Concentrations, Sources, and Influential Factors of Water-Soluble Ions in Atmospheric Particles at the Dunhuang Mogao Grottoes, a World Heritage Site in China Postprint

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Abstract

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Full Text

Preamble

Concentrations, Sources, and Influential Factors of Water-Soluble Ions of Atmospheric Particles in Dunhuang Mogao Grottoes, a World Heritage Site in China

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Abstract: Atmospheric particle pollution is one of the major factors leading to degradation of ancient wall paintings, particularly at heritage sites in arid and semi-arid regions. However, current systematic research on the changes, sources, and influential factors of atmospheric particulate matter and its water-soluble ion concentrations remains insufficient. This study investigated major water-soluble ion concentrations, sources, and influential factors of atmospheric particles PM2.5 and PM10 (particulate matter with aerodynamic equivalent diameters $ $2.5 and 10.0 m, respectively) collected from Cave 16 and its ambient exterior environment in the Dunhuang Mogao Grottoes, China, between April 2015 and March 2016.

Results showed that PM2.5 and PM10 concentrations inside and outside the cave were highest in March 2016 and lowest in December 2015. Higher particle concentrations from March to May were related to frequent sand and dust events, while lower concentrations from June to September were associated with favorable diffusion conditions, increased precipitation, and an established cave shelterbelt. Particulate matter concentrations inside the cave were affected by outdoor concentrations. Ca^{2+} and NH_4^+ were the main components of total ions in PM2.5 and PM10 both inside and outside the cave. Total ion concentrations inside the cave were frequently affected by tourist activity disturbances during the peak season from May to August. Under dust influence, total concentrations of Cl^-, SO_4^{2-}, and Ca^{2+} in different particle sizes increased both inside and outside the cave, while concentrations of Cl^-, SO_4^{2-}, Na^+, and Ca^{2+} decreased during precipitation periods. Backward air mass trajectory analysis suggested that pollutants mainly originated from Xinjiang, China. Pollutant sources included straw burning, secondary pollution sources, soil dust, dry spring rivers, and tourist activities.

Keywords: grotto temple; atmospheric particulate matter pollution; water-soluble ion; water and salt transport; heritage preventive conservation

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1 Introduction

Cultural heritage represents the common wealth of humankind, yet climate change, natural disasters, environmental pollution, and unreasonable management have caused serious damage to heritage conservation [?, ?, ?, ?, ?, ?, ?].

Air particulates significantly impact global and regional climate change and environmental systems [?, ?, ?], and damage cultural relics through coverage pollution and chemical corrosion [?, ?, ?]. Deposition of atmospheric particulates on cultural relic surfaces alters their color and texture, affecting aesthetic value and visual effects [?, ?], while certain chemicals in dust also affect murals and painted sculptures. Acidic components such as sulfate, nitrate, and small molecular organic acids react with mineral pigments in painted layers during spreading and sedimentation. Long-term accumulation causes corrosion and damage to cultural relics in caves [?, ?], and carbon and acid components react with $CaCO_3$ to form black or grey crusts that further corrode pigment layers [?, ?]. The cleaning process itself causes additional mechanical wear. Numerical simulations by Tétreault [?] showed that for preserving cultural relics for 100 years, the maximum allowable PM2.5 concentration should be limited to 0.1 g/m^3. Under environmental conditions of 10.0 g/m^3 PM2.5, the time for nondestructive preservation of cultural relics is only one year.

As early as the mid-19th century, the National Gallery of England began studying the corrosive effects of indoor atmosphere on cultural relics [?]. Ghedini et al. [?] analyzed water-soluble ion composition in atmospheric particulate matter surrounding Florence Cathedral buildings. Singh and Sharma [?] studied seasonal changes and sources of PM10 at the Taj Mahal in India, finding obvious seasonal variation with sources mainly from soil crust, vehicles, and industrial emissions.

Chinese scientists conducted comprehensive monitoring of indoor and outdoor air quality at Emperor Qin Shihuang's Mausoleum, the Terra-cotta Warriors and Horses Museum, Exhibition Hall Museum, and Jinsha Site Museum, finding that water-soluble components have caused long-term harm to cultural relics [?, ?, ?, ?].

