

Characteristics of Water-soluble Organic Nitrogen of Ambient PM_{2.5} at Yungang Grottoes in Winter

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Abstract:

The aim of the study is to better understand the nitrogen-containing particles in the atmosphere of Yungang Grottoes, China for the sake of protecting the stone carvings and improving the air quality therein. In December 2021, using a medium flow sampler for 24-hour PM_{2.5} sample collection, the water-soluble organic carbon (WSOC), water-soluble total nitrogen (WSTN), water-soluble organic nitrogen (WSON) and inorganic ion measurements were determined and their concentrations, compositions, temporal characteristics and sources were analyzed. The results showed that during the winter period the averaged daily concentration of WSON in PM_{2.5} was $7.8 \pm 4.7 \mu\text{g} \cdot \text{m}^{-3}$, accounting for 39% of WSTN. Concentration of WSON were $(1.1 \pm 1.0) \mu\text{g} \cdot \text{m}^{-3}$, $(2.1 \pm 2.8) \mu\text{g} \cdot \text{m}^{-3}$ and $(11.5 \pm 4.5) \mu\text{g} \cdot \text{m}^{-3}$ in excellent days ($\text{AQI} \leq 50$), good days ($51 \leq \text{AQI} \leq 100$) and mild pollution days ($101 \leq \text{AQI} \leq 150$), respectively. There was a strong linear correlation between WSON and NH_4^+ , NO_3^- and SO_4^{2-} ($R^2 > 0.80$). Principal component analysis (PCA) showed that in winter, the main sources of WSON in PM_{2.5} were the secondary conversion of man-made pollutants and biomass combustion at Yungang Grottoes. It is suggested to optimize the regional energy structure and introduce policies for controlling biomass combustion in the Yungang region.

Keywords:

PM_{2.5}, Water-soluble Organic Nitrogen (WSON), Principal Component Analysis (PCA), Water-soluble Total Nitrogen (WSTN)

1. Introduction

The Yungang Grottoes (40.11°N, 113.26°E) are located in the western suburbs of Datong City, Shanxi Province, China. As a famous world cultural heritage, it has very high historical and artistic value. However, due to rich coal resources, special terrain

and climatic background in the Datong region, the ambient air quality of the Yungang Grottoes is at a relatively low level, with main pollution from particulate matter [1,2].

Previous studies focused on the inorganic nitrogen in atmospheric aerosols, while ignored the components of organic nitrogen that exists in land rainwater [3] and atmospheric particles [4]. In fact, organic nitrogen is a quantitatively important component of nitrogen in atmospheric aerosols, contributing to 10%~47% of the total nitrogen in atmospheric aerosol [5,6,7,8]. In general, the dissolved nitrogen in organic forms which come from rainwater on land contributes approximately 30% to water-soluble total nitrogen (WSTN) [9], while the water-soluble organic nitrogen (WSN) contributes 63% to WSTN in rainwater [9]. The organic nitrogen deposited into the sea by the atmosphere is biologically available because the WSON in rainwater can be used by bacteria and plankton [10]. Until now, no researches on WSON and WSTN in atmospheric aerosols at the Yungang Grottoes were reported.

In order to get knowledge of effects of ambient N-containing particles on stone heritages, explore the pollution characteristics, sources and forming mechanism of WSON in them, and better protect the statues of Yungang Grottoes against the particulate matter pollution, we took the open environment in front of Cave 20 of the Yungang Grottoes as the research site, sampling through a medium-flow sampler to analyze the time-varying trends of WSON in PM_{2.5}.

2. Materials and Methods

2.1. Sample Collection

The samples were taken at a height of 1.5 meters above the ground, 25 meters south to Cave 20 of the Yungang Grottoes (40.11°N, 113.26°E, Figure 1), Datong City, China in December 2021. Using the H-150C medium flow air PM_{2.5} sampler (100L·min⁻¹) produced by Wuhan Tianhong Instrument Co., Ltd., a total of 32 PM_{2.5} samples were collected at every 23 hours and 30 minutes per day. The quartz fiber filter membrane (Whatman QM/A, England) were used to collect the samples. They were burned at 450°C in muffle furnace for 6 hours to remove volatile organic compounds in prior to use, and were stored in a refrigerator at -4°C before and after sampling.

