

## Airborne Pollutants in the Buddhist Cave Temples at the Yungang Grottoes, China

Lynn G. Salmon, Christos S. Christoforou, and Glen R. Cass\*

Environmental Engineering Science Department and Environmental Quality Laboratory, California Institute of Technology, Pasadena, California 91125

The Buddhist cave temples at the Yungang Grottoes, China, experience rapid soiling due to the deposition of airborne particles. Contributing sources include coal mining and combustion, fugitive road dust, and regional dust storms. Both particle and gas-phase air pollutants are characterized at that site. Annual average coarse (diameter,  $d_p > 2.1 \mu\text{m}$ ) particle concentrations outdoors average  $378 \mu\text{g}/\text{m}^3$ , increasing to more than  $1200 \mu\text{g}/\text{m}^3$  during peak 24-h periods. These coarse airborne particles include crustal dust (e.g., soil dust; over 80% of coarse mass) and carbon-containing particles (10%). Fine airborne particle concentrations ( $d_p \leq 2.1 \mu\text{m}$ ) outdoors average  $130 \mu\text{g}/\text{m}^3$  and consist mainly of carbon-containing particles (45.5%) and crustal dust (24%). Airborne particle concentrations inside cave 6 average approximately 60% of those outdoors.  $\text{SO}_2$  is the principal gas-phase air pollutant averaging 31 ppb outdoors and 19 ppb inside cave 6 over the year studied. Other pollutant gases are present at lower average concentrations:  $\text{NH}_3$  (4–10 ppb),  $\text{NO}_2$  (4–6 ppb),  $\text{HNO}_3$  (0.1–0.2 ppb), and HCl (<0.1 ppb).

### Introduction

Recent studies have shown that museum collections that are not protected by deliberate air purification systems may become soiled at a rapid rate (1–3). Certain archaeological sites suffer from similar problems, for example, the Buddhist cave temples at the Yungang Grottoes in the People's Republic of China, which are located in a region with high outdoor airborne particle concentrations. The Yungang Grottoes are carved into the side of a cliff in the Wuzhou hills overlooking a river valley located approximately 16 km west of the industrial city of Datong near the Inner Mongolian border and contain approximately 50 000 carvings on the walls and ceilings. Work on the caves began during the Northern Wei Dynasty in the 5th century A.D. The Yungang Grottoes belong to a string of early Buddhist cave temples that stretch across northern China, today receiving hundreds of visitors on a daily basis (4–6).

Many of the caves are built with entrances open to the outdoor air, allowing abrasive windblown dust and air pollution present in one of China's largest coal-mining districts to enter the caves without restriction followed by particle deposition onto the sculptures. The sources of airborne particles are many and include operations at the mines, dust generated by coal trucks on a nearby highway, dust generated by traffic on dirt roads in the village of Yungang in front of the caves, combustion of coal for home cooking and heating, and coal combustion by railroad locomotives and other industry. In addition, the caves are not far from the edge of the Gobi Desert, and desert dust storms can affect the site.

An extensive cleaning project was undertaken in 1986, and photos were taken of the carvings within the caves at that time (7). Comparing the sculptures today with the photographic record from 1986, there is a visible buildup of deposits, especially on upward-facing horizontal surfaces. In some places, deposits as much as 0.8 cm deep were measured during the present study at locations that are known to have been cleaned in 1986 (8). Unless such severe particle deposition processes can be abated, any attempt to preserve or restore the sculptures in the caves may well be defeated by a continuing assault of abrasive and possibly chemically reactive airborne contaminants.

The purpose of this paper is to report the results of a field experimental program designed to obtain baseline data on air quality both inside and immediately outside of the Yungang Grottoes. Filter-based air sampling methods were used to determine the concentration and chemical composition of airborne particles in both the fine (diameter,  $d_p \leq 2.1 \mu\text{m}$ ) and coarse ( $d_p > 2.1 \mu\text{m}$ ) particle size ranges as well as the concentrations of selected reactive gases:  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$ , and HCl. These measurements reveal the chemical and physical nature of the pollution problem to which the Grottoes are exposed and help to identify the likely sources of the air quality problem in a way that can help to guide remediation efforts.

### Experimental Section

During April and May 1991, a series of air pollutant measurement experiments were conducted by Caltech personnel at the Yungang Grottoes, China. The ambient samplers employed to obtain data on fine and total airborne particle concentrations and chemical composition are illustrated schematically in Figure 1 (9–11). A map of a section of the Grottoes site indicating sampler location is shown in Figure 2. Three samplers were deployed in April 1991. One of these samplers was located outside cave 9 at a site protected from rain by the overhanging cliff above the entrance to that cave. A second sampler was placed within the main chamber of cave 9, which is a room hollowed out behind the face of the cliff having horizontal dimensions approximately  $9 \text{ m} \times 8 \text{ m}$  and a height of 8.5 m. Analysis of a sample of the cliff rock by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer and by X-ray diffraction shows the rock to be a sandstone consisting of quartz, feldspar, some dolomite, and a few percent calcite; the pore spaces in the rock are filled with secondary kaolinite from decomposition of the feldspar. Cave 9 shelters an 8-m-high seated statue of the Buddha. Both the central statue and the many smaller carvings on the cave walls are polychromed. Cave 9 has a thick layer of deposited dust on its floor. That cave is closed to the public, and care was taken to exclude personnel from this cave during sampling so as not to disturb the deposited dust.