Ancient murals constitute important cultural relic components. The Dunhuang Mogao Grottoes (40°05$'17''$N, 94°40'16"E; 1334$ma.s.l.$), $famous for ancient murals, are situated at the western$ of murals, and 2400 painted sculptures [?], and were designated a World Heritage Site by UNESCO in 1987 [?]. Located on the southeastern edge of the Kumtag Desert at the eastern foot of Mingsha Mountain, the dry climate provides unique natural conditions for long-term mural preservation. The study area experiences strong northwesterly and southwesterly winds that transport large amounts of sand to and into the caves, causing serious harm to murals both outside and inside [?]. Sand particles carried by high-velocity southeasterly winds may contribute to deterioration of paintings on the eastern wall of Mogao Grotto Cave 285 [?]. Windblown sand causes mural detachment and flaking [?]. Small air particles with large specific surface areas easily carry heavy metals, acidic oxides, organic pollutants, and microorganisms [?]. When humidity is high, shell-like coatings readily form on cultural relic surfaces. Small particles enter mural gaps, accelerating flaking. When visitors enter caves, air currents change [?], and air particles repeatedly settle and adsorb on cultural relic surfaces, aggravating mural coverage and affecting tourist and

staff health.

Current research on atmospheric particulate matter pollution in the Mogao Grottoes mainly focuses on microbes, elements, organic carbon, and water-soluble ions [?, ?, ?, ?]. This study addresses the current situation of atmospheric particulate matter pollution based on analysis of temporal and spatial changes in particulate matter and its water-soluble ions, characteristics under extreme conditions (precipitation and sandstorms), and ion changes. Through airflow backward trajectory analysis, we speculated on pollution sources during dusty weather and changes in particle and water-soluble ion concentrations inside and outside the caves. We systematically analyzed their sources and influential factors based on three questions: (1) What are the differences in particle changes inside and outside caves? (2) What are the sources of water-soluble ions in atmospheric particles? (3) What are the effects of natural factors and visitor activities? The results provide important information for air pollution control and treatment in the Mogao Grottoes and serve as a reference for building monitoring and early warning systems for cultural relic protection and tourism management.

2.1 Study Area

The Mogao Grottoes are located 25 km from Dunhuang City, surrounded by Gobi area and river systems. Sampling sites were positioned in front of Cave 72 (outside) and inside Cave 16 (inside the open cave), which is 1 km west of the Daquan River, with the Kumtag Desert to the east (Fig. 1 [Figure 1: see original paper]). The climate is extremely arid, with average annual precipitation of 39 mm, of which more than 59% concentrates from June to August. Annual relative humidity is 31%, annual average temperature is 11.2°C, and annual evaporation is about 4348 mm [?].

2.2 Plane Section and Air Exchange Rate of the Cave

During the sampling period, total tourist numbers in the Mogao Grottoes reached 1,147,735. Monthly average tourist numbers from April to December 2015 were 36,920, 66,065, 101,503, 216,793, 283,197, 168,084, 202,511, 22,699, and 8,275, respectively. From January to March 2016, monthly averages were 7,605, 17,275, and 16,808, respectively.

Without tourists, the air exchange rate of small and medium-sized caves is generally less than 10 minutes. With tourists, the air exchange rate inside and outside caves doubles, demonstrating obvious tourist impact on cave air exchange [?]. Cave 16 has a door width of 4.0 m, a 7.5 m distance between cave door and tunnel, and a 14.5 m distance between tunnel entrance and sampling instrument. The cave door has screen windows and wooden floors. Particles enter the cave through three main pathways: infiltration, natural ventilation, and tourists (Fig. 2 [Figure 2: see original paper]).

2.3 Air Particulate Matter Data

PM2.5 and PM10 samples were collected on quartz fiber filter papers (47 mm, Whatman, USA) using two parallel medium-volume air samplers (Dichotomous Partisol-Plus Model 2025, Thermo Scientific, USA) at each sampling site, at flow rates of 15.00 and 1.67 L/min for 24 h, respectively, with separate sampling during dust and precipitation events. At least 316 replicate samples were obtained from the two sites. To remove carbonaceous contaminants, quartz filters were pre-heated at 500°C for 4 h in a muffle furnace before sampling. Before and after sampling, filters were equilibrated for 24 h in a balance dish at 20°C ($\pm 1°C) and 50 \pm 5\%$) relative humidity. Filter membranes were weighed three times with an electronic balance (AUY220, Shimadzu, Japan) before and after sampling. After sampling, filter membranes were stored below 0°C prior to weighing and water-soluble ion analysis.

