

Air Pollutant Intrusion into the Wieliczka Salt Mine

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The Wieliczka Salt Mine World Cultural Heritage Site contains many rock salt sculptures that are threatened by water vapor condensation from the mine ventilation air. Gaseous and particulate air pollutant concentrations have been measured both outdoors and within the Wieliczka Salt Mine, along with pollutant deposition fluxes to surfaces within the mine. One purpose of these measurements was to determine whether or not low deliquescence point ionic materials (e.g., NH_4NO_3) are accumulating on surfaces to an extent that would exacerbate the water vapor condensation problems in the mine. It was found that pollutant gases including SO_2 and HNO_3 present in outdoor air are removed rapidly and almost completely from the air within the mine by deposition to surfaces. Sulfur isotope analyses confirm the accumulation of air pollutant-derived sulfur in liquid dripping from surfaces within the mine. Particle deposition onto interior surfaces in the mine is apparent, with resulting soiling of some of those sculptures that have been carved from translucent rock salt. Water accumulation by salt sculpture surfaces was studied both experimentally and by approximate thermodynamic calculations. Both approaches suggest that the pollutant deposits on the sculpture surfaces lower the relative humidity (RH) at which a substantial amount of liquid water will accumulate by 1% to several percent. The extraordinarily low SO_2 concentrations within the mine may explain the apparent success of a respiratory sanatorium located deep within the mine.

Introduction

The Wieliczka Salt Mine, located in southern Poland near the city of Krakow, has been worked as a source of rock salt since the late 13th century. The mine consists of over 200

km of underground passages, connecting more than 2000 excavation chambers on nine underground levels extending down to 327 m below the surface. Over the centuries, miners have established a tradition of carving sculptures out of the native rock salt. As a result, the mine contains entire underground churches, altars, bas-reliefs, and dozens of life-size or larger statues. It also houses an underground museum and has a number of special purpose chambers such as a sanatorium for people suffering from respiratory ailments. As a testament to its historical and artistic importance, the mine has been placed on UNESCO's World Heritage List of sites designated as having "outstanding universal value to mankind". It receives up to 1 million visitors yearly, most of them during the warmer summer months.

Today, many of the salt sculptures are slowly dissolving. Water vapor present in the ventilation air in the mine is being absorbed into the rock salt at several locations in the mine, causing erosion of the carved salt surfaces. A joint team of Polish and American scientists and engineers is conducting experiments in the mine to document the environmental conditions there and to seek solutions to the water vapor condensation problem. One question faced by the study team is whether or not there is any significant soiling or chemical attack on the statuary that might alter the hygroscopic character of the salt.

The rock salt at the Wieliczka mine is composed of NaCl plus trace impurities. Sodium chloride develops a liquid film on its surface and begins to dissolve when the relative humidity of the surrounding air reaches approximately 75% (1). This is known as the relative humidity of deliquescence. Airborne ionic substances (e.g., nitrates) having relative humidities of deliquescence below that of rock salt could deposit onto the sculptures to an extent that the deliquescence point of the salt surface is lowered. If this occurs, it would influence the selection of a future dehumidification system for the mine.

The purpose of the present paper is to examine the transport of air pollutants from the outdoor atmosphere into the mine and the subsequent deposition of those pollutants onto the surfaces in the mine, with an eye toward determining whether or not the deliquescence point of the salt would be significantly affected by the pollutant deposition processes. Filter-based air sampling methods are used to determine the concentration and chemical composition of airborne particles in both fine and coarse particle size ranges as well as the concentrations of selected reactive gases: sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitric acid (HNO_3), and hydrochloric acid (HCl). Deposition plates and scrapings taken from surfaces in the mine also are used for studying particulate plus gas-phase pollutant deposition to surfaces. Sulfur isotope analyses are employed to confirm the presence of air pollutant-derived sulfur on surfaces within the mine. These measurements reveal the chemical and physical nature of the pollutants present, the rate of pollutant accumulation on surfaces, and whether or not there are significant differences in pollutant concentration from one chamber to another throughout the mine.

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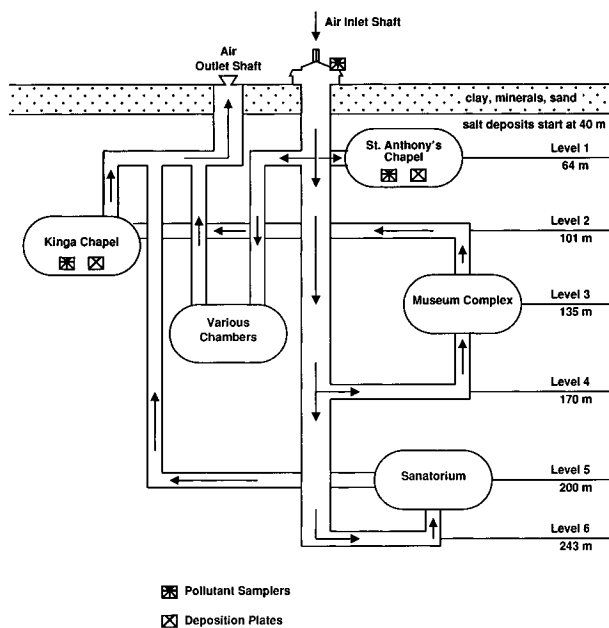


FIGURE 1. Partial schematic map showing air flow paths within the Wieliczka Salt Mine.

Experimental Section

Beginning in the spring of 1992, a team of scientists began monitoring atmospheric conditions in the Wieliczka Salt Mine. This was a cooperative effort involving several groups including the Atmospheric Turbulence and Diffusion Division of the U.S. National Oceanic and Atmospheric Administration (NOAA), the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, the Preservation Assistance Division of the U.S. National Park Service, the U.S. Geological Survey (USGS), and the California Institute of Technology (Caltech). The team from NOAA established a series of monitoring stations to track air flows, temperature, and humidity conditions throughout the mine. Data from these stations are reported elsewhere (2). A series of air pollutant measurement experiments were conducted by Caltech, USGS, and Polish Academy of Sciences personnel using filter-based samplers to measure airborne particle chemical composition and selected gaseous pollutant concentrations both in the outdoor ventilation air fed to the mine as well as within the mine itself. Deposition plates were used to measure the flux of particles plus gaseous pollutants depositing to surfaces within the mine. Surface scrapings were taken from the mine walls to determine the spatial variation of sulfur deposits leading from the main mine ventilation shaft through a portion of the mine, and sulfur isotope analyses were performed to distinguish sulfur on mine surfaces that is derived from air pollutant deposition versus sulfur compounds present naturally in the rock salt.