\* To whom correspondence should be addressed.

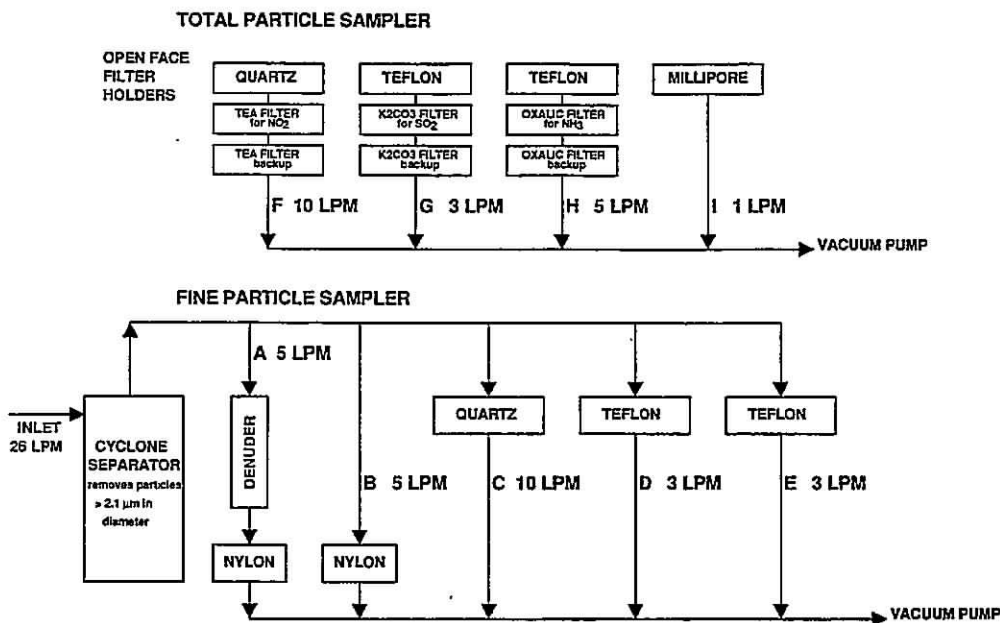


Figure 1. Schematic diagram of fine and total particle samplers.

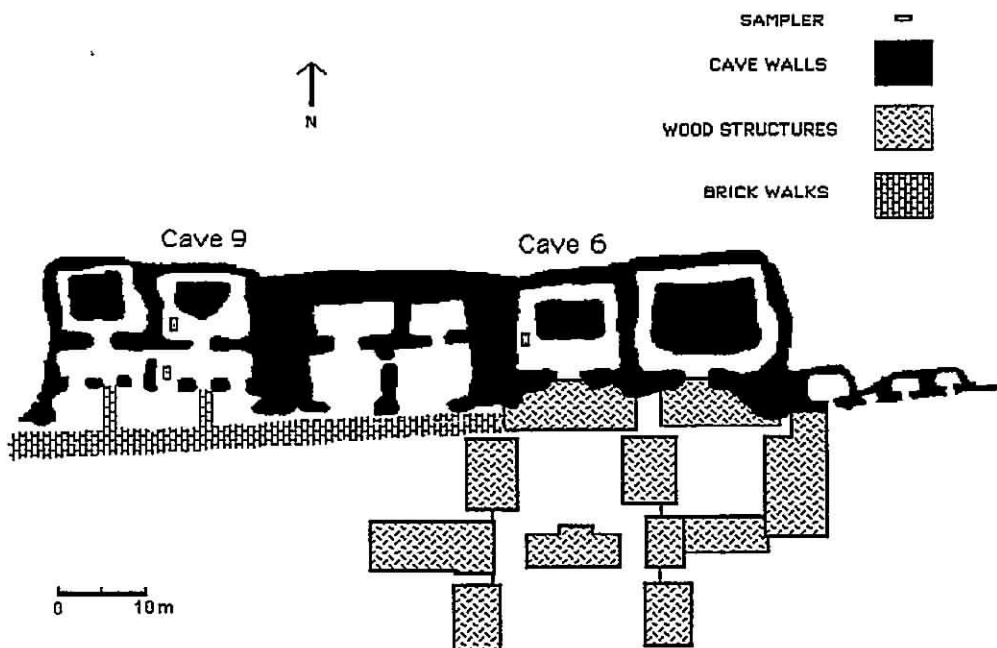


Figure 2. Map section of the Yungang Grottoes showing sampler placement.

Originally, the entrance to cave 9 was sheltered by a wooden pagoda front, one room deep, attached to the outside of the cliff into which the cave is carved and reaching up the face of the cliff to a height of several stories. That wooden temple front has since fallen away from the face of the cliff, leaving the entrances to cave 9 open directly to the outdoors. In order to examine the possible protection against air pollutant intrusion that might have been provided by the traditional wooden temple front, a second indoor sampler was placed inside cave 6, which is one of two caves that retain a wooden structure over the entrances. The dimensions of cave 6 are approximately 10.5 m × 11 m in horizontal extent and 15 m high with a 7 m × 7 m carved stone pillar standing in the center of the cave. Cave 6 routinely receives visitors, and that cave has a hard tile floor that is occasionally swept. While the floor

of that cave is relatively clean, the visitors and sweeping activity represent a possible source of resuspended dust. The caves are not presently used for organized religious purposes; the only combustion sources in cave 6 consist of a few incense sticks lit by visitors on their own initiative. We observed about three incense sticks in a 1-month period.

