. 1, a significant accumulation process occured from 19:00 on Nov 26 to 12:00 on Nov 30, while $PM_{2.5}$ concentration was increased from 185.9 µg/m³ to 812.1 µg/m³, and the increase rate is 436.8%. The high pollution process lasted to 3:00 on December 2(331.3 µg/m³). With the arrival of cold air at 7:00, $PM_{2.5}$ concentration quickly dropped to 34.4 µg/m³.



Fig. 1 PM_{2.5} concentration during from Nov 26, 2015 to Dec 3, 2015

Correlations between PM_{2.5} and meteorological factors

The analysis showed a significant correlation between meteorological factors and $PM_{2.5}$ concentration. There was a significant positive correlation between the relative humidity and the concentration of $PM_{2.5}$, the correlation coefficient R = 0.79 (corresponding $R^2 = 0.6184$), as shown in Fig 2, which indicated that $PM_{2.5}$ and relative humidity were strongly correlated.

There exist a negative correlation between wind speed and $PM_{2.5}$ concentration, the correlation coefficient R= -0.78 (corresponding R²=0.6208), as shown in Fig 3. When the wind speed is less than 0.5 m/s, the average concentration of $PM_{2.5}$ is more than 300 µg/m³; while wind speed is greater than 2.0 m/s, the average concentration of $PM_{2.5}$ was lower than 50 µg/m³, which achieved excellent standards, because high wind speeds are conductive to the spread and elimination of air pollutants.



Fig. 2 Correlation between PM_{2.5} concentration Fig. 3 Correlation between PM_{2.5} concentration and relative humidity and wind speed

Correlations between PM_{2.5} and VOCs

According to the analysis report, there are $20\% \sim 90\%$ of the ingredients are of secondary organic aerosol (SOA) in PM_{2.5}. SOA from the VOCs through a series of chemical changes transformed from physical.

Gaseous VOCs generate primary oxide of different volatility and vapor pressure by gas-phase oxidation mechanism. Products with high vapor pressure come into the ambient atmosphere; Products with low vapor, namely semi-volatile organic compounds (SVOCs) may be generated SOA in two ways. The one is nucleation, and the another are condensation process and gas / particle distribution process. These two approaches produced SOA can chemically react in the surface or in the interior of the particles and then generate a new SOA. This process begins by changing the composition of SOA thus changing the nature of its volatility and refractive index, so that the hygroscopic growth, and the formation of cloud condensation nuclei, called SOA aging process. Similarly, the primary SVOCs can also generate SOA through nucleation, condensation process gas / particle distribution process and particulate phase chemical reaction ^[4].

The orrelation between concentration of VOCs and $PM_{2.5}$ concentrations also plotted in Fig.4, and a good correlation (R = 0.804, corresponding R²= 0.6474) was found.

As shown in Fig. 5, the concentration of VOCs followed a similar variation trend as $PM_{2.5}$. This finding further proved that VOCs may be one of the main sources of $PM_{2.5}$.



Fig. 4 Correlation between PM_{2.5}andFig. 5 PM_{2.5}versus VOCs during from VOCsconcentrations Nov 26, 2015 to Dec 2, 2015

When the value of OC/EC is more than 2.0, indicating the presence of $SOC^{[5]}$. According to all the monitoring data, it shows that OC/EC in PM_{2.5} is more than 2.0 (Fig. 6), which indicates the presence of SOC in air pollution of Shijiazhuang. Therefore, SOA have a great contribution to PM_{2.5}.

According to the formula proposed by Odum and so, the concentration of SOC was calculated as follows:

 $OC_{sec} = OC_{tot} - EC \times (OC/EC)_{min}$ (1)

Where OC_{sec} , OC_{tot} and EC represented the concentrations of SOC, total OC and EC, respectively; and $(OC/EC)_{min}$ is the minimum value of the ratio of OC to EC.



Fig. 6.Ratio of OC to ECduring from Nov 26, 2015 to Dec 3, 2015

As shown in Fig. 6, $(OC/EC)_{min}$ was 2.12, according to formula (1), the average concentration of SOC was $20\mu g/m^3$, which accounted for 50.5% of OC, indicating serious SOC pollution in Shijiazhuang. The serious SOC pollution in winter may be related to the increase of coal combustion with the beginning of heating period, resulting in elevated emissions of volatile and semi-volatile organic compounds, making a higher concentration of organic precursors in the secondary reaction. And complex reactions related to the contamination from the periphery convey will happen during transmission, leading to the formation of SOC which further converted to SOA.

Conclusion

In this study, the chemical compositions of $PM_{2.5}$ and its correlations with the concentration of volatile organic compounds(VOCs) and meteorological parameters during severe air pollution period in Shijiazhuang were investigated. The correlation analysis showed that $PM_{2.5}$ had the significant positive correlation with relative humidity, while the negative correlations with wind speed. During this period, the average concentration of SOCwas 20 µg/m³ accounted for 50.5% of OC, indicating serious SOC pollution occurred in Shijiazhuang.

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