Atmospheric monitoring equipment was placed in the mine at the locations shown in Figure 1. One particle sampler was placed outdoors on the roof of the building that houses the main air inlet to the historical section of the mine. A second sampler was positioned inside the 17th century chapel carved out of solid rock salt in honor of St. Anthony, the patron saint of miners, on underground level 1. The sculptures in this chapel are affected by the most severe deterioration problem in the mine. St. Anthony's Chapel experiences distinct dry and wet seasons. During the wet summer period, warm humid air from outdoors

enters the mine and as it cools, it loses moisture which is absorbed by the surfaces within St. Anthony's Chapel. Surface liquification at that point in the mine in the summer is so serious that water drips from the carved salt statues. During the dry period in winter there is no noticeable wetness of the surfaces. In a previous attempt to reduce this moisture condensation, St. Anthony's Chapel was closed off from its most direct connection to the main ventilation shaft in the mine, but moisture still reaches the chapel by a more circuitous route and water condensation continues. The third location chosen for sampling was within the monumental Kinga Chapel on underground level 2. This 54 m long chapel dedicated to Princess Kinga contains numerous statues carved from rock salt, bas-reliefs depicting biblical scenes, stairs and railings of salt, and salt crystal chandeliers: all in good condition. It is located near the exit of the ventilation system in the mine and does not experience the fluctuations in humidity and the water condensation problems that are found within St. Anthony's Chapel.

Airborne particle samples were collected over 24-h periods every sixth day during 4 months encompassing a full year's seasonal cycle. Sampling took place during June, September, and December 1992 and March 1993. The sampling system used during this experiment is illustrated schematically in Figure 2 and has been described previously in the literature (3–5). The ambient samplers measured airborne particle concentrations and chemical composition in two size ranges: fine particles (diameter, $d_p \leq 2.1 \mu\text{m}$) and total particles (no size discrimination). Coarse particle concentrations ($d_p > 2.1 \mu\text{m}$) were calculated by subtracting the fine particle concentrations from the total particle concentrations. In each particle size range, samples were taken on three filter substrates—one quartz fiber filter (Pallflex 2500 QAO) and two Teflon membrane filters (Gelman Teflo). The quartz fiber filters were baked before use at 550 °C for 15 h to lower their carbon blank. Samples collected on quartz fiber filters were subjected to thermal evolution and combustion analysis for carbonaceous species (i.e., organic carbon, elemental carbon, and carbonate carbon). Samples collected on one of each pair of Teflon filters were analyzed by ion chromatography (IC) for nitrate, sulfate, and chloride ion concentration; for ammonium ion concentration by colorimetry; and for water-soluble sodium and magnesium concentration by atomic absorption spectroscopy (AA). The second Teflon filter from each set was analyzed by X-ray fluorescence (XRF) for 34 elements: Ag, Al, As, Ba, Br, Ca, Cd, Cl, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Mn, Mo, Ni, P, Pb, Pd, Rb, S, Sb, Se, Si, Sn, Sr, Ti, V, Y, Zn, and Zr. The elemental concentrations were converted into the concentrations of their stable oxides where appropriate. Noncarbonate crustal element (mineral dust) mass concentrations were then estimated by summing the estimated concentrations of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , and MnO . Both Teflon filters of each pair also were weighed before and after sampling to determine airborne particle mass concentrations gravimetrically.

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_3 and HCl concentrations (6, 7) and tandem filter packs were used for collection of gas-phase SO_2 and NO_2 (8). In the filter pack or tandem filter method, gas-phase species were collected on treated backup filters after particles are removed on Teflon or quartz fiber prefilters that were held

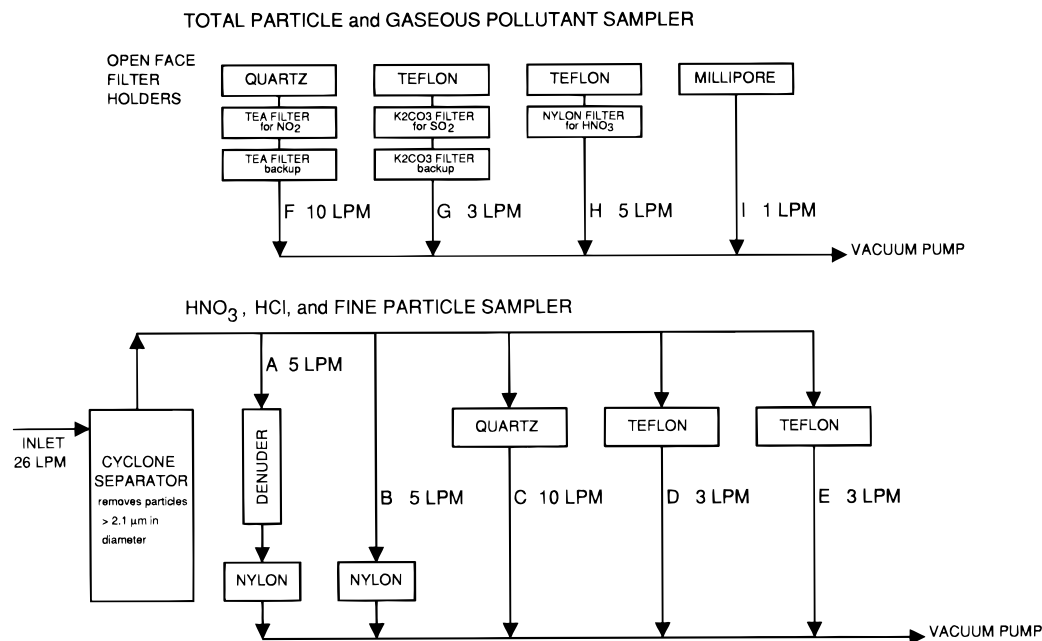


FIGURE 2. Diagram of air pollutant samplers.

in open-face filter holders. SO₂ was collected using K₂CO₃-impregnated Whatman 41 paper filters. NO₂ was collected using triethanolamine (TEA)-impregnated Whatman 31ET chromatography filters. These sampling techniques have been described previously, and the interested reader is directed to the original references (6–8).

