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Project Summary

Chemistry and Visual Impact of the Plumes from the Four Corners Power Plant and San Manuel Copper Smelter

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This paper presents a study of the conversion of SO_2 to particulate sulfur in a western power plant plume and in a western copper smelter plume, the impact of these plumes on visibility, and the relative contributions of primary and secondary aerosols to this impact. For plume ages greater than 3 h, the rates of conversion in the power plant and smelter plumes were similar (0.4 to 0.8% h^{-1}) with the higher rate in the smelter plume. For very young plumes, the conversion rates differed substantially. The low conversion rate (0-0.1% h^{-1}) in the very young plume of the power plant appeared to be related to the depletion of oxidant by nitrogen oxides. The very high conversion rate (2-4% h^{-1}) in the smelter plume of less than 1 h plume age was due in part to the absence of nitrogen oxides in the smelter plume. In the Four Corners region, most of the particulate sulfur was in the form of ammonium sulfate during the sampling period. The data suggest that most but not all of the particulate sulfur in the San Manuel plume and background was in the form of sulfate.

The major contribution to excess light extinction due to the plumes at the Four Corners power plant and the San Manuel smelter was light scattering by primary particles. This accounted for about 90% of the excess extinction from 5 km to 10 km downwind and decreased to about 70% at 25 km to 30 km downwind. Light scattering by primary sulfate particles was found to contribute very little to the extinction in the Four Corners power plant plume—2% of extinction at 5 and 25 km from the plant. In the San Manuel smelter plume, light scattering by primary sulfate particles contributed much more—55% of extinction at 10 km and 22% at 35 km from the smelter. Light scattering by secondary sulfate particles made a minor contribution to the plume excess extinction at Four Corners (2 to 5%), while at San Manuel it contributed ~7 to ~34%. The larger contribution in the smelter plume was due to higher conversion rates and the lack of NO_2 in the plume. Light absorption due to NO_2 did not contribute to the San Manuel plume excess extinction but made a modest contribution to the Four Corners plume excess extinction, increasing from 6% at 5 km to 18% at 25 km downwind.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

It is now generally recognized that haze is present in all parts of the continental United States, even in the relatively pristine desert of the Southwest. The U.S. Environmental Protection Agency undertook Project VISTTA (Visibility Impairment Due to Sulfur Transport and Transformation in the Atmosphere) in order to study the haze in the Southwest and to assess the

contributions of various sources to visibility reduction.

In this paper, we discuss the results of the second VISTTA field program (Fall of 1978) in which the plumes from a western coal-fired power plant and from a copper smelter were studied to determine the important components of the visibility reducing aerosol from these two sources.

Five days were spent studying the plume and background of the Four Corners (NM) power plant located 30 km SW of Farmington (NM). The plant has five units and produces a maximum output of 2100 MW. During the study period, the plant output varied from 900 to 2100 MW. The SO_2 emissions during the study period were estimated to range from 182 to 384 tons/day. The San Manuel (AZ) smelter plume was studied on two days with the most useful data coming from the flights on September 27, 1978, at downwind distances of 10 to 90 km.

The measurements, made by aircraft-based sampling of the plumes, were carried out on 11 days as summarized in Table 1. The aircraft was equipped with the instruments listed in Table 2.

Results

Sulfur conversion rate calculations from the Four Corners data fell into a pattern of low conversion rates of 0.1 to 0.2% h^{-1} from 0.2 to 1 h plume age rising to a maximum of 0.4% h^{-1} from 3 to 5 h plume age. Alternately, the limited San Manuel smelter data indicated a maximum sulfur conversion rate of 4% h^{-1} from 0.5 to 1 h plume age, which leveled off to 0.8% at 1 to 10 h plume age.

