RELATIONSHIP OF TRENDS IN REGIONAL SULFUR DIOXIDE EMISSIONS TO PARTICULATE SULFATE CONCENTRATIONS IN THE SOUTHWESTERN UNITED STATES

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Abstract

A large component of atmospheric light extinction is due to fine ammonium sulfate aerosol, a byproduct of sulfur dioxide emissions. Large variations in sulfur dioxide emissions from copper smelters in the last decade have provided an opportunity to study the relationship between sulfur dioxide emissions and ammonium sulfate concentrations at various receptor sites. A particular point of interest is the extent to which changes in sulfur dioxide emissions are reflected as changes in ammonium sulfate concentrations. Using a relationship between fine ammonium sulfate concentrations and atmospheric extinction, the impact of controlling emissions on visibility may be examined. To this end, data from the National Park Service particulate monitoring network has been synchronized in time with monthly and seasonal averages of smelter emissions. Empirical results show a relationship between smelter emissions and particulate sulfate concentrations at three sites, Grand Canyon National Park, Tonto National Monument, and Chiricahua National Monument.

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Introduction

The relation between changes in emissions of sulfur dioxide (SO_2) and ammonium sulfate aerosol in the Southwestern United States has been investigated during the last several years[1,2]. Empirical models have been developed that examine source-receptor relationships between SO_2 emissions and sulfate concentrations[3,4]. Due to emissions from other anthropogenic sources and meterological variability, isolation of the effect of one source or source area on a particular receptor is difficult. Efforts to overcome such difficulties have utilized extensive data bases of aerosol concentrations at various receptors, emission inventories, and meterological data. Many methods used to identify sources of anthropogenic precursors to atmospheric sulfate have involved the use of back trajectories of air parcels arriving at receptors[5,6].

The western United States has provided a unique arena for analysis of source-receptor relations. Large fluctuations in smelter emissions have occurred in the last decade. For three months in 1980, a strike virtually eliminated smelter emissions, cutting regional emissions in half. In the middle part of this decade a good portion of the Western smelter emissions were on the road to elimination through implementation of controls or by plant shutdowns. However, the decrease in U.S. smelter emissions has been offset by more recent increases in Mexican smelter emissions.

This article focuses on two questions: Do large fluctuations in SO_2 emissions cause measurable changes in ammonium sulfate aerosol concentrations; and, how well do linear empirical models describe the relationship between changes in SO_2 emissions and changes in ammonium sulfate concentrations? Special attention is given to a method of reducing variability in ammonium sulfate aerosol concentration data.

Data description

SO_2 emissions

Monthly SO_2 emissions data were obtained from the State of Arizona Department of Environmental Quality for the seven Arizona copper smelters that operated during the last decade, detailed information regarding the operation of

two Mexican smelters located at Nacozari and Cananea in the State of Sonora was also provided[7]. The information about the Mexican smelters included: estimates of monthly emission rates for January and February of 1987; whether or not emissions were controlled; and, maximum capacity uncontrolled emission rates. Figure 1 details the study area and show the locations of the smelter sources and receptor sites.

In the intermountain region between the Sierra Nevada and the Continental Divide, before the smelter at Nacozari began operations, about 90% of the anthropogenic SO_2 emissions could be attributed to 15 major powerplants and 12 copper smelters[3,4]. Non-smelter emissions for this time period were estimated to be 1084 tons per day[4]. Based on mean values for the smelter data given in Table I, the seven Arizona smelters accounted for about 33% of the total anthropogenic SO_2 emissions in the intermountain region. Non-smelter emissions are dominated by electric power plant emissions, which deviate from their annual mean values in any given month by no more than 10% of total regional emissions, and are constant to within a few per cent from year to year[3]. However, the Mohave electrical generating station was not operating for six months in the first part of 1986 and emission controls were implemented at Four Corners electrical generating station in late 1984.

In the course of this decade, four of the smelters have shut down. The Kennecott smelter at Hayden closed in the spring of 1982. Two smelters operated by Phelps Dodge at Ajo and Morenci closed in March of 1985 and December 1984, respectively. The other Phelps Dodge smelter at Douglas closed in January of 1987. The three remaining smelters have controls on their emissions capable of about 90 percent control; they are the Asarco smelter at at Hayden, Inspiration at Miami, and Magma at San Manuel.

