Distribution characteristics and sources of two water-soluble inorganic ions in $PM_{2.5}$ of Liuzhou City

Lian Feng [1], Shaohao Li [2,*] and Xiaoling Lu [3]

[1]Liuzhou Center for Disease Control and Prevention, Liuzhou 545005, China.

[2]Guangxi Zhuang Autonomous Region Center for Disease Control and Prevention, Nanning 530028;

[3]School of Medicine, Guangxi University of Science and Technology, Liuzhou 545006, China.

Abstract

Objective To understand the distribution characteristics and sources of secondary water-soluble inorganic ions in $PM_{2.5}$ of Liuzhou, it provides a reference for further comprehensive analysis of the composition of $PM_{2.5}$ in Liuzhou and its harm to human body. According to the atmospheric particulate matter, sample collection standard. Technical specifications for gravimetric measurement methods for $PM_{2.5}$ in ambient air. The secondary water-soluble inorganic ions in the 88 samples of $PM_{2.5}$ which were collected in Liuzhou from June 2017 to May 2018 were determined by ion chromatography ($N0_3^-$, SO_4^{2-} and NH_4^+) .The average concentrations of $N0_3^-$, SO_4^{2-}, NH_4^+ in $PM_{2.5}$ are (4.79±3.70),(8.86±5.15) and(2.63±2.29)μg·m^{-3},which accounted for (10.9±8.5)%, (20.2±11.8)% and (6.0±5.2)% of the mass of $PM_{2.5}$, respectively. The sum of those three accounted for (37.2±12.7) % of the mass concentration of $PM_{2.5}$. The seasonal variation characteristics of $N0_3^-$, $SO_4^{2-}$and NH_4^+ in $PM_{2.5}$ were obvious, that the mass concentration of the mixture of $N0_3^-$, $SO_4^{2-}$and NH_4^+ was as follows: Autumn > winter > spring > summer and the sum of the total concentration of $PM_{2.5}$ was autumn (49.2%). > Spring (40.5%) > winter (34.9%) > summer (26.1%).

Keywords

Distribution characteristics, source, $PM_{2.5}$.

1. Introduction

With the rapid development of economy, the problem of environmental pollution in China is becoming more and more prominent, and urban smog weather has occurred frequently. The haze weather was first included in the natural disaster information in 2013.General Secretary put forward a request to Beijing to control haze. Controlling $PM_{2.5}$ is the primary task of improving air quality. Exposure to high concentrations of $PM_{2.5}$ for a long time will have adverse effects on human health[1-2]. $PM_{2.5}$ is complex in composition and has a variety of pollutants. Long-term exposure to high concentrations of $PM_{2.5}$ can have adverse effects on human health [1-2].$PM_{2.5}$ is closely related to the formation and pollution of haze. $PM_{2.5}$ is closely related to the formation of ash. The scattering and absorption of visible light is the main reason for the decrease of atmospheric visibility[3-6],in which water-soluble inorganic ions are important substances in the atmosphere and various factors affecting the extinction coefficient of the atmosphere [7]. It has been found that the secondary water-soluble inorganic ions occupy a large proportion in the water-soluble inorganic ions and are the main components of the water-soluble inorganic ions.

As an important industrial city in Southwest China, Guangxi Liuzhou is mainly engaged in traditional manufacturing industries such as metallurgy, automobile and machinery manufacturing. The air pollution caused by high production capacity cannot be ignored. From 1985 to 1995, the acid rain

pollution in Liuzhou was serious. The frequency of acid rain reached 98.5% when it was the highest. According to the theory of " nine acids in ten rains ", it was listed as one of the four major acid rain cities in China. Liang Hongwen et al[22]. analyzed the chemical characteristics and genesis of acid rain in central of Liuzhou, and confirmed that the chemical characteristics of acid rain were most affected by ions, and the concentration accounted for 63.8% of the total ion concentration in precipitation. The monthly frequency of acid rain increases with the increase of atmospheric sulfation rate, and the correlation coefficient is 0.98, which is a typical sulfuric acid type acid rain. However, in the study of atmospheric particulate matter in Liuzhou, There are only the analysis of the characteristics of polycyclic aromatic hydrocarbons and heavy metal pollution which is still blank in the research of water-soluble inorganic ions of atmospheric particulate matter, and especially there is no research report on secondary water-soluble inorganic ions of $PM_{2.5}$.In view of the importance of secondary water-soluble inorganic ions in $PM_{2.5}$ on the atmospheric environment and human health, the pollution characteristics of secondary water-soluble inorganic ions in $PM_{2.5}$ in urban area of Liuzhou City will be obtained for the first time through the research of this subject, and the existing forms and influencing factors of NO_3^-,SO_4^- and NH_4^+ in $PM_{2.5}$ will be discussed by relevant analysis. Above information provides a reference for further more comprehensive analysis of the composition of $PM_{2.5}$ in Liuzhou and its harm to human body, and provides a scientific basis for future scientific prevention and control of air pollution in Liuzhou.