Horizontally and vertically oriented deposition plates were deployed at the beginning of June 1992 and left in place for 11 months at St. Anthony's Chapel and at Kinga Chapel. Deposition plates were deployed having substrates similar to those used for airborne particle sampling. The vertically oriented plates were mounted on the mine walls while the horizontally oriented plates were placed near the ambient samplers in the two chapels. The 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 for SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, and Mg²⁺ in the same manner as the airborne particle samples collected on Teflon filters. Additional dry deposit samples collected on Teflon material were acid-digested and analyzed for certain elements including Al, Ba, Ca, Cu, Fe, K, Mg, Mn, P, Pb, Si, Sn, Sr, Ti, and Zn by inductively coupled plasma mass spectrometry (ICP/MS). Quartz fiber filter material (102 mm diameter) mounted in aluminum holders with bevelled edges also was used as a dry deposition surface. These quartz fiber surfaces were analyzed to determine organic carbon, elemental carbon, and carbonate carbon particle deposition rates.

Sulfur isotope analysis was employed in order to distinguish air pollutant-derived sulfur present in samples taken at the mine from sulfur compounds present naturally in the rock salt. A variety of samples were collected for this purpose: SO₂ from outdoor Krakow air collected as described earlier on treated filters, particulate sulfates collected from outdoor air at the mine, airborne particle samples collected within St. Anthony's Chapel and Kinga Chapel, surface deposits collected on Teflon deposition plates in those chapels, liquid drippings from surfaces in

St. Anthony's Chapel, surface scrapings from the mine shaft, and a sample of native rock salt from the mine that had not been exposed to the atmosphere in the mine.

Sulfur isotopic analysis techniques require that the specific form of sulfur be isolated and converted to pure SO₂. Sulfate was leached from the samples with hot water and adjusted to a pH of approximately 2 with HCl, the solution was filtered, and the dissolved sulfate in the filtrate was precipitated as BaSO₄ (9, 10). BaSO₄ was collected by filtration and dried. BaSO₄ was next combusted to SO₂ in a custom vacuum line, purified by cryogenic techniques, and analyzed by stable isotope mass spectrometry (11, 12).

Sulfur isotopic compositions are reported by using standard δ -notation, $\delta^{34}\text{S}$, the per mil or parts per thousand deviation of the ³⁴S/³²S ratio of the sample relative to the ³⁴S/³²S ratio of the Canyon Diablo Triolite (CDT) standard (13). The δ -value is defined as

$$\delta^{34}\text{S} = \frac{R_{(\text{sample})} - R_{(\text{standard})}}{R_{(\text{standard})}} \times 1000$$

where R represents the ³⁴S/³²S ratio. Analytical precision is approximately ±0.2‰ (per mil). Thus a $\delta^{34}\text{S}$ value greater than zero indicates that the sample is enriched in ³⁴S relative to the standard, and $\delta^{34}\text{S}$ less than zero indicates that the sample is relatively depleted in ³⁴S.

Results

Gas-Phase Pollutants. SO₂ is the principal gas-phase air pollutant present in the outdoor atmosphere near Wieliczka. SO₂ concentrations measured over the year are shown in Figure 3a. Outdoor levels are below 20 ppb during the warmer summer months, with higher values up to 40 ppb (24-h average) measured during the winter. These higher winter values suggest higher concentrations of the combustion products of local coal during the winter heating season. The annual average SO₂ concentration outdoors is 15 ppb. Figure 3a also shows that the levels of SO₂ inside the mine are negligible; the annual average SO₂ concentrations inside St. Anthony's Chapel and Kinga Chapel are only 0.51 and 0.18 ppb, respectively. In the absence of any

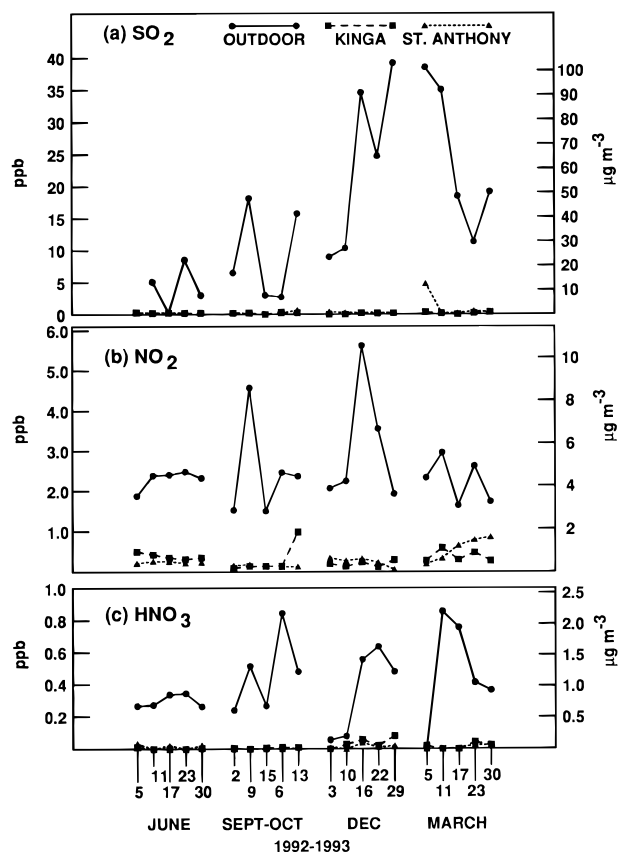


FIGURE 3. 24-h average pollutant concentrations in outdoor ventilation air supplied to the Wieliczka Salt Mine compared to pollutant concentrations within the mine at St. Anthony's Chapel and at Kinga Chapel: (a) sulfur dioxide concentrations, (b) nitrogen dioxide concentrations, (c) nitric acid concentrations.

deliberate pollutant removal systems, this decline in SO_2 concentrations within the mine suggests almost complete loss of SO_2 to interior surfaces. St. Anthony's Chapel is located near the air inlet to the mine, and SO_2 concentrations there are only 3% of those outdoors, showing that SO_2 removal at the mine walls occurs quickly.