The Mexican smelters at Cananea and Nacozari came on line in 1977 and 1985, respectively. Cananea is uncontrolled and could produce 348 tons per day of SO_2 emissions at its maximum operating capacity. Similarly, Nacozari's estimated maximum uncontrolled emission rate is 1267 tons per day. Today, Nacozari has continuous SO_2 emission controls with greater than 90 percent efficiency; however, as recently as February of 1987 Nacozari was uncontrolled with an estimated release rate of 380 tons of SO_2 per day, well below its maximum[7].

Nacozari, with an uncontrolled maximum emission rate of 1267 tons per day of SO_2, is potentially the largest source in the west. Estimating the impact of changes of SO_2 emissions on concentrations of ammonium sulfate at receptor sites is difficult without access to Nacozari's monthly emission rates. Assuming a constant emission rate of 300 tons per day for Cananea, Figure 2 shows time lines of total smelter emissions without Nacozari and with Nacozari at four constant

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values. Of particular interest is the strike period in 1980 during the months of July through September when all Arizona smelter emissions were eliminated. The second time line (Figure 2) has Nacozari at its maximum uncontrolled capacity and shows its potential impact on total smelter emissions. The third and fourth time lines show total smelter emissions with Nacozari at two intermediate values, 700 tons per day and 380 tons per day. The fifth time line with Nacozari at 100 tons per day indicates about what the maximum smelter SO_2 emissions would have been were Nacozari controlled since startup. By inspection, under these scenarios, if Nacozari emits SO_2 at 700 tons per day or greater there is not a long term reduction in smelter SO_2 emissions. Because the scenario with Nacozari at 380 tons per day shows a slight but significant long term decrease in smelter emissions, the level of Nacozari emissions that would cause no apparent long term decrease in smelter emissions is somewhere between 380 and 700 tons per day.

Aerosol data

The National Park Service (NPS) has established a network of aerosol monitors at several National Parks (NP) and National Monuments (NM). Except for a brief period in the winter of 1987/88, when a new sampling network was established, some sites have been continuously monitored since 1979. The monitors employed from August 1979 until November of 1987 were stacked filter units (SFU) that segregate the aerosol into two size categories, fine (0-2.5 microns in diameter) and coarse (2.5-15 microns). Aerosol particles are collected on teflon substrates. The concentrations of several elements, including sulfur, are determined by proton induced x-ray emission (PIXE), and total aerosol mass for each size fraction is determined gravimetrically[8]. For this study it is assumed that all particulate sulfate existed as ammonium sulfate.

Fine elemental sulfur data, in units of nanograms per cubic meter (ng/m^3), were extracted from the NPS data base for seven sites; Chiricahua NM, Tonto NM, Hopi Point (Grand Canyon NP), Chaco Culture NM, Bryce Canyon NP, Mesa Verde NP, and Canyonlands NP. Until June of 1986, the data were collected in two 72 hour periods per week yielding about 9 observations per month. After June of 1986 two 24 hour samples per week were collected. Because the finest resolution of smelter data is monthly, the sulfur concentrations were averaged to monthly values. Figure 1, which details the study region, shows that Chiricahua NM is in the middle of the smelter region and that Tonto NM is on the northern fringe on the south side of the Mogollon rim. The approximate order of distance from the smelters for the remaining sites is Hopi Point, Chaco Culture NM, Mesa Verde NP, Bryce Canyon NP, and Canyonlands NP.

A very noticeable feature of the data is the seasonal behavior of the sulfur concentrations. Figure 3 shows the time line for the Hopi Point sulfur concentration

data. At all sites, as at Hopi Point, sulfur concentrations exhibit local maxima during the late summer or early fall. The only exception to this is in the year 1980 when almost all smelters were shut down for up to 3 months by a strike.

Presuming that the periodic variation is due to seasonal changes in regional photochemistry and meteorology, and not to periodic variation in smelter emissions, the data were de-seasonalized to remove the annually periodic component of sulfur concentration variability. The data were de-seasonalized on a monthly basis for each site by first calculating a grand mean $(\overline{C})$ and a mean for each month of the year[9] $(\overline{C}_j)$. The de-seasonalized values $(\widehat{C}_j)$ are the grand mean plus the departure of the actual monthly values (C_j) from the mean monthly values as given by the equation:

$$\widehat{C}_j = \overline{C} + (C_j - \overline{C}_j). \tag{1}$$

Table II has descriptive statistics of the seasonal component extracted from each site's data and gives the grand mean, the maximum and minimum monthly means, and the range of annual variation. The grand means are highest at Chiricahua and Tonto and roughly decrease as we move away from the smelter region. Similarly, the range of annual variation is greatest for Chiricahua and smallest for Canyonlands.