2.4 Meteorological Data

Air temperature, relative humidity, rainfall, wind speed, and wind direction were obtained from the weather station in front of Cave 72. Gobi area data were provided by the monitoring and early warning system platform of the Cave Monitoring Center of Dunhuang Academy.

2.5 Water-Soluble Ion Sample Preparation and Detection

Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and $NH_4{}^{+}$) and major anions (F^{-}, Cl^{-}, $NO_3{}^{-}$, and $SO_4{}^{2-}$) in selected air particulate matter samples were measured using an ion chromatograph (Dionex-6000, Dionex, USA) [**?**].

2.6 Quality Assurance and Control

All analytical procedures complied with strict quality assurance and control protocols. Correlation coefficients of standard working curves for the nine water-soluble ions all exceeded 0.9990. All water-soluble ion concentrations were corrected by eliminating field blank values to remove errors caused by gas adsorption artifacts. The detection limit was 1 ng/mL, with standard deviation less than 5%. Determination limits for ions were: F^{-} (0.002 g/m^3), Cl^{-} (0.001 g/m^3), $NO_3{}^{-}$ (0.004 g/m^3), $SO_4{}^{2-}$ (0.004 g/m^3), Ca^{2+} (0.003 g/m^3), Mg^{2+} (0.003 g/m^3), Na^{+} (0.003 g/m^3), K^{+} (0.006 g/m^3), and $NH_4{}^{+}$ (0.003 g/m^3).

2.7 Statistical Analysis

Statistical analysis was performed using SPSS v.22.0, and graphs were drawn using Origin v.16.0. The Pearson method analyzed correlations among air temperature, air pressure, relative humidity, wind speed, precipitation, tourist numbers, and atmospheric particulate matter concentrations inside and outside the cave.

3.1 Air Particulate Matter Concentration

Monthly average PM2.5 and PM10 concentrations at the two monitoring points showed similar trends with large monthly variations (Fig. 3 [Figure 3: see original paper]). Concentrations were highest in March 2016 (339.4677, 421.6259, 708.2016, and 754.6400 μg/m^3) and lowest in December 2015 (15.4841, 23.6697, 21.4576, and 27.7507 μg/m^3). Low PM2.5 and PM10 concentrations were concentrated from November 2015 to February 2016 (inside cave variation ranges: PM2.5 15.4841–49.5065 μg/m^3, PM10 23.6697–74.0431 μg/m^3; outside cave variation ranges: PM2.5 21.4576–113.8568 μg/m^3, PM10 27.7507–132.8765 μg/m^3). From June to September, PM2.5 and PM10 concentrations inside the cave differed from outside (inside cave variation ranges: PM2.5 49.8075–60.6085 μg/m^3, PM10 70.0128–82.1617 μg/m^3; outside cave variation ranges: PM2.5 58.7113–88.8595 μg/m^3, PM10 69.1679–118.4600 μg/m^3).

PM2.5/PM10 ratios inside and outside the cave were both less than 1, indicating that atmospheric particulate matter pollution at the Mogao Grottoes mainly originated from coarse particles larger than PM10. PM2.5/PM10 increased from the beginning of the period to August 15, then decreased with a jump in January 2016 inside the cave, while fluctuating outside.

Correlation analysis revealed that PM2.5 mass concentration inside the cave was significantly and positively correlated with outside concentration (r=0.867, P<0.01), and PM10 mass concentration was also significantly and positively correlated (r=0.903, P<0.01), showing that cave particulate matter concentration was mainly affected by outdoor atmospheric particulate matter concentration.

Table 1 shows correlation analysis between PM2.5 and PM10 concentrations and various meteorological elements and tourist numbers. Concentrations at both sampling points were negatively correlated with air temperature, relative humidity, and precipitation. During the sampling period, outdoor and indoor temperatures varied from -16.66°C to 40.71°C and -3.36°C to 23.00°C, respectively. Cave particulate matter concentration showed higher correlation with temperature than outdoor concentration, as temperature difference promotes air exchange. Annual precipitation at the Mogao Grottoes is 39 mm, concentrated in May-September. PM2.5 and PM10 concentrations were positively correlated with air pressure, wind speed, and tourist numbers. Cave particulate matter concentration showed strong correlation with tourist numbers and wind speed, indicating that tourists contributed significantly to cave air pollution.