To understand the effect of UV radiation on the conversion of SO_2 to particulate sulfur, the sulfur-particle to sulfur-gas ratio (S_p/S_g) values were plotted against UV radiation (2950 to 3850 Å) for the Four Corners and San Manuel data. The Four Corners data were separated into two groups. The group with the higher slope [0.09% $(W\ h\ m^{-2})^{-1}$] was from the September 16, 1978, measurements. Two features in particular distinguish this day from the others in the Four Corners Plume Study: the plume was dispersed early in the morning beyond 12 km from the stack and the water vapor pressure was the highest. The data from the other days at Four Corners were much lower.

For the San Manuel smelter, S_p/S_g ratios plotted against UV radiation produced slopes of 0.13 to 0.16% $(W\ h\ m^{-2})^{-1}$, which were slightly greater than those for

Table 1. *Sampling Schedule at Four Corners and San Manuel Plants*

Date	Flights	Flight Times (MDT) Start	Stop	Flight Hours	Plume Sampling Distances (km)
9/12/78	Los Angeles to Farmington	14:40	19:08	4.5	Regional
9/14/78	Four Corners power plant (NM) plume	6:50	11:30	4.7	20,40
9/15/78	Four Corners plume	10:17	14:00	3.7	5,25
		16:00	20:05	4.1	5
9/16/78	Four Corners plume	7:49	11:35	3.8	2,12,34.55
9/18/78	Four Corners plume	6:31	8:15	1.7	20
9/20/78	Four Corners plume	7:54	13:37	5.7	20,40,65
		16:00	17:38	1.5	0-5
9/21/78	Regional sampling near Four Corners plant	8:23	12:15	3.9	Regional
	Farmington (NM) to Tucson (AZ)	14:38	17:40	3.0	Regional
9/23/78	San Manuel copper smelter (AZ) plume	9:12	13:25	4.2	10
9/26/78	Regional Sampling near smelters	11:43	20:33	8.8	Regional
9/27/78	San Manuel copper smelter plume	9:29	16:43	7.2	10,35,90,Bkg
9/28/78	Tucson to Los Angeles	15:53	20:43	4.8	Regional

Table 2. *Aircraft Instrumentation*

Parameter	Sampler Manufacturer and Model	Analysis Technique	Particle Size Range (μm)
Aerosols Integral Size			
Light Scattering Coefficient	MRI 1569	Integrating Nephelometer	~0.1-1
Aerosol Charge Acceptance	Washington University	Aerosol Charge Acceptance	~.01-.1
Condensation Nuclei	Environment One Rich 100	Light Attenuation	~.005-.8
Aerosols Differential Size	Thermal Systems, Inc. 3030[a]	Aerosol Charger-Mobility Analysis	.0056-1
	Royco 218[a]	Optical Particle Counter with Multichannel Analyzer	0.56-18
	Knollenberg ASSP	Axial Scattering Spectrometer Probe	3-45
Aerosol Samples			
Total Sulfur	MRI TWOMASS Sampler/Glass Fiber Filter	Flash Vaporization/ Flame Photometric Detection	<3
Sulfate and Nitrate	Bendix 240. Cyclone/Teflon Impregnated Glass Fiber Filters	Ion Chromatography	<3

[a]*Automatic bag sampling system for TSI 3030 and Royco 218;bagfill requires about 4.5 seconds.*

Table 2. *(cont'd)*

Parameter	Sampler Manufacturer and Model	Analysis Technique	Particle Size Range (μm)
Total Mass	Bendix 240 Cyclone/Teflon Impregnated Glass Fiber Filters	Gravimetric Weighing	<3
Total Sulfur	Low Pressure Impactor/ Vaseline-Coated Stainless Steel	Flash Vaporization/ Flame Photometric Detection	0.05 - 0.075 0.075 - 0.12 0.12 - 0.26 0.26 - 0.50 0.50 - 1.0 1.0 - 2.0 2.0 - 4.0
Al-Pb	Lundgren Impactor/Greased Mylar Stages Followed by Nuclepore after Filter	Particle-Induced X-Ray Emission Some Samples Analyzed by X-Ray Fluorescence	<0.5 0.5 - 1.0 1.0 - 2.0 2.0 - 4.0 >4.0
Gases			
Sulfur Dioxide	Meloy 285	Flame Photometric	
Ozone	Monitor Labs 8410	Chemiluminescence	
Nitrogen Oxides	Monitor Labs 8440	Chemiluminescence	
Other			
Dew Point Temperature	Cambridge Systems 137		
Turbulence			
Altitude Indicated Air Speed	MRI Airborne Instrument Package		
Position	Aircraft Navigation System		
Visual Range	Optical Photography Telephotometer		
UV Radiation	Eppley Radiometer	Barrier-Layer Photocell	