Other pollutant gases are present at lower average concentrations outdoors: NO_2 (2.5 ppb), HNO_3 (0.42 ppb), and HCl (0.62 ppb). NO_2 levels inside the mine are lower than outdoors and remain less than 1 ppb during the year as shown in Figure 3b. Nitric acid and hydrochloric acid concentrations inside the mine are negligible, neither exceeding 0.1 ppb on any measurement day. Nitric acid concentrations are plotted in Figure 3c; a plot for HCl is not included as it would appear very similar to that for HNO_3 . The complete loss of HNO_3 within the mine is expected since salt is known to be a nearly ideal sink for HNO_3 ; indeed NaCl -impregnated fiber filters have been used in the past to sample for HNO_3 in ambient air. When HNO_3 reacts with NaCl , HCl vapor could be released, but the air monitoring data do not indicate any accumulations of HCl vapor within the mine.

Airborne Particle Mass Concentrations. The mass concentrations of both coarse and fine airborne particles are shown in time series in Figure 4 for each season outdoors and at the two locations sampled within the mine. 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 $30.4 \mu\text{g m}^{-3}$, and annual

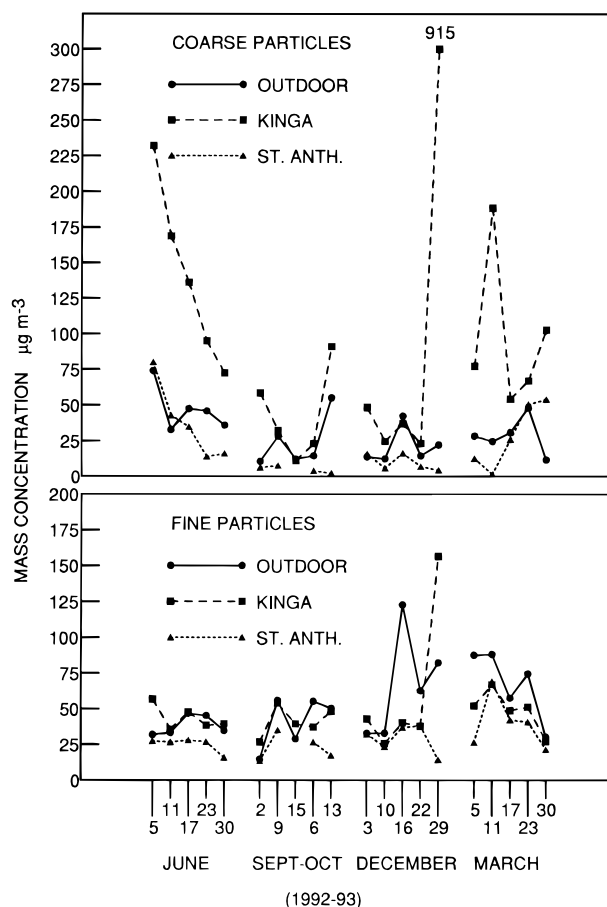


FIGURE 4. 24-h average coarse particle and fine particle mass concentrations in outdoor ventilation air supplied to the Wieliczka Salt Mine compared to concentrations within the mine at St. Anthony's Chapel and at Kinga Chapel.

average outdoor fine particle concentrations were found to be $53.3 \mu\text{g m}^{-3}$. By comparison, coarse particle concentrations in the air outside museums in downtown Los Angeles, CA, average about $78 \mu\text{g m}^{-3}$, while fine aerosol concentrations in Los Angeles average about $32\text{--}46 \mu\text{g m}^{-3}$ (4, 14). Los Angeles is widely recognized as experiencing high airborne fine particle loadings; it is clear that fine particle concentrations are comparable at Wieliczka.

Levels of both coarse and fine particles inside St. Anthony's Chapel are lower than those outdoors with annual average coarse particle concentrations of $20.4 \mu\text{g m}^{-3}$ and annual average fine particle concentrations of $29.1 \mu\text{g m}^{-3}$. St. Anthony's Chapel has been closed off from the main ventilation system in the mine by a series of doors that are only opened to allow tour groups to pass through. There is no air filtration system in the mine; therefore, the reduced particle concentrations observed in St. Anthony's Chapel when compared to the ventilation air fed to the mine provides evidence for particle losses due to dry deposition within the mine as there is no other mechanism for particle removal. Kinga Chapel, on the other hand, has annual average coarse particle levels of $123.0 \mu\text{g m}^{-3}$, much higher than those measured outdoors and thus arising in part from sources within the mine. The annual average fine particle concentration in Kinga Chapel is $48.5 \mu\text{g m}^{-3}$, similar to that outdoors.

Aerosol Chemical Composition. Figure 5 depicts the annual average chemical compositions of the fine and coarse particles at all three sampling locations. Organic

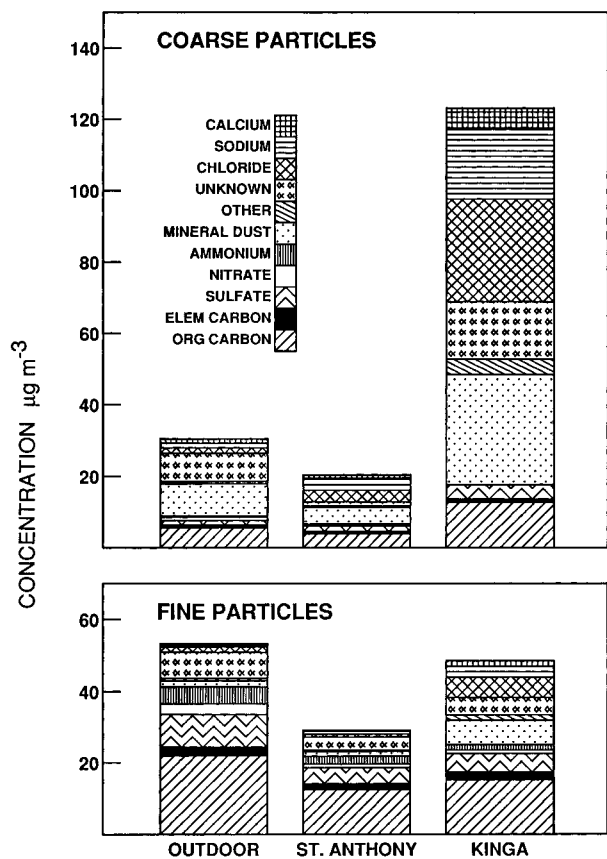


FIGURE 5. Annual average chemical composition and mass concentration of coarse particles and fine particles in outdoor ventilation air supplied to the Wieliczka Salt Mine compared to annual average airborne coarse particle and fine particle composition and concentration within the mine at St. Anthony's Chapel and at Kinga Chapel.

carbon compounds are the most abundant contributor to the fine particle concentrations, with noticeable amounts of aerosol ammonium, sulfate, and elemental (black) carbon. A large fraction of the airborne coarse particle material and some of the fine particle material in the atmosphere of Kinga Chapel is composed of sodium and chloride (i.e., salt dust) and mineral dust. This salt dust and rock dust arises from operations within the mine and is stirred up by numerous tourists.