3.2.1 Concentration of Water-Soluble Ions

As shown in Table 2 , total water-soluble ion concentrations in PM2.5 and PM10 inside the cave were 11.0106 ($\pm$5.4744)and22.3576($\pm$10.5183)$g/m^{3}, respectively, withionranking: Ca^{2+}$ > NH_4^+ > Cl^- > Na^+ > SO_4^{2-} > K^+ > NO_3^- > Mg^{2+} > F^-. Outside the cave, concentrations were 11.7001 ($\pm$7.1713)and25.3878($\pm$15.7937)$g/m^{3}, respectively, withranking: Ca^{2+}$ > Cl^- > NH_4^+ > SO_4^{2-} > Na^+ > NO_3^- > K^+ > Mg^{2+} > F^-. Results showed that Ca^{2+}, NH_4^+, Na^+, Cl^-, and SO_4^{2-} were main components of total

water-soluble ions both inside and outside the cave. PM2.5/PM10 ratios were 0.42–0.62 inside and 0.37–0.62 outside, showing that nine water-soluble ions had different enrichment degrees in different particle sizes. NH_4^+ concentration in fine particles inside the cave was relatively high, while Cl^-, NO_3^-, and NH_4^+ outside the cave were relatively high in fine particulate matter.

The ratio of each ion to total ion content remained basically unchanged, indicating relatively stable composition either inside or outside the cave (Fig. 4 [Figure 4: see original paper]). Cl^- concentrations accounted for 16.48% and 14.76% in PM2.5 and PM10 inside the cave, and 18.30% and 14.40% outside, respectively. NH_4^+ accounted for 16.74% and 13.05% inside, and 14.26% and 10.73% outside, respectively. Ca^{2+} accounted for 35.89% and 41.01% inside, and 34.48% and 41.74% outside, respectively.

3.2.2 Monthly Change of Water-Soluble Ions

Figure 5 [Figure 5: see original paper] shows that total ion concentration in PM2.5 and PM10 inside the cave generally increased during the measurement year, fell to the lowest point in September, and increased to peak or secondary peak in January or March. Concentrations of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+} increased from January to March 2016. F^- concentration was higher in July-August 2015, NO_3^- was higher in November 2015-January 2016, and NH_4^+ was higher in October 2015-January 2016.

Total ion concentration in PM2.5 and PM10 outside the cave decreased from June 2015 to October, then increased until January 2016, showing an increasing trend from January to March 2016. Monthly distributions of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+} outside the cave were similar to those inside. F^- changed from January to March 2016, while NH_4^+ concentration was high from October 2015 to March 2016. Both inside and outside the cave, ion mass loss was lowest in September and highest in January or March.

3.3 Air Particulate and Water-Soluble Ions in Particles of Different Sizes Inside and Outside the Cave in Extreme Conditions

3.3.1 Influence of Sandstorm and Precipitation on Atmospheric Particulate Matter

A sandstorm occurred in Dunhuang from 01:00 to 19:40 LST on 29 April 2015, with wind speed of 7.83 m/s at the cave top, reaching a maximum instantaneous wind speed of 12.72 m/s at 15:40. During the sandstorm, wind direction varied from 0.0° to 355.2°, with main direction NNE (north-north-east), conducive to pollutant movement into the cave. Continuous precipitation occurred from 17:30 to 21:10 on 29 April, with cumulative precipitation reaching 2.3 mm (17.04% of total 2015 precipitation) and relative humidity reaching 84.56%. Samples were

collected to analyze effects of special weather on atmospheric particulate and water-soluble ion concentrations.