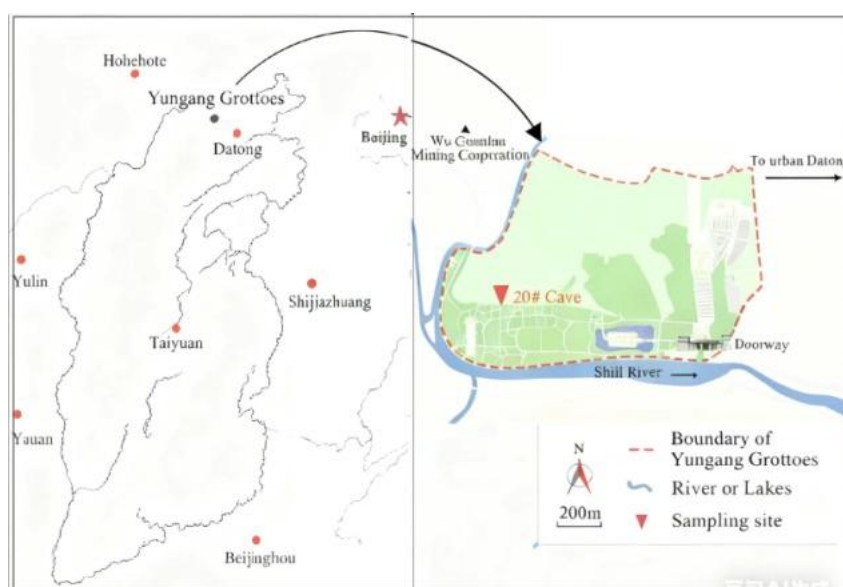


Figure 1. A schematic of the sampling site.

2.2. Sampling Analysis and Testing Methods

2.1.1. Analysis of Water-soluble Inorganic Ions

The inorganic ions were measured using Diana ICS-90 ion chromatograph, cation analysis column (4×250mm), CG12A cation protection column (4×50mm), CSRS-300 suppressor (4nm), anion analysis column (4×250mm) and AG14A anion guard column (4×50mm). The conductivity detector was DS5, the mobile phase flow rate was 1mL·min⁻¹, the suppressor current was 60mA, the loop was 10μL, and the column temperature was set at 25°C.

2.1.2. Analysis of Water-soluble Organic Nitrogen

WSTN was measured with TOC-2100s analyzer (Analytik Jena AG). The concentration of water-soluble organic nitrogen (WSN) can be determined by the difference between WSTN and WSIN, WSON= WSTN – WSIN. The concentration of WSIN was calculated by the sum of NH₄⁺, NO₃⁻, NO₂⁻ measured by ion chromatography, namely:

$$WSON=WSTN-14\times\left(\frac{[NO_3^-]}{62}+\frac{[NH_4^+]}{18}+\frac{[NO_2^-]}{46}\right)$$

2.2. Error Control and Guarantee

In order to ensure the accuracy of the experiment during the sampling process, the experiment set up a blank control group, and all the measured sample data were subtracted from the blank value and then averaged. The scissors and tweezers used to treat the sample were disinfected with alcohol, and washed with ultrapure water many times to remove possible pollution without interference.

3. Results and Discussion

3.1. Mass Concentrations of Major Components

According to the air quality index (AQI) data of Datong City in December 2021, the sampling period was divided into “excellent days” (AQI ≤ 50), “good days” (51 ≤ AQI ≤ 100), and “mild pollution days” (101 ≤ AQI ≤ 150).

Table 1. Concentrations of the measured species of PM_{2.5} in Yungang Grottoes /μg·m⁻³ in winter.

Component	Winter (N=32)	Excellent days (N=10)	Good days (N=16)	Mild pollution days (N=6)
Na ⁺	8.5±4.5 (0.4~26.4)	3.1±3.0 (0.4~6.5)	14.8±3.2 (3.2~19.5)	15.9±5.3 (11.4~26.4)
K ⁺	4.3±1.6 (0.7~8.0)	1.1±1.8 (0.7~2.0)	2.6±1.7 (1.2~4.5)	6.2±1.2 (3.7~8.0)
NH ₄ ⁺	10.4±6.7 (0.3~31.0)	1.7±2.1 (0.3~10.2)	13.0±3.7 (0.6~15.9)	27.6±5.2 (14.4~31.0)
Mg ²⁺	1.2±1.0 (0.1~4.8)	0.4±1.3 (0.2~1.4)	1.2±0.9 (0.1~2.8)	1.7±1.9 (0.1~4.8)
Ca ²⁺	1.8±1.6 (0.2~9.1)	0.9±1.0 (0.2~1.7)	1.3±0.4 (0.4~2.0)	2.6±2.1 (0.9~9.1)
F ⁻	1.1±0.9 (0~5.1)	0.2±0.2 (0~1.4)	0.6±0.2 (0.1~1.9)	2.0±1.4 (0.8~5.1)
Cl ⁻	10.6±9.6 (1.4~50)	7.3±5.1 (1.4~20)	9.2±5.5 (1.5~35)	20.1±8.2 (9.2~50)
NO ₂ ⁻	0.04±0.3	0.01±0.2 (0~0.05)	0.03±0.03	0.07±0.1 (0.03~0.4)