The seasonal variation in the chemical composition of the airborne particles is illustrated in Figure 6. It is seen that fine organic carbon particle concentrations outdoors are similar to those within the mine during the months of June and September. Outdoor levels of both organic and elemental (black) carbon particles more than double during the colder winter months outdoors and are also present in greater quantities within the mine during this time. Fine particulate matter composition within Kinga Chapel would be much like that in St. Anthony's Chapel if the excess sodium, chloride, and mineral dust were not present in the atmosphere within Kinga Chapel.

Among coarse particles shown in Figure 6, there is more variation from site to site than from season to season. Coarse particle concentrations in the Kinga Chapel are always much higher than either in St. Anthony's Chapel or outdoors. The higher coarse particle concentrations in Kinga Chapel are caused by coarse salt dust and rock dust, and the concentrations of these depend on activities occurring within the mine. In early June, a team of photographers

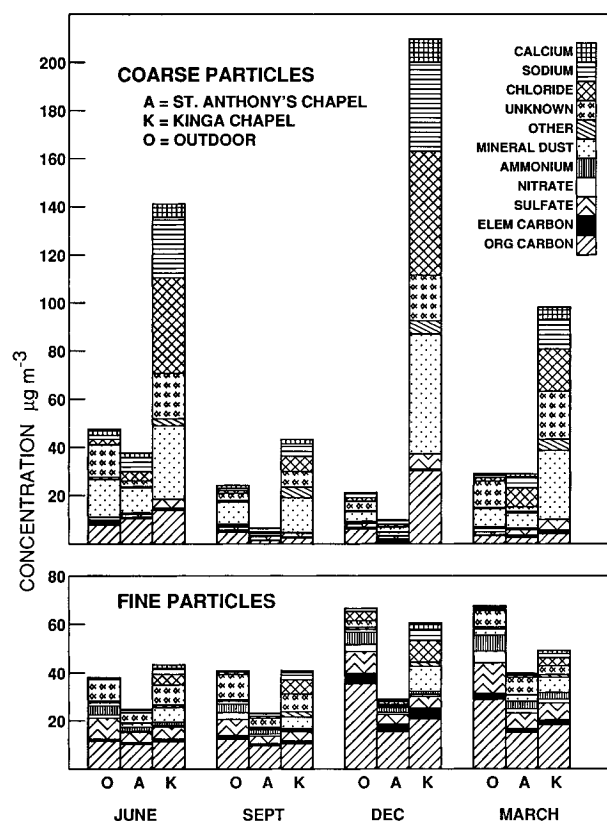


FIGURE 6. Seasonal changes in chemical composition and mass concentration of coarse particles and fine particles in outdoor ventilation air supplied to the Wieliczka Salt Mine compared to airborne coarse particle and fine particle composition and concentration within the mine at St. Anthony's Chapel and at Kinga Chapel.

was working in Kinga Chapel, and additional electrical wiring was installed at that time, which may have contributed to some of the increased particle levels found there during that month. During September, the lower levels of the mine experienced flooding that caused the mine to be closed to tourism at that time. The very high average coarse particle concentration in December is due to a single day in late December (see Figure 4). The exact cause of this excursion is not certain. However, throughout the entire period following the flooding of the lower levels of the mine, a great deal of drilling activity occurred in the mine as miners proceeded to erect barriers to arrest water intrusion. It is possible that such repair work in the mine caused the high dust values observed in Kinga Chapel.

Dry Deposition Samples. Dry deposition to vertical surfaces occurs largely by convective diffusion. Coarse particles by virtue of their large size have negligible diffusivity in air and hence do not deposit readily to vertical surfaces. Instead, dry deposits on vertical surfaces should be due to the flux of smaller diameter fine particles plus any gaseous material that is still in the air by the time that the air reaches the two chapels.

Table 1 shows the dry deposition flux of selected chemical species to vertically oriented deposition plates in St. Anthony's Chapel and in Kinga Chapel over the 11-month period of this investigation. Examination shows that the chemical composition of the vertically oriented dry deposit samples is consistent with our prior expectations. The chemical composition of the dry deposits on vertical surfaces is similar to that of the airborne fine

TABLE 1

Accumulation on Vertical Deposition Substrates ($\mu\text{g cm}^{-2}$) during 11 Months from June 1992 through April 1993

	Kinga Chapel	St. Anthony's Chapel
sodium ^a	0.46 ± 0.05	1.67 ± 0.17
chloride ^b	0.79 ± 0.09	1.90 ± 0.21
sulfate ^b	0.10 ± 0.01	0.11 ± 0.02
nitrate ^b	0.03 ± 0.01	0.03 ± 0.01
ammonium ^c	0.02 ± 0.01	0.03 ± 0.01
magnesium ^a	0.04 ± 0.01	0.08 ± 0.01
organic carbon ^d	3.78 ± 0.33	3.42 ± 0.31
elemental carbon ^d	0.03 ± 0.14	0.36 ± 0.16
aluminum ^e	0.02 ± 0.01	0.03 ± 0.01
calcium ^e	0.06 ± 0.01	— ^f
potassium ^e	—	0.05 ± 0.01
other ^g	0.01	—

^a Teflon substrate analyzed by atomic absorption spectroscopy. ^b Teflon substrate analyzed by ion chromatography. ^c Teflon substrate analyzed by colorimetry. ^d Quartz filter material deposition surface subjected to thermal evolution and combustion analysis. ^e Teflon substrate analyzed by inductively coupled plasma mass spectrometry (ICP/MS). ^f Less than blank value, indicated by —. ^g Other species measured by ICP/MS: Ti, Mn, Fe, Zn, Ga, Sr, Ba, Cr, Sn, Pb, Cu, and P.

particulate matter shown in Figure 5; organic carbon is a major contributor to the deposition samples, sodium and chloride are the next most abundant elements, followed by sulfates.