Figure 6 [Figure 6: see original paper] shows that during sunny weather, PM2.5 and PM10 concentrations inside and outside the cave were 83.3333 and 270.8333 μg/m^3, and 64.8148 and 170.8333 μg/m^3, respectively, with outdoor concentrations being 0.78 and 0.63 times corresponding indoor concentrations. During precipitation, concentrations were 55.5556 and 95.8333 μg/m^3, and 18.5185 and 24.5370 μg/m^3, respectively, with outdoor concentrations being 0.33 and 0.26 times indoor concentrations. During sandstorm, concentrations were 287.6157, 367.2535, 474.5370, and 547.9167 μg/m^3, representing 3.45, 1.36, 7.32, and 3.21 times sunny weather values, and 5.18, 3.83, 25.63, and 22.33 times precipitation period values, respectively. Outdoor concentrations were 1.65 and 1.49 times corresponding indoor concentrations. Sandstorm and precipitation rapidly affected atmospheric particulate concentrations at both monitoring points, especially outdoor pollutant concentrations.

3.3.2 Influence of Sandstorm and Precipitation on Water-Soluble Ions

Water-soluble ion concentrations in PM2.5 and PM10 differed inside and outside the cave (Fig. 7 [Figure 7: see original paper]). On sunny days, total concentrations of Cl^-, SO_4^{2-}, Na^+, NH_4^+, and Ca^{2+} in PM2.5 and PM10 were 6.9426, 12.3699, 8.5362, and 12.7496 μg/m^3, accounting for 95.24%, 93.80%, 95.28%, and 93.88% of total water-soluble ions, respectively. Total mass concentrations of other ions (F^-, NO_3^-, K^+, and Mg^{2+}) were 0.3469, 0.8180, 0.4225, and 0.8311 μg/m^3, accounting for only 4.76%, 6.20%, 4.72%, and 6.12%, respectively.

During sandstorm, total concentrations of Cl^-, SO_4^{2-}, Na^+, NH_4^+, and Ca^{2+} in PM2.5 and PM10 were 9.5812, 15.7339, 18.0314, and 25.8900 μg/m^3, accounting for 95.51%, 94.91%, 96.28%, and 95.51% of total water-soluble ions, respectively. Total mass concentrations of other ions (F^-, NO_3^-, K^+, and Mg^{2+}) were 0.4502, 0.8434, 0.6971, and 1.2170 μg/m^3, accounting for only 4.49%, 5.09%, 3.72%, and 4.49%, respectively.

During precipitation, total concentrations of Cl^-, SO_4^{2-}, Na^+, NH_4^+, and Ca^{2+} in PM2.5 and PM10 were 3.0384, 5.4094, 1.3198, and 2.6671 μg/m^3, accounting for 91.89%, 91.25%, 90.31%, and 89.39% of total water-soluble ions, respectively. Total mass concentrations of other ions (F^-, NO_3^-, K^+, and Mg^{2+}) were 0.2681, 0.5188, 0.1416, and 0.3166 μg/m^3, accounting for only 8.11%, 8.75%, 9.69%, and 10.61%, respectively.

Further analysis showed that under dust weather influence, concentrations of Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were 1.72–2.75, 1.63–2.29, 1.54–2.41, and 2.12–3.62 times sunny day values, with proportions increasing significantly. Concentrations of F^-, NO_3^-, and NH_4^+ changed little. While proportions of NH_4^+, K^+, Mg^{2+}, and Ca^{2+} decreased, F^- proportion increased inside the cave but decreased outside. Cl^- and Na^+ varied the most. Sandstorm period concentrations of Cl^-, SO_4^{2-}, Na^+, and Ca^{2+} were 4.65–36.51, 4.73–41.91,

6.30–24.87, and 2.65–13.28 times precipitation period values. Proportions of Cl^-, $SO_4{}^{2-}$, and Na^+ decreased significantly, while Ca^{2+} proportion increased inside the cave but decreased outside.

3.3.3 Backward Trajectory of Air Flow

To identify potential transport pathways and possible source regions of aerosols over the Mogao Grottoes, we used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://ready.arl.noaa.gov/HYSPLIT_{traj}.php) to simulate sand and dust transport, calculating a 24-h backward trajectory (Fig. 8 [Figure 8: see original paper]). Heights of 500, 1000, and 1500 m were selected, with back-calculation time at 17:00 UTC on 28 April and 01:00 LST on 29 April 2015. Combined with ion concentrations in Figure 7, arriving air masses were classified into two types: (1) those arriving on 29 April that originated from or were transported through arid regions of Hami City, Xinjiang Uygur Autonomous Region, via the Taklimakan Desert; and (2) those transported through the Kumtag Desert to the sampling site, which may have resulted in desert dust input and some anthropogenic pollution. Thus, concentrations of Cl^-, $SO_4{}^{2-}$, Na^+, $NH_4{}^+$, and Ca^{2+} were very high.

