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Chemical Features of Atmospheric Particulate Matter in Longmen Grottoes

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In recent years, the pollution of fine particulate matter (PM2.5) has been increasing in China. Particularly in the northern heating season, dust-haze has been very serious. Air pollution has a wide range of influence, which not only poses a hazard to human health, but also has a negative impact on the landscape of the scenic spot. This paper, by selecting the scenic spot- Longmen Grottoes as the object of research, applies the whole-sample analysis technique to determine the concentration of PM2.5 in the scenic spot. Then it analyses water-soluble ions, carbonaceous substances, and heavy metal elements one by one. Finally, it's concluded that: (1) The concentration of PM2.5 in the Longmen Grottoes area exceeds the limit, esp., in winter, which may be related to coal burning; (2) The calculation of the cation-anion balance shows that the atmospheric PM2.5 in the scenic spot is acidic, acidifying the precipitation, and causing corrosion and damage to the grottoes surface; (3) The linear correlation of OC (organic carbon) and EC (elemental carbon) concentrations in the atmospheric PM2.5 of the scenic spot is relatively high, indicating that their sources of pollution are the same; (4) Zn, Pb, and Cr in the atmospheric PM2.5 components are the main heavy metal elements.

1. Introduction

Longmen Grottoes is located in Longmen Town, Luolong District, Luoyang City, Henan Province (34.6 degrees north latitude and 112.5 degrees east longitude). It was established in the Emperor Xiaowen period of the Northern Wei Dynasty, after which it was continuously built by the dynasties of the Eastern Wei, Western Wei and Northern Qi etc. for more than 400 years. It reflected various changes in ancient politics, economy, literature, and art in ancient China with a large number of physical images and written materials. In 2000, it's listed as World Cultural Heritage by UNESCO, which has a high research value (Cassee et al., 2013). Due to natural weathering and man-made damages, the landscape of the Longmen Grottoes has been damaged to varying degrees. Besides, Luoyang is located in the coal-fired area, close to Jincheng, Jiaozuo, and Pingdingshan. Energy consumption is dominated by coal. So, the air pollution is more serious, with the main pollutants: sulfur dioxide, nitrogen oxides, PM2.5, and PM10, which are coal-smoke pollution (Pant and Harrison, 2013; Robert et al., 2013). In recent years, the number of visitors to the Longmen Grottoes has been increasing year by year, and the content of PM2.5 in the scenic spots has also gradually received more attention (Hoffman and Duce, 2013).

Table 1: Pm2.5 concentration limits in different countries and organizations

Countries or organizations	setting time	Average annual concentration limit / mg/m^3	Average daily concentration limit / mg/m3
WHO	2006	0.010	0.025
USA	1997-2006	0.015	0.035-0.065
EU	2008	0.025	—
China	2012	0.035	0.075

PM2.5, also known as fine particulates, refers to suspended particulate matter with an aerodynamic equivalent diameter less than or equal to 2.5 microns in the ambient air. It has a small particle size, a large specific

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surface area, and strong adsorptivity. It is also easy to attach toxic and harmful substances (heavy metals, microorganisms, etc.), and remains long-time suspension in the atmosphere, resulting in a serious impact on human health (Burnett et al., 2014). In addition, PM2.5 can also cause a series of problems such as acid rain, climate warming, and crop damage etc. (Bell et al., 2013). Based on the above hazards, scholars and research institutes in various countries have conducted in-depth studies on the concentration of PM2.5 and set limits (Table 1).

Studies show that the main components of PM2.5 in the atmosphere include water-soluble inorganic salt ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, $NH4^+$, F^-, CL^-, NO^{3-}, $SO4^{2-}$, etc.), and carbonaceous substances (organic carbon (OC), elemental carbon (EC), and trace element (mainly metallic element) (Grahame et al., 2014; Bell et al., 2012). The influence of PM2.5 on cultural relics includes two inseparable aspects: physical action and chemical action, and the two make mutual promotion. PM2.5 deposits on the surface of the cultural relics, causing it to lose original lustre and reduce the ornamental value. The acidic components in the fine particulate matters can corrode the surface materials of the cultural relics, and also be used as a carrier for various types of microorganisms, which shall rot and spoil the cultural relics under certain temperature and humidity (Mansha et al., 2012). Besides, it's also found through the studies that PM2.5 in the Longmen Grottoes area is acidic, and the acidity in winter is much higher than in summer; the acid particles may cause corrosion damage to cultural relics (He et al., 2013). The stone of the Longmen Grottoes is limestone, which has the relatively stable structure. Neutral water has limited damage to the grottoes, but the erosion of the cultural relics is obvious when the precipitation is acidic. The main pollutant in the Longmen Grottoes is SO_2, which dissolves in water to form an acidic solution and reacts with $CaCO_3$ on the surface of the cultural relics to produce $CaSO_4 \cdot 2H_2O$. This is the important cause of cultural.