Airborne particle samples were collected over 24-h periods every third day for eight sampling events in April and May 1991. Measurements were also made of the concentration of certain gas-phase pollutants that could affect the stone or the painted surfaces including SO<sub>2</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>, and HCl. Particle deposition samples were collected over the month-long period (on both vertical and horizontal surfaces) and for shorter times (sequential 4- and 24-h periods) on horizontal surfaces. Additional measurements were made of air-exchange rates between

the outside atmosphere and the inside of the caves. Air velocities and temperatures in the near-wall region that govern particle deposition processes likewise were measured.

At the close of the experiments in early May, arrangements were made for the staff at the Yungang Grottoes to continue atmospheric sampling for three additional 1-month periods to complete a full seasonal cycle (July 1991, October 1991, and January 1992). Two abbreviated ambient samplers were placed at the site, one outdoors and one inside cave 6, to continue monitoring fine and coarse airborne particle concentration and chemical composition and gas-phase SO<sub>2</sub> concentration. During these months, 24-h average samples were taken at 6-day intervals.

Fine particle samples were collected on 47-mm-diameter filters located downstream of an AIHL-design cyclone separator that removed particles with aerodynamic diameter greater than 2.1 μm (12). A complete fine particle sample set for a single sampling event consisted of two Teflon membrane filters (Gelman Teflo, 0.5-μm pore size) through which air had been drawn at a rate of 3 Lpm each and one quartz fiber filter (Pallflex, 2500 QAO) through which air had been drawn at a rate of 10 Lpm for 24 h (see Figure 1). The Teflon filters were weighed before and after sampling for gravimetric determination of aerosol mass concentration. One Teflon filter sample from each set was analyzed by X-ray fluorescence (XRF) for 34 elements. The other Teflon filter sample of each set was analyzed by ion chromatography (IC) for nitrate, sulfate, and chloride ion concentration (13, 14), for ammonium ion concentration by colorimetry (15), and for water-soluble sodium and magnesium by atomic absorption spectroscopy (AA) (16). All quartz fiber filters were baked at 550 °C for at least 4 h prior to use in order to reduce their carbon blank. Following sample collection, the quartz fiber filters were analyzed to determine the organic carbon, elemental carbon, and carbonate carbon particle concentration by a thermal evolution and combustion technique (17, 18). Detailed descriptions of the filter preparation and analytical methods have been reported previously (3, 9). A second set of Teflon and quartz fiber filters placed in open-face filter holders were used for total particle (without any size separation) collection and analysis. Coarse particle characteristics were determined by difference between the fine particle and the total particle concentration data.

In addition to the fine and total particle filter samples mentioned above, the denuder difference method employing nylon filters was used to measure atmospheric HNO<sub>3</sub> and HCl concentrations (19, 20), and tandem filter packs were used for the collection of gas-phase SO<sub>2</sub>, NO<sub>2</sub>, and NH<sub>3</sub> (10, 21). In the filter pack, or tandem filter method, gas-phase species are collected on treated backup filters after particles are removed on Teflon or quartz fiber prefilters that are held in open-face filter holders. SO<sub>2</sub> was collected using K<sub>2</sub>CO<sub>3</sub>-impregnated Whatman 41 paper filters. NO<sub>2</sub> was collected using triethanolamine (TEA) impregnated Whatman 31ET chromatography filters. The NH<sub>3</sub> samples were collected on oxalic acid-impregnated Gelman AE glass fiber filters. These sampling techniques have been described previously, and the interested reader is directed to the original references (10, 19-21).

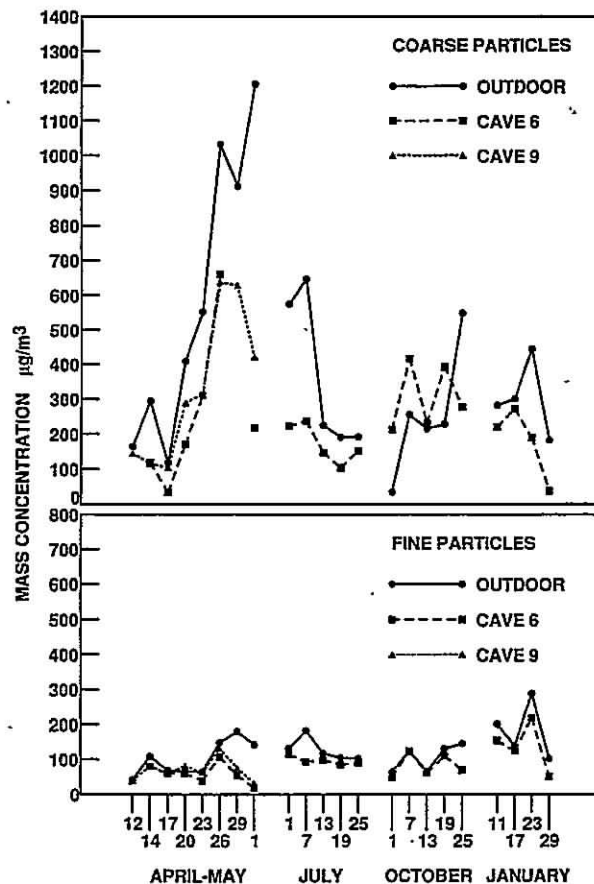


Figure 3. Mass concentration of coarse and fine particles outdoors and inside of cave 6 at Yungang Grottoes over four seasons and inside of cave 9 during April 1991.