Figure 4 shows the de-seasonalized data for the seven receptor sites. The strike period in 1980 is clearly identified. All sites, except Mesa Verde, have local minimums during the strike period. The time lines suggest that the strike period minimum is the extreme minimum for all sites except Mesa Verde, Bryce Canyon and Canyonlands. At Bryce Canyon and Canyonlands the extreme minimum occurs late in 1986; moreover, Canyonlands has two local minima in 1981 that are lower than the strike period minimum. In late 1986, large swings in monthly sulfur concentrations with very low concentrations in September are seen at all sites that had data during this period. Since there was no interruptions of smelter emissions a regional cause due possibly to meteorological phenomena is suggested.

By inspection, the de-seasonalized data show two prominent trends in sulfur concentrations that occurred after the 1980 strike period. First, at all sites except Bryce Canyon NP, there are increasing trends in sulfur concentrations that peak in the the years 1983 through 1985. However, sulfur concentrations at Bryce Canyon are essentially constant from 1982 through the middle of 1985. By 1986 a decreasing trend that continues through the end of the data record in 1987 is evident at all sites. The down trend is least evident at Bryce Canyon NP and Canyonlands NP. At Mesa Verde NP sulfur concentrations peak in 1983 and then exhibit a steady down trend; a trend no doubt enhanced by the controls implemented in late 1984 at the Four Corners power plant which is in close proximity to the south of the park.

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Regression results

Assuming a linear relationship between total smelter SO_2 emissions as the independent variable, and sulfur concentration data as the dependent variable a suite of ordinary least squares (OLS) regression models were explored. When the independent variables are uncertain, as is the case with the smelter data, OLS regression can give lower R^2s and flatter slopes than orthogonal departure regression (OD) which explicitly considers the error variances of all variables. As we are dealing with monthly averages of sulfur concentrations and monthly smelter emission data, the biggest uncertainties are not directly accessible. Rather than assuming uncertainties for OD regression, OLS regression was used to obtain conservative estimates of the relation between smelter SO_2 emissions and sulfate sulfur concentrations.

First, the strike period was explicitly examined by using only data from 1980 through 1981. De-seasonalized sulfur concentration data were used as the dependent variable for all sites except Mesa Verde. Figure 5 has scatterplots of sulfate sulfur against smelter emissions with the OLS regression line for two of the six sites with strike period data, Tonto NM and Canyonlands NP. Table III gives the results of the regressions for all six sites.

Chiricahua (Table III), in the center of the smelter region, has the highest sulfur concentration, the second steepest regression line with a slope of 0.345, and an R^2 of 0.63. Tonto, on the northern fringe of the smelter region, has the steepest regression line with a slope of 0.491 and an R^2 of 0.76. Moving away from the smelter region the maximal sulfur concentrations decrease, the slopes of the regression lines become flatter, and the R^2's decrease. Hopi Point and Chaco Culture, being about equidistant from the smelter region, have similar slopes of 0.097 and 0.134 and R^2's of 0.57 and 0.48, respectively. Bryce Canyon, even further away, has a slope of 0.071 and an R^2 of 0.29. Finally, Canyonlands has a slope of 0.075 and an R^2 of 0.24 and is the furthest from the smelter region.

The flattening of the slopes, decreases in maximal concentrations, and decreases in R^2s are consistent with the relative distances of the receptors from the smelters. Although the R^2s become very low for distant receptors the significance of the regression coefficient associated for the slopes are very high as indicated by their small standard errors and correspondingly low p-values (Table III). One can argue that low R^2s at distant receptors suggest not a poor causal relationship between smelter emissions and sulfur concentrations but rather an attenuation of influence from smelter emissions as distance increases.