	(0~0.4)		(0.01~0.2)	
NO ₃ ⁻	18.6±10.7 (0.22~42.1)	2.2±1.5 (0.22~8.4)	16.8±4.4 (1.3~20.3)	29.2±6.4 (19.5~42.1)
SO ₄ ²⁻	21.5±16.2 (3.8~65.2)	7.3±2.0 (3.8~11.2)	17.8±9.8 (5.9~41.1)	48.1±12.3 (21.1~65.2)
WSTN	20.1±13.5 (1.2~54)	2.9±1.7 (1.2~14.2)	15.0±7.8 (3~25.9)	39.6±11.7 (18~54)
WSON	7.8±4.7 (0.1~21.6)	1.1±1.0 (0.1~5.2)	2.1±2.8 (0.4~10.2)	11.5±4.5 (5.7~21.6)
WSIN	12.3±6.2 (0.2~33.1)	1.8±1.6 (0.2~9.5)	13.9±7.8 (1.2~16.4)	28.1±6.4 (19.3~33.1)
NH ₄ ⁺ -N	8.1±5.0 (0.2~24)	1.3±1.6 (0.2~7.96)	10.1±7.6 (0.5~12.4)	21.5±4.1 (11.2~24)
NO ₃ ⁻ -N	4.2±4.3 (0.05~9.5)	0.5±0.3 (0.05~1.9)	3.8±1.5 (0.3~4.6)	6.6±1.5 (4.4~9.5)

Table 1 show the concentration levels of each component. The daily average concentration of WSON, NH₄⁺-N and NO₃⁻-N in winter mild pollution were 7.8±4.7, 8.1±5.0 and 4.2±4.3 μg·m⁻³, respectively. The daily concentration range of WSTN was 1.2~54 μg·m⁻³, with the average concentration of 20.1±13.5 μg·m⁻³. By caculation, the contribution rates of WSON, NH₄⁺-N and NO₃⁻-N to WSTN were 39%, 40% and 21% respectively. It indicates that the concentrations of each component showed an increasing trend from good days to mild pollution days.

3.2. Analysis of Possible Sources of WSON during the Sampling Period

3.2.1. Correlation Analysis between WSON and Water-soluble Ions

The water-soluble ions are important components of atmospheric particulate matter. And SO₄²⁻, NO₃⁻, NH₄⁺ are the main water-soluble ions, most of which are secondary products.