Horizontally and vertically oriented deposition plates were deployed having substrates similar to those used for airborne particle sampling. The vertically oriented plates were mounted on the cave walls in caves 6 and 9 plus outdoors where they were mounted on the side of a stand located near the ambient sampler. Horizontally oriented plates likewise were placed near the ambient samplers. Teflon filter material (Gelman Zefluor, 20 cm × 25 cm) onto which particle deposits accumulated was clamped into aluminum holders having bevelled edges designed to minimize the disruption of the boundary layer air flow over the collection plates. The dry deposit samples were analyzed in the same manner as ambient Teflon filters for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Mg<sup>+</sup>, Ca<sup>+</sup>, and K<sup>+</sup>. Quartz fiber filter material (102-mm-diameter) mounted in aluminum holders with bevelled edges also was used as a dry deposition surface. Those quartz fiber surfaces were analyzed to determine organic carbon, elemental carbon, and carbonate carbon particle deposition rates. Other particle collection substrates deployed included glass slides and Millipore filters for use in a single particle counting and sizing experiment designed to determine the particle size distribution and size-dependent deposition velocity, which is described in a separate paper (8).

### Results and Discussion

**Particle Mass Concentrations.** The mass concentrations of both coarse and fine particles are shown in time series for each season both inside and outside the caves in Figure 3. Annual average concentrations were

estimated by first averaging the data within each season and then averaging the four seasonal periods. Annual average outdoor coarse particle concentrations were found to be  $378 \mu\text{g}/\text{m}^3$ , and annual average outdoor fine particle concentrations were found to be  $130 \mu\text{g}/\text{m}^3$ . By comparison, coarse particle concentrations in the air outside museums in downtown Los Angeles, CA, average about  $78 \mu\text{g}/\text{m}^3$ , while fine aerosol concentrations in Los Angeles average about  $46 \mu\text{g}/\text{m}^3$  (3, 9). While Los Angeles is widely recognized as experiencing high airborne particle loadings, it is quickly seen that levels of both coarse and fine particles are higher at Yungang. By comparison to Los Angeles, the coarse aerosol concentrations are very high, confirming the observer's visual impression that Yungang is quite dusty.

The annual average concentration of coarse particles inside cave 6 was calculated to be  $228 \mu\text{g}/\text{m}^3$ . Thus, the coarse particle concentrations within cave 6 are almost 60% as high as those outdoors, as can also be seen in Figure 3. Coarse particle concentrations within cave 6 exceeded outdoor levels on several occasions during October, which may be due to the previously mentioned visitors and cleaning activity in that cave. During the April sampling period, coarse particle concentrations in cave 9 averaged 57% of those outdoors, a value intermediate between the outdoor and the cave 6 concentrations, which averaged 43% of those outdoors in April. Since cave 9 does not possess any air filtration system, this differential between the indoor and outdoor concentrations represents a depletion of coarse airborne particles by deposition onto surfaces within that cave. In the case of cave 6, concentrations lower than in cave 9 may be due to a combination of deposition within the cave and to removal of some particles as air passes through the wooden temple front structure that covers the entrance to cave 6.

Fine particle concentrations inside caves 6 and 9 are close to the fine particle concentrations outdoors. Outdoor fine particle concentrations averaged  $130 \mu\text{g}/\text{m}^3$  over the year while concentrations inside cave 6 averaged  $94 \mu\text{g}/\text{m}^3$  for the year. April fine particle concentrations averaged  $102 \mu\text{g}/\text{m}^3$  outdoors,  $70 \mu\text{g}/\text{m}^3$  inside cave 9, and  $60 \mu\text{g}/\text{m}^3$  inside cave 6. The deposition velocity for fine particles typically is much lower than the gravitational settling velocity for coarse dusts (1, 22, 23). Thus, with higher indoor coarse particle concentrations than fine particle concentrations, most of the mass flux of deposited material onto horizontal surfaces inside the caves will be due to coarse particle deposition.

**Aerosol Chemical Composition.** A material balance on the chemical composition of each aerosol sample was constructed based on the ion chromatography data for ionic species, thermal evolution, and combustion analysis for carbonaceous species, and X-ray fluorescence analysis for trace metals. The concentrations of silicon and aluminum measured by XRF were corrected for the size-dependent response of the XRF system to coarse particles based on the actual particle size distribution counted by optical microscopy on Millipore filters taken on the same day (24). The crustal element concentrations were converted into the concentrations of their stable oxides where appropriate. Non-carbonate crustal element mass concentrations were then estimated by summing the estimated concentrations of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{MnO}$ , plus the calcium, potassium, sodium, and magnesium oxide compound concentrations in excess of that needed to

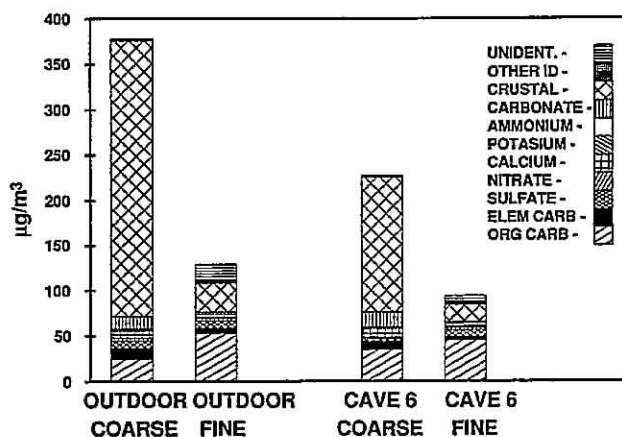


Figure 4. Annual average composition of coarse and fine particles outdoors and inside cave 6 at Yungang Grottoes.

account for the carbonate minerals present. Organic carbon concentrations were converted into estimates of the mass of organic compounds present by multiplying measured OC levels by a factor of 1.2 (25, 26).