2. Pollution particulate matter concentration in Longmen Grottoes

Taking the comprehensive factors into consideration such as terrain, surrounding environment, number of tourists, installation of instruments, etc., the following sampling sites were selected. No. 1 sampling site was the famous tourist spot-Xishan Grottoes with higher number of tourists. No. 2 sampling site was the main entrance of Longmen Grottoes Research Institute with less visitors and vehicle flow. Samples of fine particulate were collected on December 22-28, 2016, April 20-24, July 8-11, and October 25-28, respectively. The sampling time was the same: 9 am to 5 pm daily for 8 hours, and the temperature and humidity for the relevant sampling site and sampling time were recorded simultaneously. A total of 40 samples were obtained (Table 2).

Table 2: Sampling time, number and temperature records

Sampling period	Sampling time	Number	mean temperature/℃	mean humidity/%
December	2016.12.22-28	12	-8.4	36.2
April	2017.4.20-24	9	14	44.7
July	2017.7.8-11	8	28	60.4
October	2017.10.25-28	11	7.8	57.1

Analysis of the samples showed that the variation trend of the concentration for fine particulate matter in the sampling periods at the two sampling sites was basically similar. The sampling point at Xishan Grottoes ($238.6 \mu g \cdot m^{-3}$) in December was measured to be the maximum value, and the sampling point at Institute ($30.2 \mu g \cdot m^{-3}$) in Judy was the minimum value, and the overall average concentration was $112 \pm 64.8 \mu g \cdot m^{-3}$. For most of time in the sampling period, the concentration of fine particulate matter at the sampling site of the research institute was lower than that at the Xishan Grottoes. This may be due to the large passenger flow and the great impact of the human activities (burning incense and praying etc.) near the Xishan Grottoes; but the flow of visitors and traffic in the vicinity of the Institute was relatively small, without obvious source of pollution, so the concentration of fine particulate matter was low. The Longmen Grottoes belongs to the class I air quality functional area according to *Ambient Air Quality Standards* (2012), where, it's specified that PM2.5 applies to the daily average concentration limit of $35 \mu g \cdot m^{-3}$. Therefore, the scenic spot exceeded the standard for most of the time, and it was particularly serious in winter.

Generally, it can be seen in Fig.1 that from the perspective of the time range, the variation trends at the sampling sites of Xishan grottoes and the institute are the same. The PM2.5 mass concentration is December> October> April> July. Luoyang enters the heating period in early November every year, and pollutants are not easily diffused. In summer, the amount of coal is reduced while the amount of precipitation is large, so, pollutants are not easy to accumulate. This has caused a higher concentration of PM2.5 in winter and a lower concentration of PM2.5 in summer.

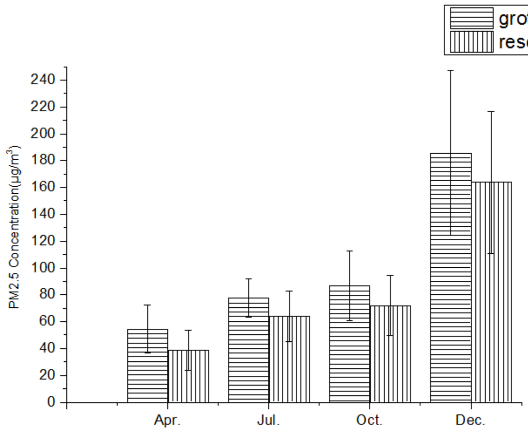

Figure 1: Average quality concentration of air pm2.5 in sampling periods

3. Chemical features of atmospheric particulate matter in Longmen Grottoes

In order to comprehensively analyse the pollution characteristics of each component of the atmospheric fine particulate sample, the whole-sample analysis method was applied to obtain the average level of some chemical components in the samples. The analysis mainly includes water-soluble inorganic ions, carbonaceous substances, and heavy metal elements.