the Four Corners data set of September 16, 1978. The higher slope for data collected close to the smelter indicates that some factor besides or in addition to UV radiation, perhaps heterogenous conversion on the primary particulate emissions, is important to the conversion in the young smelter plumes.

If the plume is oxidant limited, SO_2 is expected to compete with NO and NO_2 for oxidant species, and the faster reactions NO_x will be favored. This competition was evident in the Four Corners plume when the S_p/S_g ratio (an indicator of SO_2 conversion) was examined against the NO_2/NO_x ratio (an indicator of NO oxidation). An increase in S_p/S_g due to secondary particulate sulfur formation appeared only at relatively high NO_2/NO_x ratios (low NO concentrations).

In the San Manuel smelter plume, no measureable NO_x above background was observed. This was also observed in passes near smelters during regional flights and is consistent with other VISTTA measurements.

The concentrations of gaseous nitrogen compounds and ozone for the various plume and background orbits at the Four Corners power plant are consistent with the generally accepted photostationary steady state model which leads to the conservation of the sum of NO_2 plus O_3. This conservation relationship can be tested with our data using the ratio $(\Delta NO_2+\Delta O_3)/\Delta NO_x$. The values of the ratio near the plant ranged from 0.04 to 0.09. While fluctuations were probably due to experimental uncertainties, negative values may be related to HNO_3 production. The photostationary steady state reactions are not the only reactions involving O_3, NO, NO_2, but the invariance of the ratio indicates that they are the most important.

The chemical composition of both the power plant and smelter plume aerosol showed obvious differences between the two plumes at the same downwind distances. These differences may be useful in determining the contribution of each type of source to the regional haze. The power plant always had higher concentrations of Al, Si, Ti, and V while the smelter always had higher concentrations of S, K, Cr, Cu, Sn, and Pb.

A trimodal mass size distribution of particulate sulfur with an ultrafine aerosol peak at 0.09 μm, a fine aerosol peak at 0.9 μm and coarse aerosol peak at 9 μm was seen in aerial plume measurements close to the Four Corners power plant (5 km) on the morning of September 15, 1978. The ultrafine mode was also present in morning ground-based plume measurements at 3 km and 25 km from the stacks. The ultrafine mode was not present in late afternoon aerial plume measurements when temperatures were 10 to 20°C higher than the morning measurements. This small particle mode might be due to condensation of sulfuric acid vapor into droplets.

The average percentage of coarse particle sulfur (diameter >2 μm) to total gaseous sulfur in the plume at 5 km was 0.08% which can be used as an indication of primary particulate sulfur from the flyash. No significant particle sulfur concentrations were observed on the ground because of the low cutpoint of the cyclone used.

The sulfur concentration associated with particles of aerodynamic diameter >1 μm was quite low in all background measurements. The mass mean size of particle sulfur in the background was about 0.24 μm. The Stokes mass mean diameter was 0.10 to 0.15 μm.

In the Four Corners plume and in the background, the sulfur appeared to be in the form of ammonium sulfate. Ammonium ion concentrations were determined only for the ground site sampling. For the samples in which ammonium, sulfate, and nitrate ion concentrations were determined, the average concentrations were 14 nmol sulfate/m^3, 34 nmol ammonium/m^3, and 2 nmol/m^3 of nitrate. These balance to within the sampling errors, indicating that sulfur was in the form of ammonium sulfate at the ground site near the Four Corners power plant. At the San Manuel copper smelter, most of the sulfur appeared to be in the form of water-soluble sulfate except close to the plant where large primary sulfur particles (>4 μm) made a significant contribution.