Table 1 shows that nitrate ion accumulation on vertical surfaces in these two chapels is quite small. This is important because a principal motivation for the present study was to determine whether or not low deliquescence point salts such as ammonium nitrate were accumulating on surfaces due to air pollutant intrusion into the mine. Table 1 shows that only minor amounts of nitrate ion and ammonium ion are making their way to surfaces in the two important chapels studied here.

Dry deposition to horizontal surfaces generally is dominated by gravitational sedimentation of large (coarse) airborne particles. Since the coarse particles shown in Figure 5 contain large amounts of salt dust and mineral dust, one would expect those species to be enriched in the deposits collected on horizontally oriented deposition plates within the mine. The horizontal deposition samples analyzed indeed are enriched in sodium chloride and mineral dust, but quantitative interpretation of those samples is prevented by confounding factors. In St. Anthony's Chapel, the horizontal deposition plate was heavily encrusted with salt out of all proportion to its presence in ambient air. This was due to salt-containing liquid dripping off the roof of the chapel due to the previously mentioned deliquescence problem there.

Samples Taken from Surfaces in the Mine. In addition to the dry deposition samples collected on Teflon and quartz deposition plates, it is also possible to examine samples taken from surfaces in the mine. Table 2 shows such an examination of the surface of one of the eroded statues in St. Anthony's Chapel. That statue is carved from a free standing block of white salt that is not the same material as the green salt walls of St. Anthony's Chapel (15). Material scraped from the surface of the statue is compared to the composition of the native salt below the surface. All species except for sulfate, nitrate, and chloride were analyzed by inductively coupled plasma/mass spectrometry. Sulfate,

TABLE 2

Comparison of Interior of Salt Sculpture with Surface Deposit on Sculpture

	interior ^a (ppm)	surface ^b (ppm)
aluminum	59.0 ± 8.9	11 060 ± 1,600
calcium	88.9 ± 13.3	6 236 ± 935
potassium	73.7 ± 11.0	5 052 ± 758
titanium	14.9 ± 2.2	616 ± 92
chromium	— ^b	18.7 ± 2.8
manganese	0.5 ± 0.2	112.0 ± 16.8
iron	—	7 234 ± 35.1
lead	—	8.0 ± 1.2
magnesium	20.3 ± 3.0	2 710 ± 406
zinc	—	34.8 ± 5.2
copper	1.5 ± 0.2	18.7 ± 2.8
strontium	0.3 ± 0.2	72.3 ± 10.8
sulfate	724.0 ± 201.0	894 ± 231
nitrate	—	—
sodium	375 000 ± 75,000	358 000 ± 72,000
chloride	651 000 ± 55,000	484 000 ± 18,000

^a μg of species/g of total mass. ^b None detected, indicated by —.

nitrate, and chloride analyses were performed by ion chromatography on a separate sample. The exposed surface material was extremely dark in color, while the interior material from which this statue was carved was composed of translucent rock salt. Table 2 shows that the surface of this statue has become covered with mineral dust deposited from its surroundings plus some sulfate in excess of the sulfate content of the parent salt from which the statue was carved.

Having established that SO₂ present in the outdoor atmosphere is rapidly removed by deposition within the mine, an attempt was made to map the deposition of SO₂ to the mine walls along the path from the main ventilation shaft to St. Anthony's Chapel. Surface scrapings were taken at several locations starting near the elevator doors where the main ventilation shaft intersects the first level of the mine 64 m below the surface. The second location where surface scrapings were taken was at the top of the Antonia Shaft 30 m down the corridor toward St. Anthony's Chapel. Finally, samples were taken inside St. Anthony's Chapel. In Table 3, these surface scrapings are compared to the composition of bulk rock salt from the mine that has not been exposed to the atmosphere in the mine.

Referring to Table 3, it is seen that bulk interior material from the mine walls that has not been exposed to the atmosphere in the mine has a sulfate/chloride ratio in the range of 0.08 to 0.014. The translucent rock salt from which the statue examined in St. Anthony's Chapel was made has a very low sulfate/chloride ratio of 0.001. The areas of white salt efflorescence where water has modified the salt likewise have low sulfate/chloride ratios in the range 0.006–0.007. In contrast, the surface of the solid salt mine walls that have not been brine-washed by liquified surface runoff show much higher sulfate to chloride ratios than the bulk salt behind the surface, suggesting a possible accumulation of sulfur transferred from the mine ventilation air to the surface of the mine. In addition, several of the mine wall surface scrapings contained large amounts of foreign material apparently deposited from the surrounding atmosphere, labeled as "gray fuzzy deposit" and "thick deposit" in Table 3.

Sulfur Isotope Analyses. Isotopic analyses were undertaken to confirm the origin of the excess sulfate seen on

TABLE 3
Wieliczka Surface Scrapings—Sulfate/Chloride Ratio

location	surface orientation	sulfate/chloride ratio
Bulk Interior Material ^a		
salt block, light color	interior	0.014
salt block, dark color	interior	0.080
sculpture, translucent	interior	0.001
Surface Scrapings Taken near Elevator Shaft ^b		
gray fuzzy deposit	vertical	0.208
gray salt	horizontal	0.513
fuzzy material only	horizontal	0.043
Surface Scrapings Taken at Antonia Shaft ^b		
white efflorescence	vertical	0.014
dark surface	vertical	0.007
Surface Scrapings from St. Anthony's Chapel ^b		
white efflorescence	vertical	0.006
dark surface	vertical	0.399
gray thick deposit	horizontal	0.866

^a Native rock salt not previously exposed to the atmosphere in the mine. ^b Scrapings taken from the solid native salt walls of the mine are labeled as having a dark surface or a gray surface, while the white deposits refer to areas of salt efflorescence that exist on the walls at many places in the mine due to water vapor condensation/evaporation cycles.

some surfaces within the mine. The results of that study are shown in Table 4. Sulfur derived from outdoor SO₂ shows a value of δ³⁴S equal to 0.67, the lowest of any of the source materials studied. Native rock salt from the mine that has never been exposed to the atmosphere in the mine has a δ³⁴S value of 21.56, the highest of any sample analyzed. This is similar to values previously reported for sulfate from salt in the Wieliczka Mine (+21.6 to +21.9) (16). All other samples lie between these two extremes. Assuming that each sample studied consists of a two end member mix of sulfur from ambient SO₂ mixed with sulfate from native salt, the fraction of the sulfur in each sample that is derived from atmospheric sulfur, *f_a*, can be calculated and is shown in Table 4.