2. Materials and methods

2.1 Sample source

The sampling site (Fig. 1) is located on the 4 storey roof,about 15m away from the ground, and there is no industrial pollution source within 5km. It is a typical urban air observation site. Samples were collected according to the Technical Specification for Manual Monitoring Method (Gravimetric Method) of Environmental Air Particulate Matter ($PM_{2.5}$) (HJ 656-2013).In spring, 20 samples were collected from March to May.18 samples were collected from June to August in the summer, and 17 samples were collected in the autumn from September to November. In winter, there were 33 in December and February, and 88 valid samples were finally collected.

2.2 Experimental instruments

ICS-5000 ion chromatograph(Thermo Fisher Scientific, USA) ,PB303-A/FACT Electronic analytical balance (METTLER TOLEDO, USA);Milli-Q Advantage A10 Ultra-pure water device (Millipore, USA).

2.3 Experimental reagents

Sulfate standard substance(GBW(E)080266,Concentration value:1000mg·L^{-1}, National institute Metrology , China), Nitrate standard substance(GBW(E)080264 Concentration value:1000mg·L^{-1}, National institute Metrology ,China), Ammonia in water (NH_4^+) component analysis standard substance (GBW(E) 080525, Concentration value:1000mg·L^{-1}, National Defense Technology Industry Applied Chemistry Level I Metering Station),Methane sulfonic acid(Chromatographic purity, Shanghai Ampere Laboratory Technology Co., Ltd.), Potassium hydroxide (Guarantee Reagent, Sino pharm Chemical Reagent Co., Ltd.)

2.4 Sample determination

After weighing, the filter membrane was shredded, and 50 mL ultrapure water was extracted by ultrasonic cleaner. The blank solution was prepared simultaneously with the same batch of blank filter membrane. The content of secondary water-soluble inorganic ions (NO_3^-, SO_4^{2-} and NH_4^+) in the sample was determined by ion chromatography after being filtered with the 0.45 mm pinhole filter. Reference conditions for ion chromatograph: Dionex IonPac CG12A, Anion protection column: Dionex IonPac CG12A, Anion analysis column: Dionex IonPac CS12A,Cation suppressor: Dionex

CSRS300,T Eluent flow velocity: 1.0mL·min^{-1};Concentration of eluent: 30mmol·L^{-1} MSA;Sample volume: 25μL.

3. Result

3.1 Mass concentration characteristics of secondary water-soluble inorganic ions

3.1.1 Overall air quality status in Liuzhou during the study period (already counted)

According to the air quality index and level judgement criteria , first grade (excellent): 154 days, accounting for 42.2%,second grade (good): 153 days, accounting for 41.9%,third grade (light pollution): 49 days, accounting for 13.4%,fourth grade (moderate pollution): 8 days, accounting for 2.2%,fifth grade (severe pollution): 1 day, accounting for 0.3%,the overall mild pollution above 20%, So Liuzhou is a city with more serious air pollution. See Figure 1,the maximum daily mass concentration of $PM_{2.5}$ was 170μg·m^{-3},the minimum was 8μg·m^{-3},and the average annual concentration was (53.5±46. 5)μg·m^{-3}.See table 1.According to the secondary standard of $PM_{2.5}$ mass concentration of Environmental Air Quality Standard (GB 3095-2012) (daily average was 75 μg·m^{-3}. The number of days exceeding the standard was 53 days, and the rate of exceeding standard was 14.5%.