3.1 Concentration of water-soluble ions in the fine particulate matter at sampling sites

In PM2.5, the average mass concentration of 9 water-soluble ions at the two sampling sites of Longmen Grottoes is shown in Table 3. The concentration at the sampling site of Xishan grottoes was December (112.84μg·m^{-3})> October (32.86μg·m^{-3})> April (18.85μg·m^{-3})> July (11.32μg·m^{-3}), while the concentration at the sampling site of research institute was December (103.68μg·m^{-3})>October (11.71μg·m^{-3})>4 months (11.84μg·m^{-3})>7 months (6.12μg·m^{-3}); the total ion concentration at the grotto sampling point 176.83μg·m^{-3} was greater than that at the sampling site of the institute, which was 133.51μg•m^{-3}, both accounting for 38.7% and 34.9% of the fine particulate concentration respectively.

The percentage of 9 water-soluble ions in the total mass concentration of ions at two sampling sites was basically the same, which may be due to the close distance between the two sites and the same causes of pollution. By taking the sampling point of the Xishan Grottoes as an example, it’s found that among the 9 water-soluble ions, the secondary ions content of the SO_4^{2-}, NO_3^-, and NH_4^+ is the highest (Table 3). These three types of ions are mainly converted from the surrounding industrial areas and fossil fuel-burning gaseous precursors (O_2, NO_X, NH_3, etc.) through a series of chemical reactions. SO_2 is generated mainly from the combustion of fossil fuels such as coal etc. NO_X mainly comes from the exhaust gas generated by the combustion of motor vehicles, and a small amount from the combustion of coal. NH_3 may be derived from the surrounding rural livestock breeding, organic matter degradation, agricultural fertilization, etc.

Table 3: Average concentration of 9 water-soluble ions in PM2.5 (mean ± sd, unit: μg·m^{-3})

	Grotto				Researcher			
	Apr.	Jul.	Oct.	Dec.	Apr.	Jul.	Oct.	Dec.
F^-	0.05±0.03	0.06±0.03	0.04±0.03	0.25±0.12	0.03±0.01	0.03±0.02	0.02±0.03	0.21±0.10
Cl^-	0.43±0.41	0.54±0.05	1.29±1.12	2.38±1.38	0.29±0.31	0.35±0.19	0.91±0.61	2.38±1.54
NO_3^-	3.51±3.21	1.19±0.34	8.49±6.45	5.21±2.97	1.78±1.49	0.81±0.42	2.29±1.28	4.71±2.74
SO_4^{2-}	8.61±3.09	6.58±2.21	8.49±5.39	74.2±18.9	5.34±3.98	3.21±1.19	3.69±2.14	66.5±16.8
Na^+	0.12±0.07	0.12±0.07	0.41±0.71	1.29±1.02	0.09±0.10	0.05±0.02	0.13±0.08	2.07±1.58
NH_4^+	3.95±0.09	2.19±1.09	11.74±4.31	16.45±4.21	2.59±1.39	1.01±0.87	3.38±1.08	15.98±4.57
K^+	0.29±0.10	0.20±0.17	1.69±0.47	1.59±0.49	0.22±0.04	0.11±0.09	0.48±0.18	1.48±0.42
Mg^{2+}	0.08±0.04	0.05±0.06	0.05±0.04	4.71±1.06	0.08±0.06	0.04±0.01	0.02±0.01	4.47±1.38
Ca^{2+}	1.59±0.79	0.46±0.32	1.12±0.64	5.42±1.58	1.28±0.62	0.42±0.12	0.69±0.19	5.07±1.81

he pH of atmospheric fine particulate matter has a significant impact on the pH of precipitation. In this paper, the cation and anion balance analysis were performed to explore the pH issue of atmospheric PM2.5 in the scenic area of Longmen Grottoes. Based on the above ideas, the cation balance is calculated as:

$\mathrm{CE} = \mathrm{Na}^{+}/23 + \mathrm{NH_4}^{+}/18 + K^{+}/39 + Mg^{2+}/12 + Ca^{2+}/20.$

Anion balance is calculated as:

$\mathrm{AE} = SO_4^{2-}/48 + NO_3^{-}/62 + Cl^{-}/35.5 + F^{-}/19.$

The linear fitting results of the cation and anion balance at the two sampling sites are shown in Fig. 2 and 3. At the sampling site of Xishan Grottoes, the goodness of fit for the cation and anion linear regression equation was 0.9435, and the slope was 1.1508, that is, the ratio of AE to CE was obviously greater than 1, indicating that the cations account for a majority and the fine particles are acidic. At the sampling site of institute, the goodness of fit for the cation and anion ion regression equations was 0.9236, and the slope was 1.0065, which is roughly equal to 1, indicating that the anionic and cationic ions of the fine particulate matter are basically in equilibrium and are approximately neutral. Thus, it can be seen that the PM2.5 in the Longmen Grottoes area is acidic, which may cause acid rain, to corrode or damage the cultural relics.

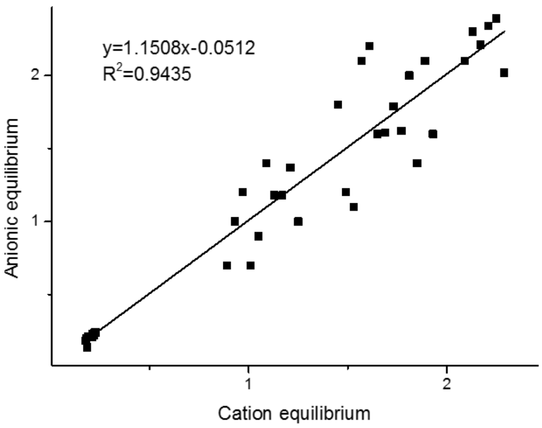

Figure 2: The correlation of CE and AE at grotto sampling site

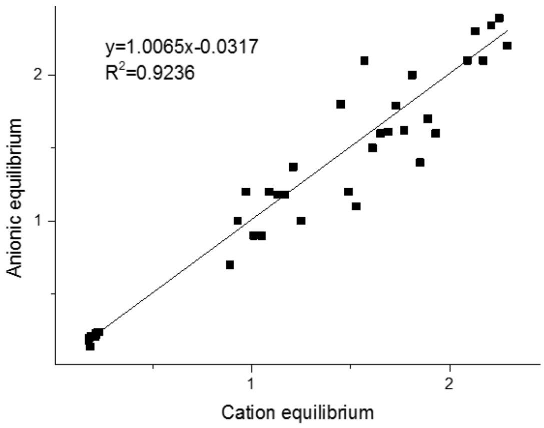

Figure 3: The correlation of CE and AE at research institute sampling site

3.2 Concentration of carbonaceous materials in fine particulate matter at sampling sites

Analysis of the carbon concentration in the samples showed that the OC (organic carbon) concentration range at Grottoes was 4.96-41.73 μg·m^{-3}, accounting for 7.89%-30.73% of the PM2.5 concentration; the EC (elemental carbon) concentration range was 0.37-28.84μg·m^{-3}, accounting for 1%-19.8% of PM2.5 concentration. At the sampling site of institute, the OC concentration range was 3.07-34.93μg·m^{-3}, accounting for 8.14%-30.79% of the PM2.5 concentration; the EC concentration range was 0.26-32.82μg·m^{-3}, accounting for 1%-15.6% of the PM2.5 concentration. The average value of OC and EC concentrations at the sampling site of grotto was greater than at the institute. The total concentration of OC and EC in PM2.5 accounted for about 22.8%, OC concentration was greater than EC concentration in the sampling periods of two sites, and

the OC, EC concentration was December> October> April> July. This seasonal change is also consistent with the change in the concentration of fine particulate matter.
Next, this paper analyses the source of carbonaceous particles by establishing regression equations for OC and EC. If the correlation between these two is higher, it means that the two are more likely to have the same source of pollution, otherwise, it indicates that they come from different sources of pollution. The regression results (Fig.4 and 5) show that the correlation is good, R2 is 0.81 and 0.79, respectively, and the regression coefficients are positive, indicating that OC and EC have the common source of pollution.