3.4 Acidity and Alkalinity of Atmospheric Particles

Acidity of atmospheric particles can be determined by analyzing the balance of main anion and cation charges [**?**]:

$$AE = c(Cl^-)/35.5 + c(NO_3^-)/62 + c(SO_4^{2-})/48 + c(F^-)/19,$$

$$CE = c(NH_4^+)/18 + c(Mg^{2+})/12 + c(K^+)/39 + c(Ca^{2+})/20 + c(Na^+)/23,$$

where c is ion concentration (µg/m^3), AE is anion equivalent (eq/m^3), and CE is cation equivalent (eq/m^3).

Figure 9 [Figure 9: see original paper] shows fitting lines for cation versus anion equivalent values in PM2.5 and PM10. Slopes of anion-cation balance for PM2.5 and PM10 inside and outside the cave were greater than 1 (3.48, 6.06, 1.90, and 6.49, respectively), showing anion deficiency and alkalinity in the Mogao Grottoes.

3.5 Source Analysis of Water-Soluble Ions

Principal component analysis and orthogonal rotation factor load matrix results are shown in Tables 3 and 4. For PM2.5 inside the cave (Table 3), three factors contributed 76.22%. Factor 1 loaded with Na^+, K^+, Cl^-, $NO_3{}^-$, and $SO_4{}^{2-}$ accounted for 40.73% of total variance. Factor 2 was dominated by Mg^{2+} and

Ca^{2+}. Factor 3 was dominated by F^-. For PM10 inside the cave (Table 4), three factors contributed 84.57%. NH_4^+ predominance in Factor 1 accounted for 33.89%. Na^+, K^+, F^-, and Cl^- in Factor 2 had significant effects. Factor 3 significantly affected Mg^{2+} and Ca^{2+}.

For PM2.5 outside the cave (Table 3), three factors contributed 82.90%. Factor 1 dominated by F^-, Cl^-, NO_3^-, and SO_4^{2-} had significant effects, accounting for 33.89%. Factor 2 showed significant effects from Na^+, K^+, Mg^{2+}, and Ca^{2+}. Factor 3 showed significant F^- effects. For PM10 outside the cave (Table 4), three factors contributed 88.28%. Factor 1 showed significant effects from Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}, accounting for 51.27%. Factor 2 showed significant NH_4^+ and NO_3^- effects. Factor 3 showed significant F^- effects.

4.1 Effects of Climatic Factors and Visitors

Besides pollution sources, atmospheric particulate matter concentration is affected by meteorological elements such as temperature, air pressure, wind speed, and precipitation [**?**, **?**]. Precipitation is considered a major factor in long-term mural preservation [**?**]. When relative humidity exceeds 75%, it increases mural crack frequency and influences material transformation processes [**?**]. In Figure 3, the difference between indoor and outdoor PM2.5 concentrations in March was much higher than reported by Li et al. [**?**] at the Pottery Depot of the Terracotta Warriors and Horses Museum (inside: 76.1 µg/m^3; outside: 153.9 µg/m^3) and by Deng et al. [**?**] at the Jinsha Site Museum (inside: 33.3 µg/m^3; outside: 39.4 µg/m^3). This difference can be attributed to windy, sandy weather in northern China's arid environment. Cold air activity is more frequent and likely to cause sand and dust in spring (March-May) in Dunhuang. Mingsha Mountain, providing sufficient sand source for windy weather, is 1 km from the Mogao Grottoes top, although a shelterbelt located directly in front provides protection against sand and dust processes [**?**].