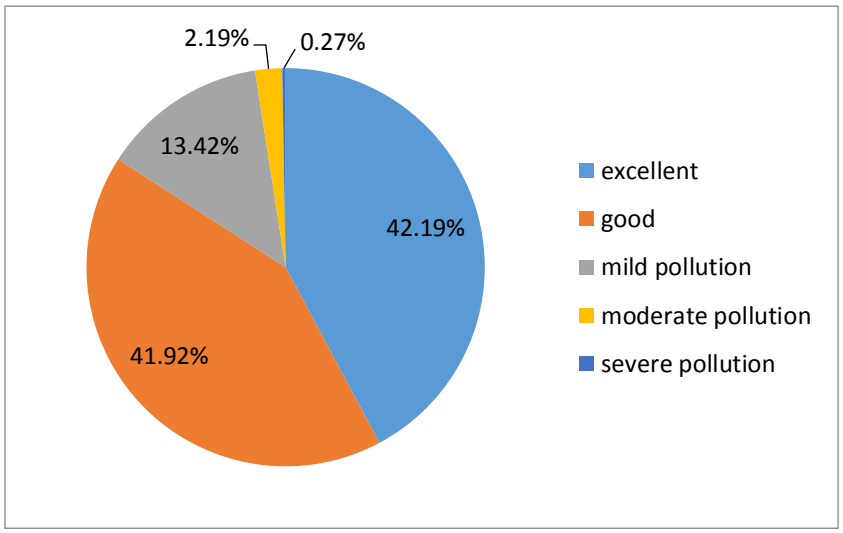

Figure 1 Overall air quality in Liuzhou during the study period

3.1.2 Seasonal variation of AQI in Liuzhou during the study period

The seasonal variation of AQI in Liuzhou is shown in Figure 2.The seasonal variation of AQI from good to poor is summer > spring > autumn > winter. Air quality in Liuzhou is best in summer. In summer, the excellent rate of AQI grade two is 95.3%.Moderate pollution 0.4%;In summer, the AQI second-level excellent compliance rate is 95.3%, the mild pollution is 4.3%, the moderate pollution is 0.4%, and the spring AQI second-class excellent compliance rate is 84.4%.In spring and summer, the weather is dominated by fine weather;There is was no severe or serious pollution and there is no severe pollution and serious pollution. The air quality in winter is the worst. The second-grade excellent rate of AQI in winter is 58.2%, the light pollution is 21.9%, the moderate pollution is 14.1%,the severe pollution is 5.6% and serious pollution is 0.4%. The AQI second-grade excellent compliance rate is 79.9%. Although most of the autumn is dominated by fine weather. There is severe pollution which began to appear in autumn.

3.1.3 Concentration level of secondary water-soluble inorganic ions

The daily average concentrations of secondary water-soluble ions (NO_3^- , SO_4^{2-} , NH_4^+) in $PM_{2.5}$ are (4.79±3.70) μg·m^{-3},(8.86±5.15) μg·m^{-3} and(2.63±2.29)μg·m^{-3},respectively,which accounted for (10.9 ± 8.5) %, (20.2 ± 11.8)% and (6.0 ± 5.2) %in $PM_{2.5}$.The sum of the three ions accounts for

(37.2±12.7) % of the mass concentration of $PM_{2.5}$, which exceeds 1/3 of the mass concentration of $PM_{2.5}$. It is indicated that the secondary water-soluble inorganic ion is the main component of $PM_{2.5}$ in Liuzhou.