The attenuation of influence as function of distance can be further supported by considering the magnitude of the intercept between sites. Assuming that the

intercept represents sulfur concentrations due to non-smelter sources the size of the intercept in relation to the average sulfur concentration indicates the average contribution of non-smelter sources to sulfur concentrations. For a particular site, multiplying its slope by the average SO_2 emission rate for the strike period gives the average contribution from the smelters; thus, the average sulfur concentrations would be the sum of the intercept and the smelter contribution. By taking the ratio of the intercept with the average concentration and multiplying by 100 to obtain percentages, intersite comparisons of non-smelter sources are possible (Table III). Tonto and Chiricahua have intercepts that are relatively insignificant and Tonto's intercept is actually negative, suggesting that their sulfur concentrations are due entirely to smelter sources. However, Chiricahua's intercept at face value, suggests that non-smelter emissions account for 20% of the average sulfur concentration there. Because Chiricahua is located the southeast corner of Arizona sources in southern New Mexico and El Paso not explicitly considered here may account for the intercept. For the remaining sites, the non-smelter contribution to sulfur concentrations roughly increase with distance indicating that more distant sites are less influenced by smelter emissions than nearby sites.

Secondly, the entire record was examined by using data stratified by season at Hopi Point, and Chiricahua. Due to lack of information about emissions from the Mexican smelters, the four scenarios for Cananea and Nacozari as presented above were used. In summary, an emission rate of 300 tons per day was assumed for Cananea, and Nacozari emissions at four different levels were examined (100, 380, 700, and 1250 tons per day). The most significant results were obtained for summer and winter data. Because meteorological conditions for transport to Hopi Point from the smelter region are most favorable during the summer only summer season results are discussed here.

The summer season analysis was done with monthly data and averaged data for the summer season. Figure 6 has scatter plots of monthly de-seasonalized sulfur data vs total SO_2 emissions at two levels of Nacozari output for Chiricahua. Table IV summarizes the results of the regressions for all levels of Nacozari output at Chiricahua and Hopi Point. There is a positive relation at both sites with the relation being strongest at Chiricahua. The intercepts obtained for Chiricahua with Nacozari at 380 tons per day or 100 tons per day are highly insignificant suggesting that the intercepts should be set to zero for those cases. At both sites, the level of Nacozari emissions that give the best fit to the data is 380 tons of SO_2 per day. Not only does 380 tons per day yield the best R^2s, the steepest regression lines go with 380 tons per day. Moreover, during the winter of 1987, the estimated emission rate for Nacozari was 380 tons/day[7].

Using a 380 tons/day as a good estimate of Nacozari emissions, Figure 7 shows

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the scatterplots of summer season sulfur and smelter emissions at Hopi Point and Chiricahua NM using monthly data. Table V summarizes the results of the OLS regression of the data using monthly and seasonaly averaged data for Hopi Point, Chiricahua, and Tonto. The scatterplots and regression results suggest that at Chiricahua NM and Tonto NM all of the summer season sulfate sulfur concentrations are due to smelter emissions. While at Hopi Point, the significant intercept and much flatter regression lines suggest that summer season sulfate sulfur are due in part to non-smelter emissions.

Conclusions

Examination of the time lines of smelter SO_2 emissions indicate that shutdowns of U.S. smelters and the implementation of controls were essentially negated by the startup of the smelter at Nacozari in 1985. Only after the Phelps Dodge smelter at Douglas ceased operations in January of 1987 is an apparent long term decrease in smelter emissions discernable. Moreover, the long term decrease in smelter emissions due to the shut down of the Douglas smelter occurs only if the emissions from Nacozari are well below 700 tons per day.

Examination of the time lines for actual and de-seasonalized sulfur concentrations indicate that sulfur concentrations have recently declined at all receptors with data. Maximal sulfur concentrations occurred from late 1983 through 1985, beginning in 1986 significant decreases in sulfur concentrations are apparent at all sites. The de-seasonalized sulfur concentration time lines also show that large fluctuations in emissions during the strike period do cause measurable changes in aerosol concentrations at several receptors.

Regression results for the strike period and show that empirical linear models can describe changes in aerosol concentrations due to changes in emissions from specific sources, both in the short and long run. Although R^2's are low for receptors that are far away from the smelter region, the models obtained are highly significant with small standard errors for the regression coefficients. The decrease in R^2s for the more distant receptor sites indicates a decrease in influence of smelter emissions on sulfur concentrations as a function of distance. Many factors not onsidered here may play a role in the decrease of the R^2s, certainly as distance from the smelters increases long range transport from other sources would be more influencial.