Bar charts that compare the annual average chemical composition of coarse and fine airborne particles inside cave 6 and outside the caves are given in Figure 4. The outdoor coarse aerosol is dominated by crustal dust, most probably soil dust, accounting for about 80% of the coarse aerosol burden on average over the year. The remainder of the coarse aerosol consists of small amounts of many different substances as shown in Figure 4.

In contrast, carbonaceous particles are the largest contributors to the outdoor fine particle concentrations with organic compounds comprising 41% and elemental (black) carbon contributing 4.5% of fine aerosol mass. The fine particle tail of the crustal dust size distribution contributes 24% of the average outdoor fine particle mass concentration. The relative chemical compositions of indoor and outdoor fine particles are fairly similar, again suggesting that the indoor aerosol is largely outdoor aerosol that has been little changed as a result of its introduction into the caves.

Time series graphs of aerosol chemical composition are shown for coarse and fine particles in Figures 5 and 6. Dust storms were observed in late April and early May. Not surprisingly, air quality during these events was characterized by large increases in outdoor crustal dust concentrations. The highest indoor 24-h average coarse particle concentration ( $660 \mu\text{g}/\text{m}^3$ ) measured in cave 6 occurred on April 26, 1991, during one of these dust storms, and chemical analysis shows that crustal oxides plus carbonate materials made up over  $450 \mu\text{g}/\text{m}^3$  of that indoor coarse particle loading. Figures 5 and 6 also show that fine carbon particle concentrations increase significantly in winter (January) both inside and outside the caves. This may reflect greater concentrations of emissions from combustion sources relative to soil dust sources at that time of year, due either to increased combustion for heating purposes during the winter or to suppression of dust entrainment into the atmosphere by the winter weather and snow cover.

**Protection Afforded by Wooden Temple Fronts.** The possible protection of the grottoes provided by the traditional wooden temple fronts present on caves 5 and 6 was examined by comparing the results of aerosol particle intrusion into cave 6 with that of cave 9, which lacked the

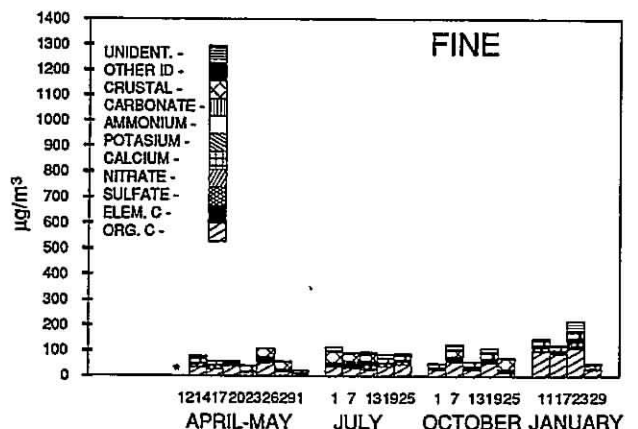
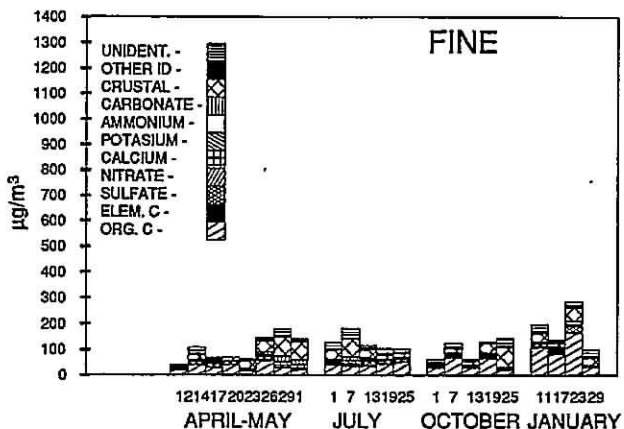
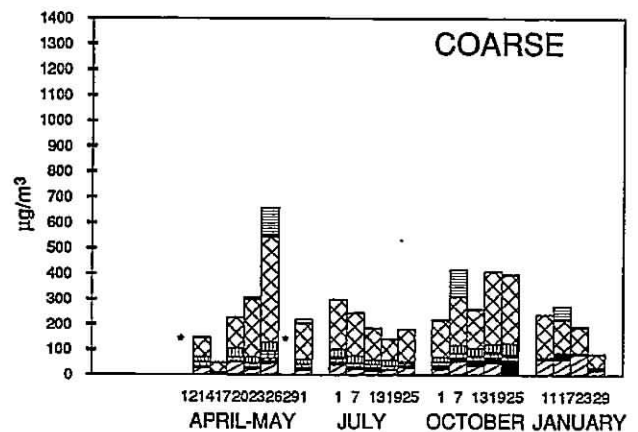
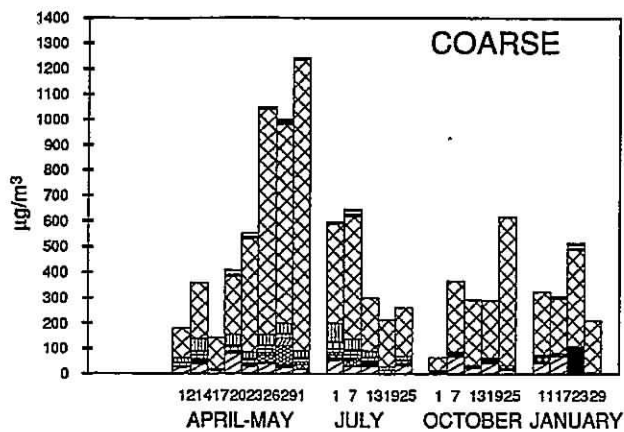