At 12 km downwind of the stack, the visual range through the copper smelter

plume was reduced from 105 km in the background to 42 km with the plume present (60% reduction). The visibility reduction decreased farther downwind of the plant. For example, at 90 km downwind, the visual range was 92 km with the plume present (13% visibility reduction relative to the background). The impact of the power plant is greatest when the plume is well defined in early morning and decreases at farther downwind distances. The impact was greatest on September 14, 1978, the only day when all five units were in operation during the VISTTA study. The reduction in visibility (51%) was significantly greater at 20 km downwind on the 14th when the load was ~2100 MW than the reduction in visibility (35%) when the load was 1200 MW.

Conclusions

The major conclusions of the study are:

1. The conversion of SO_2 to particulate sulfate in the Four Corners power plant plume and in the San Manuel copper smelter plume at ages greater than 1 h is consistent with homogeneous gas phase oxidation by OH radical. Rates of 0.4% h^{-1} for Four Corners on September 16, 1978 and 0.8% h^{-1} for San Manuel on September 27, 1978 were observed.
2. Conversion of SO_2 in the young (<1 h) smelter plume under daylight conditions is possibly dominated by heterogenous conversion on primary particles. The high conversion rate of ~4% h^{-1} was seen only close to the stacks where SO_2 and particulate concentrations were high.
3. In the Four Corners power plant plume, significant amounts of large diameter particles (>2 μm) containing sulfur were measured at 4 and 25 km downwind. Sulfur associated with fine particles (diameters between 0.1 and 2 μm) was seen in some plume samples. Very small particle sulfur (<0.1 μm aerodynamic diameter) was measured in high concentrations when ambient temperatures were below 18°C in sampling from the ground and from an airplane in the mixed layer. Sulfur was not present in the very small particle mode in samples taken at higher ambient temperatures.
4. In the background of the Four Corners power plant plume, no significant concentration of large particle sulfur (diameter > 2 μm) was present either in ground-based or aerial measurements. The aerodynamic sulfur mass median diameter from these background measurements was 0.2 μm.
5. The particulate composition in the Four Corners power plant plume was consistent with flyash analyses from this plant. Sulfur was enriched relative to iron at increasing downwind distances from the plant, indicating particulate sulfur formation in the plume.
6. The particulate composition in the San Manuel copper smelter plume was consistent with copper ore. Again sulfur enrichment indicated particulate sulfur formed from SO_2 in the plume.
7. Light scattering by primary particles was the major contribution to excess light extinction due to the plume at the Four Corners power plant and at the San Manuel smelter. This accounted for about 90% of the excess extinction from 5 km to 10 km downwind and decreased to about 70% by 25 km to 30 km downwind.
8. Light scattering by primary sulfate particles was found to contribute very little to the extinction in the Four Corners power plant plume—2% of extinction at 5 and 25 km from the plant. In the San Manuel smelter plume, light scattering by primary sulfate particles contributed much more—55% of extinction at 10 km and 22% at 35 km from the smelter.
9. Light scattering by secondary sulfate particles made a minor contribution to the plume excess extinction at Four Corners (2 to 5%), while at San Manuel it contributed ~7 to ~34%. The larger contribution in the smelter plume was due to higher conversion rates and the lack of NO_2 in the plume.
10. Light absorption due to NO_2 did not contribute to the San Manuel plume excess extinction but made a modest contribution to the Four Corners plume excess extinction, increasing from 6 to 18% from 5 km to 25 km downwind.

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***William Wilson** and **William Conner** are the EPA Project Officers (see below).*
The complete report, entitled "Chemistry and Visual Impact of the Plumes from the Four Corners Power Plant and San Manuel Copper Smelter," (Order No. PB 83-264 457; Cost $10.00, subject to change) will be available only from:
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