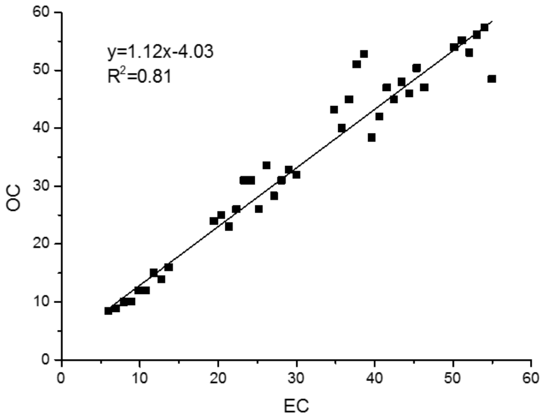

Figure 4: The linear regression of EC and OC at grotto sampling site

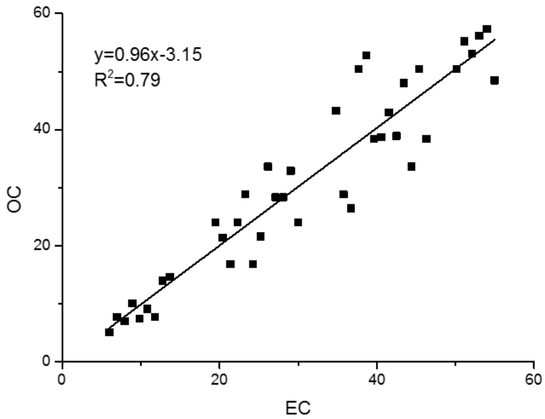

Figure 5: The linear regression of EC and OC at research institute sampling site

3.3 Concentration of heavy metal elements in fine particulate matter at sampling sites

In this paper, the concentration of main heavy metal elements at sampling sites was analysed, to find the main heavy metal elements: Zn, Pb, Cr, Cu, Ni, Cd, where the metal element contents of Zn, Pb and Cr are relatively high. In terms of average concentration, the six heavy metal elements are Zn>Pb>Cr>Cu>Ni>Cd. Among them, Zn, Pb, and Cr are significantly higher than other elements. The total concentration of main heavy metal elements above accounts for 0.29% to 1.52% of the fine particulate matter concentration, with an average of 0.59%, indicating that the proportion of heavy metals in PM2.5 is not significant.
In terms of the sample collection period, the concentration of the main heavy metal elements mentioned above was high in December and April, and low in October and July. At present, in China, the heavy metal pollution in PM2.5 comes from transportation, coal., oil consumption, manufacturing wastewater, and exhaust emissions etc. Zn is mainly derived from metallurgy, fossil fuel combustion and rubber additives. Pb mainly comes from exhaust emissions, lead battery manufacturing, and so on. The Longmen Grottoes is in the period of coal-fired heating in December; the burning of coal and other fossil fuels is the main reason for the increase in the content of heavy metal elements. In April, the sand is blown heavily, so, the heavy metal particles in the soil enter the atmosphere and result in its high content of heavy metals. In July and October, the humidity is relatively high, rainfall is abundant, and plants grow lushly, so as to promote the heavy metal deposition. Therefore, the concentration of heavy metals isn't high at these two time points.

4. Conclusions

This paper studies the atmospheric PM2 concentration and changes during the four sampling periods at the two sampling points/sites of the Longmen Grottoes, and then analyses the concentrations and changes of water-soluble ions, carbonaceous substances, and heavy metal elements one by one. The results show:

(1) The average daily PM2.5 concentration in Longmen Grottoes has far surpassed the concentration reference limit of Class I environmental function in the *Ambient Air Quality Standard* (2012), and it is the most serious during the heating period in December, when there is a lot of burning of coal. The mean concentration of atmospheric PM2.5 at the sampling sites of Grottoes is significantly higher than that at the sampling sites of the institute, which is closely related to the high passenger flow and human activities (burning licences or praying etc.) at the sampling site of grottoes.

(2) The contents of SO_4^{2-}, NO_3^-, and NH_4^+ in the PM2.5 in the Longmen Grottoes are higher, and the concentration of water-soluble ion in December is the highest. The cation-anion balance analysis shows that the atmospheric PM2.5 in the scenic area is acidic, which can make the precipitation acidified, and cause corrosion and damage to the surface of the grotto.

(3) The linear correlations of OC (organic carbon) and EC (elemental carbon) concentrations in atmospheric PM2.5 in the Longmen Grottoes area are relatively high, indicating that OC and EC have a common source of pollution. The concentration of heavy metals in PM2.5 during the sampling period is high in December and April, but low in October and July. During the sampling period, the contents of Zn, Pb, and Cr in PM2.5 are higher, far exceeding the content of Cu, Ni, and Cd.

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