Figure 5. Chemical composition of coarse and fine particles outdoors at Yungang Grottoes over four seasons.

Figure 6. Chemical composition of coarse and fine particles inside cave 6 at Yungang Grottoes over four seasons. An asterisk (\*) indicates no data.

wooden pagoda structure. The mean chemical composition of coarse and fine airborne particles during the month of April outdoors, inside cave 9, and inside cave 6 is given in Figure 7. Mean coarse particle concentrations inside cave 9 are 57% of those outdoors while coarse particle concentrations inside cave 6 are further reduced to 43% of outdoor levels. As can be seen in Figure 7, most of the reduction of coarse particles inside cave 9 is due to the loss of crustal dust with some loss of sulfate. In contrast, all species of coarse particles are somewhat reduced inside cave 6.

**Gas-Phase Pollutants.**  $\text{SO}_2$  concentrations measured over the year are shown in Figure 8. Outdoor levels range between 7 and 40 ppb for most of the year, with higher values up to 115 ppb measured during the winter. These higher winter values suggest higher concentrations of the combustion products of local coal at that time of year. Indoor  $\text{SO}_2$  concentrations inside cave 6 averaged 19 ppb over the year-long experiment compared to 31 ppb outdoors. In the absence of any deliberate pollutant removal systems, this decline in  $\text{SO}_2$  concentrations within the caves suggests some loss of  $\text{SO}_2$  to interior cave surfaces. The chemical composition of the rock surfaces within the caves and some rock weathering products have been examined previously (27). Those data show that the native rock contains 30–35% carbonates and that the cement binder between the sand grains contains 15–25% carbonates.  $\text{SO}_2$  attack on the rock walls thus is possible and should be examined further as  $\text{SO}_2$ -induced damage to sandstones has been observed elsewhere (28, 29). As part of the present study, a sample of the cliff rock that had

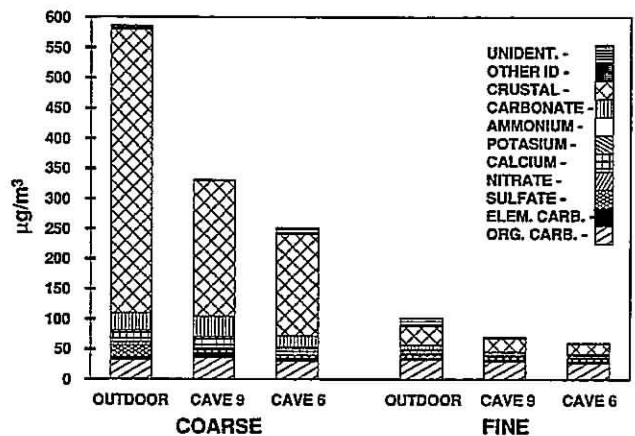


Figure 7. Average composition of coarse and fine particles outdoors, inside cave 9, and inside cave 6 at Yungang Grottoes during April 1991.

been exposed to the local atmosphere was examined by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. In addition to the quartz, feldspar, dolomite, and intergranular kaolin found on the unexposed interior of the rock, this surface sample showed abundant fine crystals of gypsum and kaolinite. Gypsum is often observed as the reaction product of  $\text{SO}_2$  with carbonate rocks.

$\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{HCl}$ , and  $\text{HNO}_3$  concentrations were measured during April 1991. Levels of each of these gases were much lower than the  $\text{SO}_2$  concentrations.  $\text{NH}_3$  concentrations averaged 4.7 ppb outdoors, 4.1 ppb inside

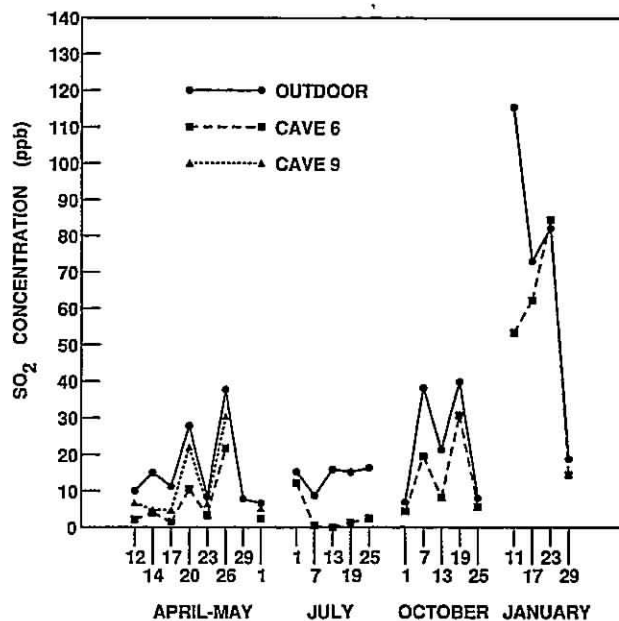


Figure 8. SO<sub>2</sub> concentrations measured over the year at Yungang Grottoes.