Summer season regression results, based on the best fit, suggest that the average SO_2 emission rate for Nacozari is less than 700 tons/day, with 380 tons/day as a good estimate. Moreover, summer season sulfate sulfur concentrations at Tonto NM and Chiricahua NM are due almost entirely to smelter emissions, while

at Hopi Point a large contribution is due to non-smelter sources. Thus, summer season regression results are consistent with the relative distances of the receptors from the smelter region.

References

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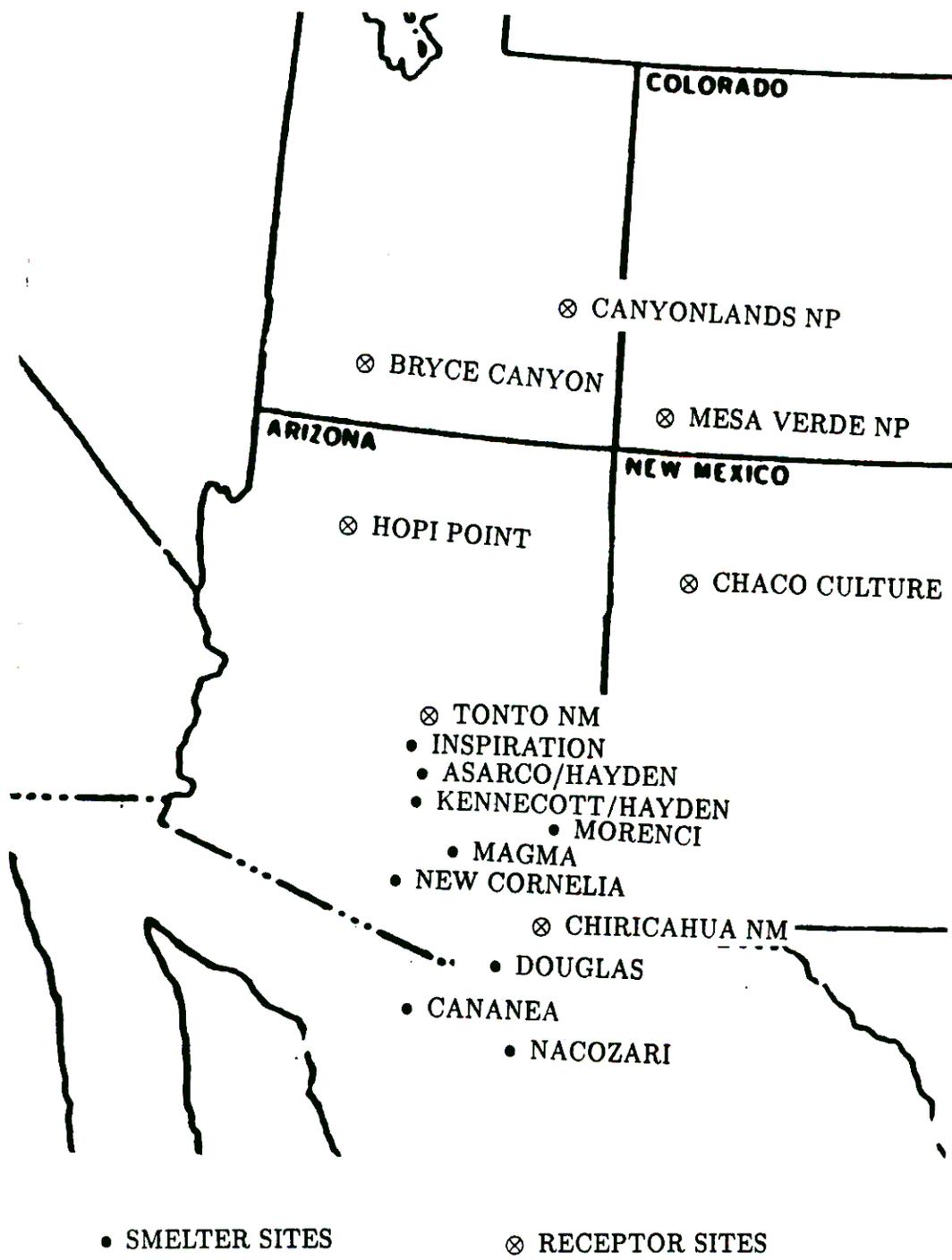9. C. Chatfield, The Analysis of Time Series, Chapman and Hall, pp. 21-30, New York, 1980.