Cave PM2.5 and PM10 concentrations were also affected by tourist numbers during the peak season (June-September 2015). Table 1 shows that large temperature differences between outside and inside promote atmospheric particle migration. Higher temperatures increase airflow activity and facilitate pollutant diffusion. When cave relative humidity is high, particles easily adsorb to water vapor surfaces, forming wet deposition that settles to the ground [**?**], thus reducing suspended particle concentration. Summer and autumn precipitation has strong scavenging effects on pollutants [**?**]. Outdoor particulate matter concentration is more likely affected by precipitation, as humidity increase in caves may cause salt damage to murals. During non-polluted periods, opening cave doors and increasing air circulation plays an important role in reducing suspended particulate concentration. Under high pressure, particulate matter does not readily diffuse, easily causing PM2.5 and PM10 accumulation [**?**]. High wind speed facilitates particulate matter migration, likely due to abundant deposits in Mingsha Mountain and the gravel Gobi area at the cave top. The average annual wind speed at the cave top is 4.23 m/s, with sand-blowing wind frequency

($ $5 m/s at 2 m height) as high as 69.80%. Higher wind speed can easily blow pollutants deposited on sand dunes into the cave [?]. Westerly winds (strong but low frequency) harm murals through sand transportation and accumulation in front of caves [?]. The valley topography between Sand Mountain and Sanwei Mountain to the east is not conducive to pollutant diffusion. The average annual wind speed inside the cave is 0.54 m/s, with sand-blowing frequency of only 0.01%, which is not conducive to pollution dispersion. Higher wind speeds facilitate particle infiltration into caves through cracks in Cave 16, increasing particle mass concentration, while tourist disturbance causes secondary particle suspension.

4.2 Sources of PM2.5 and PM10

Studies show that Gobi area soil in the top 50 cm has high salinity (4.4% average), mainly consisting of Na_2SO_4 and NaCl [?]. As shown in Table 2, Gobi area salt content may affect inorganic ion content (Na^+, Cl^-, and SO_4^{2-}) in atmospheric particulates, and effective control of unstable, dust-prone surfaces can reduce harmful salt ion sources in murals. NH_4^+ concentration in fine particles inside the cave was relatively high. Fine particles more easily enter fresco cracks, increasing contribution of enriched salt ions to mural degradation. Therefore, dust removal from pigmented layer surfaces should focus more on fine particles. NO_3^- mainly comes from secondary pollution such as coal combustion and soil dust in surrounding rural areas. NO_3^-/SO_4^{2-} can distinguish mobile from fixed pollution sources [?]. In this study, NO_3^-/SO_4^{2-} in PM2.5 and PM10 inside and outside the cave was less than 1, suggesting that coal combustion or dust contributes more pollutants than mobile sources. This is because motor vehicles are strictly prohibited in key protected areas, tourist shuttle buses park more than 200 m away, and the protective forest belt effectively reduces secondary pollutant emissions. This result is consistent with Yang et al. [?], who found significant impacts of tourist visiting patterns on water-soluble ions.

In Figure 5a and b, May-August 2015 represents the peak tourist season, accounting for over 80% of annual total. Mg^{2+} and Ca^{2+} may originate from building sites and/or soil dust and dust weather in northern China [?], coal burning for heating, and pollutants from bare ground in winter, leading to increased concentrations of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+}. K^+ is an important indicator of dust and biomass burning [?]. K^+ concentration was also relatively high from October to December 2015, mainly derived from burning crop stalks such as corn and cotton in Dunhuang's rural areas. F^- mainly comes from ceramics and coal burning [?]. Higher F^- concentration in July-August 2015 may be mainly affected by secondary suspension of particles containing coal combustion products caused by tourist disturbance. High NO_3^- concentration from November 2015 to January 2016 may be related to coal burning for heating in Dunhuang's rural areas and sandy weather. High NH_4^+ concentration from October 2015 to January 2016 was mainly related to rural coal burning for heating.

In Figure 5c and d, lack of wind and more rainfall in June-September reduced water-soluble ion concentrations outside the cave. In January-March 2016, cold winter air containing fugitive dust from bare ground pollutants and rural heating coal impacted water-soluble ions. F^- occurrence from January to March 2016 may be mainly affected by long-distance transport of crop straw combustion products [**?**]. High NH_4^+ concentration from October 2015 to March 2016 was mainly related to coal burning for heating in Dunhuang's rural areas. Content and type of water-soluble ions in semi-closed caves are mainly affected by air exchange and tourist activities, while those outside caves are mainly affected by the natural environment. Therefore, during periods of frequent sandstorms, numerous tourists and vehicles, intensive crop burning, and coal heating, air exchange can be reduced by replacing existing cave doors. When pollutant levels are high, internal air purification equipment and other measures can effectively reduce water-soluble ion concentrations inside the cave.