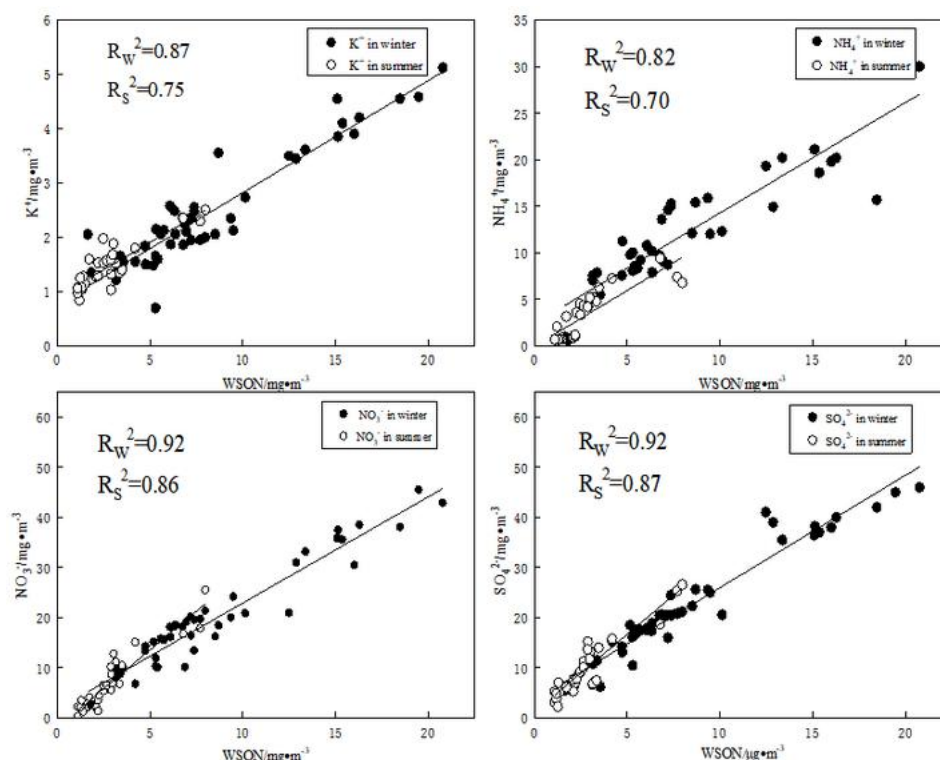


Figure 2. Relationship between WSON and NH₄⁺, K⁺, NO₃⁻, SO₄²⁻.

Their concentrations are related to the conversion of precursors SO_2 , NO_x and NH_3 , and are affected by temperature and humidity. SO_4^{2-} is mainly derived from the combustion of fossil fuels from anthropogenic sources, and K^+ mainly comes from the combustion of fossil and biomass. The concentration is higher due to the large amount of fossil combustion and biomass combustion in winter. Figure 2 shows the correlation analysis between WSON and SO_4^{2-} , NO_3^- , NH_4^+ , and K^+ . The high correlation ($R^2 > 0.8$) between WSON and this four water-soluble ions indicates that WSON has a similar source with these ions, suggesting that WSON is related to fossil fuel combustion, biomass combustion, and conversion of secondary pollution products.

3.2.2. Principal Component Analysis (PCA)

To further understand the source of WSON of ambient $\text{PM}_{2.5}$ at Yungang Grottoes, the principal component analysis was carried out based on the main water-soluble components (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- , SO_4^{2-} and WSON), as shown in Figure 3.

During the study period, there are significant correlation between NH_4^+ , K^+ , NO_3^- , SO_4^{2-} and WSON. Since NH_4^+ , NO_3^- , SO_4^{2-} are typical conversion products of secondary pollutants emitted by man-made combustion sources, and K^+ represents the source of biomass combustion, it is concluded that the main source of WSON in winter in Yungang Grottoes are secondary conversion and biomass combustion.

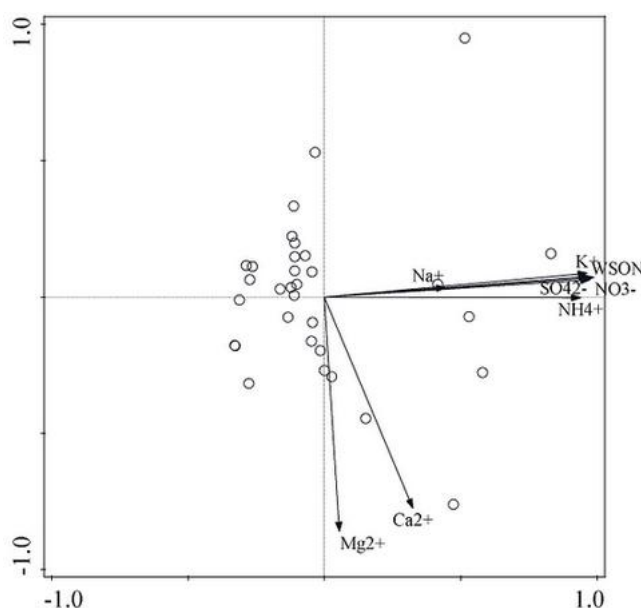


Figure 3. Relationship between WSON and NH_4^+ , K^+ , NO_3^- , SO_4^{2-} in winter.

4. Conclusions and Suggestions

(1) During the sampling period, the daily average concentration of WSON of $\text{PM}_{2.5}$ in the winter was $7.8 \pm 4.7 \mu\text{g} \cdot \text{m}^{-3}$. The contribution of WSON to WSTN was 39%.

(2) Analysis of the correlation between WSON and water-soluble ions indicates that WSON had similar sources with the ions of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- , SO_4^{2-} , suggesting WSON be related to fossil fuel combustion, biomass combustion, and conversion of secondary pollution products.

(3) PCA showed that the possible sources of WSON in winter were the conversion products of secondary pollutants discharged from typical anthropogenic combustion sources and biomass combustion.

(4) It is hoped for the local government to optimize the regional energy structure, promote clean energy to replace coal and firewood, and introduce policies for controlling biomass combustion to reduce primary emissions.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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