The sulfur isotope data are consistent with inferences drawn earlier from ambient pollutant concentration measurements and from examination of deposition plates. Liquid drippings from the surfaces in St. Anthony's Chapel show a sulfur isotopic ratio almost the same as that of outdoor SO₂. Apparently SO₂ is easily dissolved in the liquid film that forms on the surfaces of that chapel. The sulfur isotope composition found on the horizontal deposition plate in St. Anthony's Chapel also closely resembles that of the liquid dripping from surfaces in the chapel. This is

consistent with the earlier observation that that deposition plate appeared to be encrusted with material that had dripped off the ceiling of St. Anthony's Chapel rather than being dominated by particles that had deposited from the atmosphere. Particulate matter samples taken outdoors at the location where ventilation air enters the mine show δ³⁴S values higher than that of ambient SO₂. Logically, these particles could contain a mixture of sulfates formed from ambient SO₂ plus some sulfate from salt dust particles released by activities near the mine. Airborne particles measured in St. Anthony's Chapel, near the entrance to the mine, have a sulfur isotope composition nearly identical to that of the outdoor airborne particulate matter. In contrast, the airborne particles in Kinga Chapel are enriched in ³⁴S compared to the outdoor aerosol, which is consistent with our earlier observation that the aerosol in the Kinga Chapel is contaminated with larger amounts of salt dust than is found in the outdoor air that is supplied to the mine. Both of the surface scrapings taken from the mine walls that were analyzed for sulfur isotopes in Table 4 show that those particular samples contain sulfur that is largely from the native salt. The horizontal dry deposition plate sample that was collected in Kinga Chapel is dominated by sulfur from the native salt, even more so than the salt-enriched aerosol measured in that chapel. This is consistent with the data given in Figure 5, which show that much of the airborne salt dust in Kinga Chapel is present in large particles that will settle out of the atmosphere more rapidly than the fine sulfate particles arriving there from the outdoor air.

Water Uptake by Surfaces. The data discussed so far show that the surfaces of the salt sculptures are becoming soiled by deposited particles and that some excess sulfate is accumulating on surfaces within the mine. In order to address the effect that these deposits might have on the relative humidity at which a liquid layer will form, both theoretical and experimental studies were undertaken.

The deliquescence point of complex mixed salts can be predicted based on thermodynamic considerations (17-20), and experimental data are available for binary salt mixtures that can be used to confirm these calculations in some cases (17). In general, it is found that the deliquescence point for mixed salts is lower than the deliquescence point of the individual pure salts that are blended to form the mixture (17). The interior of the salt sculpture analyzed in Table 2 consists almost entirely of Na and Cl, with a fraction of a percent SO₄²⁻ and traces of other elements such as K, Ca, and Mg. The deliquescence point of that mixed salt was calculated at 15.6 °C (the summertime

TABLE 4
Isotopic Composition of Sulfur in Samples from the Wieliczka Salt Mine

sample	δ ³⁴ S	fraction of S from SO ₂ , ^a <i>f_a</i>
SO ₂ from outdoor Krakow air	0.67	1.00
horizontal deposition plate from St. Anthony's Chapel	1.87	0.94
St. Anthony's altar drippings (liquid)	2.27	0.92
St. Anthony's altar drippings (liquid, second sample)	3.29	0.87
total airborne particles from outdoors at the mine	5.31	0.78
fine airborne particles from outdoors at the mine	6.74	0.71
total airborne particles from St. Anthony's Chapel	6.93	0.70
total airborne particles from Kinga Chapel	10.28	0.54
St. Anthony's Chapel salt surface scraping (white area)	16.70	0.23
horizontal deposition plate from Kinga Chapel	17.80	0.18
surface scraping from mine shaft	20.72	0.04
native salt from mine, not exposed to air in mine	21.56	0.00

^a The fraction of sulfur derived from airborne SO₂ is estimated as $f_a = (\delta^{34}S_{\text{sample}} - \delta^{34}S_{\text{salt}}) / (\delta^{34}S_{\text{SO}_2} - \delta^{34}S_{\text{salt}})$.

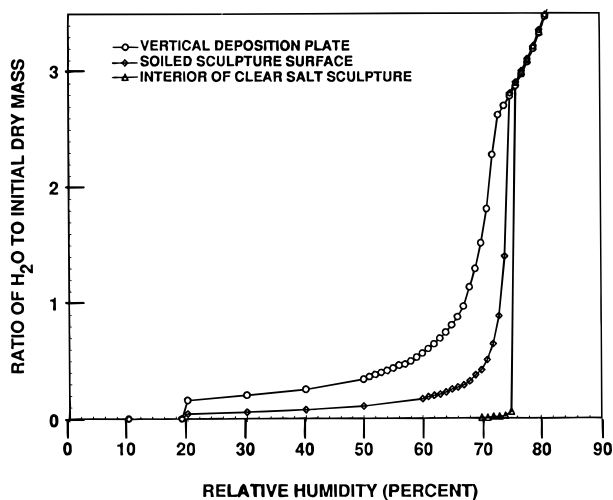


FIGURE 7. Water incorporation into samples taken from St. Anthony's Chapel as a function of ambient relative humidity: theoretical predictions for the case of multicomponent salt mixtures.

TABLE 5

Deliquescent Points of Some Compounds at 25 °C

compounds	RHD ^{a,b}
NaCl	0.7528
NaNO ₃	0.7379
NaHSO ₄	0.52
NH ₄ Cl	0.7710
NH ₄ NO ₃	0.6138
(NH ₄) ₂ SO ₄	0.7997
NH ₄ HSO ₄	0.40
(NH ₄) ₃ H(SO ₄) ₂	0.69
KCl	0.8426
K ₂ SO ₄	0.9751
KNO ₃	0.9248
CaCl ₂	0.2830
Ca(NO ₃) ₂	0.4906
MgCl ₂	0.3284
MgSO ₄	0.8613

^a Relative humidity of deliquescence. ^b Data are from refs 18 and 20.

temperature of the walls of St. Anthony's Chapel) using the SCAPE computer code of Kim, Seinfeld, and Saxena (18–20) after having reduced the measured chloride concentration by enough to satisfy electroneutrality. The salt mixture was calculated to undergo an abrupt transition from a nearly dry solid (with a few percent water) to become a liquid at just above 75% RH, as shown for the interior of the salt sculpture in Figure 7. The predicted deliquescence behavior of the interior of this statue is essentially the same as that of pure NaCl.