Table 1. Accumulation on Deposition Plates During April 1991 [in  $\mu\text{g}/(\text{m}^2 \text{ s}^{-1})$ ]

location	orientation	total mass flux <sup>a</sup>	carbon compds <sup>b</sup>	SO <sub>4</sub> <sup>2-</sup>	other species measd <sup>c</sup>
outdoors	horizontal	21.50	0.18	0.75	1.06
outdoors	vertical	0.20	0.0003	0.008	0.015
cave 9	horizontal	13.40	0.13	0.11	0.17
cave 9	vertical	0.034	0.002	0.003	0.0007
cave 6	horizontal	4.54	0.11	0.06	0.06
cave 6	vertical	0.016	0.02	0.0003	0.0008

<sup>a</sup> Mass flux based on the average of 8–24-h glass slide samples, from ref 8. <sup>b</sup> Organic carbon plus elemental carbon from quartz deposition filter material. <sup>c</sup> Other compounds measured: Ca<sup>+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, K<sup>+</sup>, Mg<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and Na<sup>+</sup>.

cave 9, and 10.4 ppb inside cave 6; the higher values inside cave 6 probably being due to the fact that it is more frequently entered by visitors than is cave 9. NO<sub>2</sub> concentrations averaged 3.9 ppb outdoors, 4.3 ppb inside cave 9, and 5.6 ppb inside cave 6. Concentrations of nitric acid were found to be less than 1 ppb each day in April with average HNO<sub>3</sub> concentrations between 0.1 ppb inside cave 6 and 0.2 ppb outdoors over the month. HCl concentrations were even lower, averaging less than 0.1 ppb both inside the caves and outdoors.

**Chemical Composition of Dry Deposition Samples.** Table 1 displays the mass accumulation results from the deposition samples. Total mass flux was calculated using the particle-counting results on glass slide samples and assuming a uniform density of 2.2 g/cm<sup>3</sup> (8). Ionic species measured based on particle accumulation on Zefluor filters plus carbon compounds (which would include coal dust and soot) measured on quartz fiber filters account for 3–10% of the total mass accumulation. The rest is assumed to be crustal dust (e.g., soil dust or cave wall material).

**Other Measurements.** One of the portable abbreviated ambient samplers was used to take ambient aerosol measurements at other locations near the grottoes. Measurements were taken at the side of the main coal haul road located approximately 0.5 km south of the grottoes on April 28, 1991. The day was sunny and windy with

winds predominantly blowing from the northwest across the road toward the location of the sampler. Vehicle traffic was fairly heavy with approximately 10 trucks/min, 45% of the trucks were laden with coal.

Mass concentrations measured at roadside were higher than those at the grottoes: coarse mass, 1710  $\mu\text{g}/\text{m}^3$ ; fine mass, 191  $\mu\text{g}/\text{m}^3$ . The chemical composition of the coarse airborne particle mass was made up primarily of crustal dust (76%), organic compounds plus elemental carbon (17%), and calcium carbonate (6%). Fine airborne particle mass was comprised of 68% organic compounds plus elemental carbon, 20% crustal dust, and small amounts of other trace compounds.

### Conclusions

High concentrations of airborne particles were measured outdoors and inside the Yungang Grottoes contributing to the rapid soiling that occurs inside the cave temples. Coarse airborne particle levels averaged 378  $\mu\text{g}/\text{m}^3$  outdoors during 1991–1992 with peak 24-h outdoor levels of more than 1200  $\mu\text{g}/\text{m}^3$ . Levels of coarse airborne particles inside cave 6 over the year were also high, averaging 228  $\mu\text{g}/\text{m}^3$ . Crustal dust (e.g., soil dust plus cave wall material) comprised most of the coarse airborne particle mass accounting for 80% of the outdoor coarse material and 66% of the coarse material inside cave 6. Carbon-containing compounds account for most of the remaining coarse material.

Concentrations of fine airborne particles at the Yungang Grottoes were also high, averaging 130  $\mu\text{g}/\text{m}^3$  outdoors and 94  $\mu\text{g}/\text{m}^3$  inside cave 6 over the year. Carbon-containing compounds are the largest contributor to the fine particle mass, accounting for 45.5% of the outdoor fine material and 53% of the fine material inside cave 6. Crustal dust accounts for most of the remaining fine material.

In summary, then, nearly all of the airborne particulate matter at Yungang, both coarse and fine, consists either of mineral dust or carbon particles. That knowledge should help focus attention on the control of local sources of such emissions.

SO<sub>2</sub> concentrations averaged 31 ppb outdoors and 19 ppb inside cave 6 over the year studied, with wintertime peak 24-h SO<sub>2</sub> concentrations outdoors of about 120 ppb. Given the loss of SO<sub>2</sub> inside the caves, a cliff rock sample was examined, and it was determined that gypsum crystals were present on the surface, which is consistent with SO<sub>2</sub> attack on the calcium carbonate content of the original sandstone. Levels of other pollutant gases measured were much lower with average concentrations as follows: NH<sub>3</sub> (4–10 ppb), NO<sub>2</sub> (4–6 ppb), HNO<sub>3</sub> (0.1–0.2 ppb), and HCl (<0.1 ppb).