4.3 Change of Water-Soluble Ion in Relation to Dust Storm

Particulate and water-soluble ion changes are closely related to extreme sand and duststorm processes. Research shows that particle concentration, especially PM10, during duststorms is much higher than during non-duststorm periods [**?**], and chemical elements inside caves are affected by outdoor weather conditions [**?**], including precipitation, clear or cloudy conditions, and wind. Furthermore, physical forces generated by large sand particles during strong duststorms cause scratches on mural surfaces [**?**]. This study found that duststorms and precipitation have greater impacts on pollutants inside and outside caves, which is why closing caves and stopping visits reduces pollutant transmission. Effects of duststorms and precipitation on water-soluble ions are similar to those reported by Xu et al. [**?**] and He et al. [**?**]. Sand and saline soil deposited by the Daquan River, Kumtag Desert, and Gobi area, redistributed by wind, influence water-soluble ions in atmospheric particles [**?**].

Mural disruption and blistering are mainly caused by NaCl and Na_2SO_4 [**?**]. If particulate matter containing large amounts of Na^+, Cl^-, and SO_4^{2-} deposits on or attaches to wall paintings and cave humidity exceeds 65%, salts in the ground and murals become activated, causing dissolution and crystallization of soluble salts and accelerating mural damage such as blistering [**?**, **?**]. During duststorms, air masses mainly originated from the Hami area of Xinjiang and were transported to Dunhuang through the Taklimakan and Kumtag Deserts. This process may cause long-distance atmospheric particle transport or short-distance local dust formation in surrounding deserts and Gobi areas. Therefore, during duststorms and sudden heavy rainfall, we recommend closing caves to reduce inward pollutant and humid air transmission. After duststorms, dust accumulation in caves and on doors, windows, floors, and other areas should be cleaned promptly. These results can serve as a reference for improving the duststorm environment early warning system and cave opening decision-making in response to extreme weather. Deposition of alkaline or acidic particles on

relics causes potential or immediate acid and salt corrosion of surfaces and colors in high-humidity environments [**?**]. This study showed alkalinity in the Mogao Grottoes, consistent with results at the Jinsha Site Museum [**?**] but contrary to Hanyang Tomb results [**?**]. Dunhuang's climate is extremely arid with low precipitation and high evaporation, and salinity remains on the surface as evaporated groundwater makes soil alkaline. With no industrial pollution sources in the protected area, atmospheric particulate alkalinity may be related to more crustal elements present in the cave and low car exhaust pollution levels.

Water-soluble ion pollution has complex origins including sea fog emissions, soil dust, biomass combustion, and fossil fuel combustion [**?**]. In Tables 3 and 4, Na^+ and Cl^- may come from the Gobi area and Daquan River, NH_4^+ mainly derives from secondary pollution sources such as rural coal combustion, and K^+ mainly derives from crop straw burning. In summary, pollution sources of different particle sizes in the Mogao Grottoes are diverse, including straw burning, secondary pollution sources, soil dust, dry spring rivers, and tourist activities. Therefore, it is necessary to strengthen control of agricultural crop burning in Dunhuang, reduce motor vehicle operation (especially employee private cars) in the protection zone, increase new energy commuter vehicle use, and reduce cracking of sand hills and dry springs on the cave top.

5 Conclusions

PM2.5 and PM10 concentrations inside and outside the cave were highest in March 2016 and lowest in December 2015. Lower particulate matter concentrations from June to September are associated with good diffusion conditions, increased precipitation, and reduced wind impact. Ca^{2+} and NH_4^+ were main components. There was consistent relationship between PM2.5 and PM10 inside and outside the cave, with pollution sources mainly from coal combustion or ground dust contributing more pollutants than mobile sources. Duststorms can cause sharp increases in air particulate concentration and predictable deterioration of mural covers. Control of atmospheric particulate matter pollution in the Mogao Grottoes should focus on improving the comprehensive wind and sand prevention system, limiting tourist numbers, adjusting cave opening schedules, timely cleaning of sand or dust deposits, and adding effective ventilation and air purification systems.

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Note: Figure translations are in progress. See original paper for figures.