The surfaces of the sculptures in the mine are contaminated with deposited particles plus some sulfate formed as SO₂ is scavenged from the mine air. The chemical composition of this material deposited on surfaces is quite complex, as shown in Table 1. In the aggregate, SO₄²⁻, NO₃⁻, NH₄⁺, Mg²⁺, Ca²⁺, and K⁺ constitute a significant fraction of the mass of these surface deposits; the deposits are far from being pure NaCl. The relative humidities of deliquescence of some of the individual salts that could be formed from these ions are given in Table 5.

Many of the most likely sulfate salts that could be present in single deposited particles, such as (NH₄)₂SO₄, have relative humidities of deliquescence greater than that of NaCl. At the same time, certain possible combinations,

such as MgCl₂ and CaCl₂, if present would have very low relative humidities of deliquescence. It is not possible from a bulk chemical analysis to know the details of the composition of individual particles on these deposition plates. The worst case situation from the point of view of water accumulation would be that of a mixed salt having the bulk composition of all of the materials shown (other than carbon and aluminum, which will be assumed to be in insoluble carbon particles and mineral dust particles, respectively). To explore that situation, thermodynamic calculations were performed for a mixed salt having the composition of the material measured on the vertically oriented Teflon deposition plate that was located in St. Anthony's Chapel (see Table 1). In this case, the measured Na concentration was reduced to satisfy electroneutrality before the calculations were performed. As seen in Figure 7, the result of this worst case calculation was that, as relative humidity increases, a mixed salt like that found on the vertical deposition plate would slowly pick up water beginning at about 20% RH. Between 67 and 68% RH, an amount of water equal to the mass of the mixed salt would be present on the deposition plate. This would amount to a few micrograms of water per centimeter squared of deposition plate surface, possibly not enough to cause runoff. Thereafter, water uptake increases rapidly, roughly matching that of the interior of the salt sculpture studied earlier at 75% RH.

The actual situation faced by the surface of a salt sculpture is somewhere between that of the pure surface deposit versus the pure sculpture interior cases just described. Thermodynamic calculations were performed for a mixed salt having the composition of the deposition-contaminated surface scrapings taken from the statue studied in St. Anthony's Chapel in Table 2 (again with measured Na adjusted downward to satisfy electroneutrality considerations). It was found that such a mixture would pick up a very small amount of water beginning at approximately 20% RH, but that water retention equal to the mass of dry salt itself would not be reached until 73–74% RH (see Figure 7). Above 74% RH, the surface would acquire water very quickly such that by 75% RH the water content would be close to that of the post-deliqescence condition of the material found in the interior of the sculpture. These calculations cannot be exact because the degree of internal mixing of the surface deposits with the underlying salt sculpture cannot be determined exactly, but it seems likely that the effect of the pollutant deposition on the surface of the sculptures may be to reduce the effective relative humidity at which a liquid layer could begin to run off the statues by 1% to several percent.

In order to check that prediction, a small piece of material from the surface of the statue examined in St. Anthony's Chapel was placed on a microbalance, and its weight gain was measured as a function of relative humidity. The piece was found to gain water at 74% RH. The approximate theoretical analysis and the experimental determination give about the same results.

Discussion and Conclusions

Examination of air pollutant concentrations within the Wieliczka Salt Mine compared to those outdoors shows that pollutant gases including SO₂ and HNO₃ are removed quickly and thoroughly from the ventilation air within the mine by deposition to interior mine surfaces. At St. Anthony's Chapel, only 64 m below ground level, SO₂

concentrations have declined to negligible levels. A corresponding enrichment in the sulfate concentration on some unwetted rock salt surfaces within the mine and on the surface of a statue in St. Anthony's Chapel combined with the finding that sulfur present in liquid dripping from surfaces in St. Anthony's Chapel has an isotope composition close to that of ambient SO₂ seems to confirm the fate of SO₂ lost from the ventilation air. Nitrate concentrations on surfaces are quite low, which is fortunate since the presence of significant amounts of low deliquescence point nitrate compounds could have aggravated the water vapor absorption problem. The rapid and complete removal of SO₂ from the mine air may, however, explain a different feature of mine operations. The apparent success of the respiratory sanatorium on level 5 deep within the mine (see Figure 1) might be due to having access to air with some of the lowest SO₂ concentrations in Eastern Europe.

Fine particle concentrations measured both outdoors and within the mine show that carbonaceous aerosols are the largest single contributor to airborne fine particle levels, accompanied by noticeable amounts of aerosol ammonium and sulfate. These fine aerosol carbon and sulfate particles appear to be of outdoor origin. Coarse particles present in the air in Kinga Chapel near the exit to the mine's ventilation system show large amounts of salt dust and mineral dust that is not present in the outdoor air fed to the mine ventilation system but that instead must come from mining activities or from dust disturbed by visitors to the mine. Deposition samples collected on vertically oriented deposition plates are chemically similar to the ambient fine particle composition while accumulations on horizontal surfaces reflect deposited salt dust and mineral dust, plus material transported as contaminated water drips off overhead surfaces in St. Anthony's Chapel. Examination of one statue carved from translucent rock salt shows that it was blackened and soiled by particle deposition onto its surface.

Experiments performed by exposing a small piece of the surface of a salt sculpture from St. Anthony's Chapel to increasing humidification show that a substantial amount of liquid water accumulates on its surface beginning at about 74% RH. This is about 1% RH below the deliquescence point of pure NaCl and is consistent with approximate thermodynamic calculations performed for a mixed salt having the composition of the surface of that sculpture including its pollutant deposits.

In addition to the observation that air pollutant deposition has somewhat altered the water vapor condensation problem within the Wieliczka Salt Mine, there is compelling evidence that surfaces including the sculptures are becoming soiled by the deposition of dark-colored airborne particles. In the case of statues carved from dark-colored rock salt, these deposits may be hard to see visually, but in the case of some sculptures carved from translucent rock salt and the fixtures made from salt crystals, these deposits are both visually apparent and possibly harmful.

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