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#### Literature Cited

- (1) Nazaroff, W. W.; Salmon, L. G.; Cass, G. R. *Environ. Sci. Technol.* 1990, 24, 66-77.
- (2) Nazaroff, W. W.; Cass, G. R. *Atmos. Environ.* 1991, 25A, 841-852.
- (3) Nazaroff, W. W.; Ligocki, M. P.; Salmon, L. G.; Cass, G. R.; Fall, T.; Jones, M. C.; Liu, H. I. H.; Ma, T. *Protection of works of art from soiling due to airborne particulates*; GCI Scientific Program Report; The Getty Conservation Institute: Marina Del Rey, CA, Jan 1992.
- (4) Caswell, J. O. *Written and Unwritten: A New History of the Buddhist Caves at Yungang*; University of British Columbia Press: Vancouver, 1988.
- (5) Mizuno, S. *Arch. Chinese Art Soc. Am.* 1950, 4, 39-60.
- (6) Knauer, E. R. *Expedition* 1983, Summer, 27-47.
- (7) *The Great Treasury of Chinese Fine Arts*; Peoples Fine Arts Publishing House, Shanghai People's Fine Arts Publishing House, Cultural Relic Publishing House, and China Architecture Publishing House: Beijing, China, 1986; Vol. 10.
- (8) Christoforou, C. S.; Salmon, L. G.; Cass, G. R. *Atmos. Environ.* 1994, Part A, in press.
- (9) Ligocki, M. P.; Salmon, L. G.; Fall, T.; Jones, M. C.; Nazaroff, W. W.; Cass, G. R. *Atmos. Environ.* 1993, 27A, 697-711.
- (10) Solomon, P. A.; Fall, T.; Salmon, L. G.; Lin, P.; Vasquez, F.; Cass, G. R. *Acquisition of acid vapor and aerosol concentration data for use in dry deposition studies in the South Coast Air Basin*; EQL Report 25; Environmental Quality Laboratory, California Institute of Technology: Pasadena, CA, Final report submitted to the California Air Resources Board Mar 1988.
- (11) Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Environ. Sci. Technol.* 1992, 26, 1594-1601.
- (12) John, W.; Reischl, G. J. *Air Pollut. Control Assoc.* 1980, 30, 872-876.
- (13) Derrick, M.; Moyers, J. L. *Anal. Lett.* 1981, 9, 1637.
- (14) Weiss, J. *Handbook of Ion Chromatography*; Johnson, E. L., Ed.; Dionex Corp.: Sunnyvale, CA, 1986.
- (15) Bolleter, W. T.; Bushman, C. T.; Tidell, P. W. *Anal. Chem.* 1961, 33, 592-594.
- (16) *Analytical Methods for Flame Spectroscopy*; Varian Techtron: Melbourne, Australia, 1972.
- (17) Cary, R. Speciation of aerosol carbon using the thermal-optical method. Presented at the Third International Conference on Carbonaceous Particles in the Atmosphere, Berkeley, CA, Oct 1987.
- (18) Huntzicker, J. J.; Johnson, R. L.; Shah, J. J.; Cary, R. A. Analysis of organic and elemental carbon in ambient samples by a thermal optical method. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimisch, R. L., Eds., Plenum Press: New York, 1982; pp 79-85.
- (19) Salmon, L. G.; Nazaroff, W. W.; Ligocki, M. P.; Jones, M. C.; Cass, G. R. *Environ. Sci. Technol.* 1990, 24, 1004-1013.
- (20) Eldering, A.; Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Atmos. Environ.* 1991, 25A, 2091-2102.
- (21) Chow, J. C.; Watson, J. G.; Egami, C. A.; Frazier, C. A.; Fung, K.; Taketomo, A. Laboratory operations manual for the California acid deposition monitoring program: sample pretreatment, sample preparation, and chemical analysis. DRI Document No. 8068.3D1, prepared for the California Air Resource Board by the Desert Research Institute, Reno, NV, 1989.
- (22) Nazaroff, W. W.; Ligocki, M. P.; Ma, T.; Cass, G. R. *Aerosol Sci. Technol.* 1990, 13, 332-348.
- (23) Nazaroff, W. W.; Cass, G. R. *Environ. Int.* 1989, 15, 567-584.
- (24) Dzubay, T. G.; Nelson, R. O. Self absorption corrections for X-ray fluorescence analysis of aerosols. In *Advances in X-ray Analysis*; Pickles, W. L., Barrett, C. S., Newkirk, J. B., Ruud, C. O., Eds.; Plenum Publishing Corp.: New York, 1975; Vol. 18, pp 619-631.
- (25) Benner, W. H.; Hansen, A. D. A.; Gundel, L. A.; Novakov, T. *Sci. Total Environ.* 1984, 36, 271-276.
- (26) Grosjean, D.; Friedlander, S. K. *J. Air Pollut. Control Assoc.* 1975, 25, 1038-1044.
- (27) Studies of technical conservation in Yungang Caves, basic data (1960-1988). The Scientific & Technological Institute for Conservation of Cultural Relics, Ministry of Culture, China, July 1988.
- (28) Fobe, B.; Sweevers, H.; Vleugels, G.; Van Grieken, R. *Sci. Total Environ.* 1993, 132, 53-70.
- (29) Butlin, R. N. *Proc. R. Soc. Edinburgh* 1991, 97B, 255-272.

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