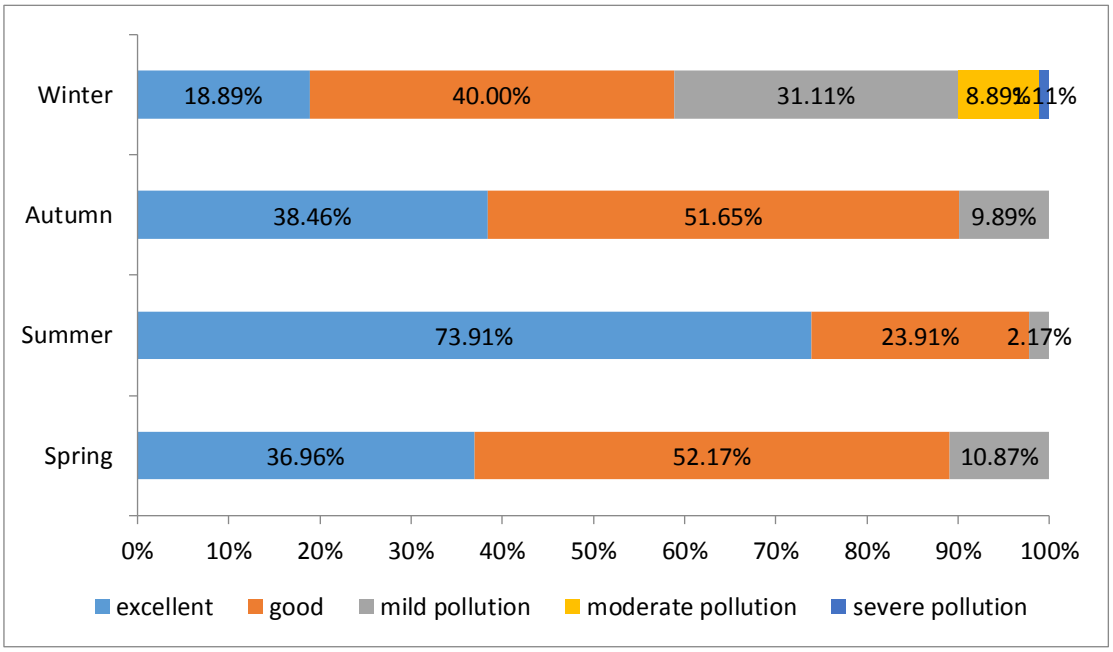

Figure 2 Seasonal Variation of AQI in Liuzhou City during the Study Period

Table 1 Concentration levels of secondary water-soluble inorganic ions during the study period

	$PM_{2.5}$ and its secondary ion concentration/μg·m^{-1}				secondary ion specific gravity/%		
	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	NO_3^-	SO_4^{2-}	NH_4^+
Maximum value	170	10.236	16.521	6.789	6.02	9.72	3.99
minimum value	14	0.852	1.658	0.728	6.09	11.84	5.20
average value	43.77	4.792	8.858	2.630	11.0	20.2	6.01

3.1.4 Seasonal variation characteristics of secondary water-soluble inorganic ions

The average concentration in spring: (12.39±4.63) μg·m^{-3}, the average concentration in summer: (6.51±3.43) μg·m^{-3}, the average concentration in autumn: (20.62±10.65) μg·m^{-3}, the average in winter Concentration value: (23.03±10.15) μg·m^{-3}.The order of the average concentration from large to small was: Winter > autumn > spring > summer; the sum of the three in each season accounts for the mass concentration of $PM_{2.5}$: spring (30.04±11.21)%,summer(26.14±13.77)%,autumn (49.19± 25.41)%, winter(24.88±15.37)%.The sum of the three values from large to small was: autumn > spring > summer > winter.

3.1.5 The existence form of secondary water-soluble inorganic ions

When $NH_4^+/SO_4^{2-}\leq0.19$(mass ratio),it indicates that these two ions are mainly in NH_4HSO_4 forms. When $NH_4^+/SO_4^{2-}\geq0.38$(mass ratio),it indicates that these two ions are mainly in the form of(NH4)2SO4[23].Table 4 shows mass ratio of NH_4^+/SO_4^{2-} in different seasons.The mass ratio of NH_4^+/SO_4^{2-}ratio in spring is higher than 0.38,which indicates that the two ions are mainly $(NH4)_2SO_4$ forms in spring.

Table 2 Mass ratio of $NH_4^+$and SO_4^{2-}in different seasons

project	NH_4^+/SO_4^{2-}
spring	0.53
summer	0.38
autumn	0.20
winter	0.29

4. Conclusions

(1)During the study period, the seasonal variation of AQI in Liuzhou showed from good to poor:summer>spring>autumn>winter.The secondary water-soluble inorganic ion is the main component of $PM_{2.5}$ in Liuzhou.The average concentration values of (NO_3^-, $SO_4^{2-}$and NH_4^+) of $PM_{2.5}$ are respectively (4.79±3.70),(8.86±5.15) and (2.63±2.29)μg·m^{-3},which accounted for (10.9 + 8.5)%, (20.2 + 11.8)% and (6 + 5.2)% of the mass of $PM_{2.5}$ respectively.The sum of the three accounts for (37.2 + 12.7)% of the mass concentration of $PM_{2.5}$.

(2)The seasonal variation characteristics of (NO_3^-, SO_4^{2-}andNH_4^+) of $PM_{2.5}$ are obvious.The mass concentrations of NO_3^-, SO_4^{2-} and NH_4^+ are all expressed as autumn > winter > spring > summer,and the concentration value is SO_4^{2-}> NO_3^- > NH_4^+.The sum of the percentage of mass concentration of $PM_{2.5}$ is autumn (49.2%), spring (40.5%), winter (34.9%) and summer (26.1%).

(3)The ratio of NH_4^+/SO_4^{2-} is higher than 0.38 in spring,which indicates that the main form of the two ions are mainly in the form of $(NH_4)_2SO_4$ in spring.

Acknowledgments

This study was financially supported by the promotion project of basic ability for young and middle-aged teachers in colleges and universities of Guangxi (Grant No. 2017KY0365).

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