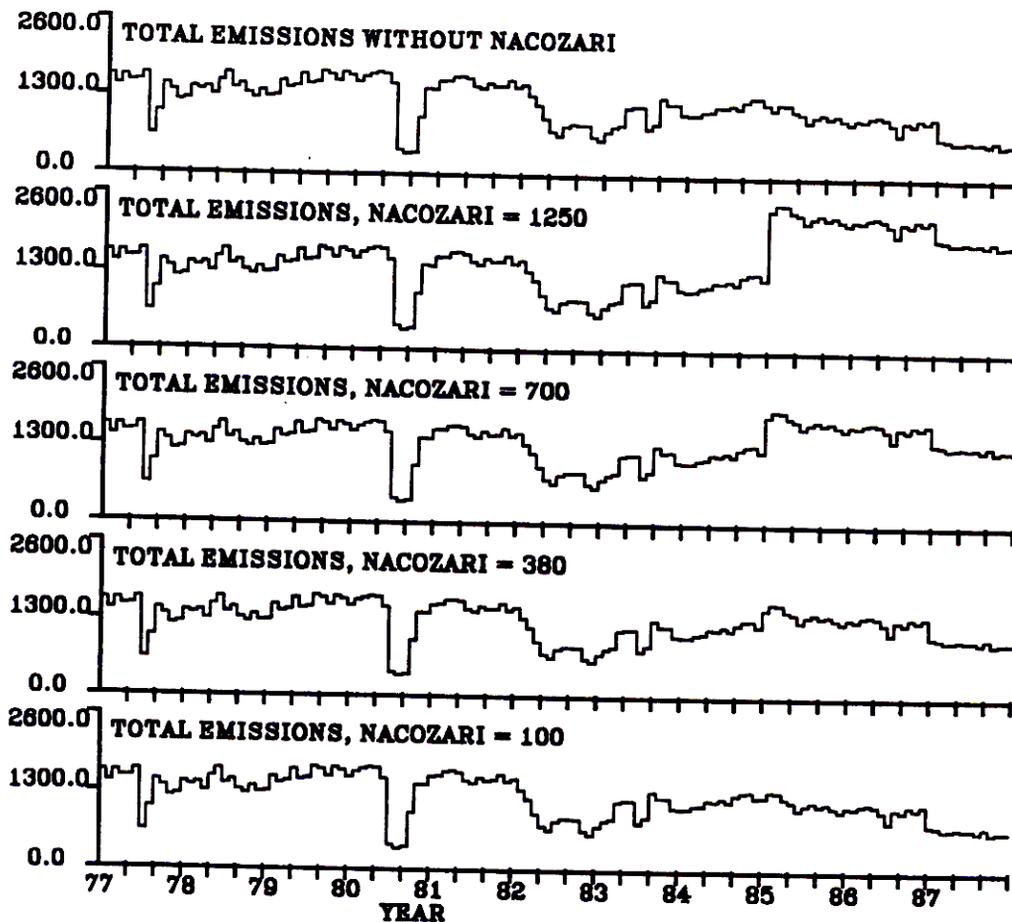Figure 1. Study area showing smelter and receptor sites.

Figure 2. Total smelter SO$_2$ emissions without Nacozari, and with Nacozari at four different levels.
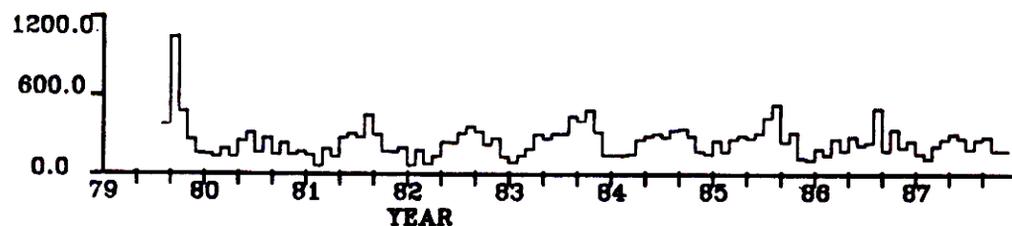

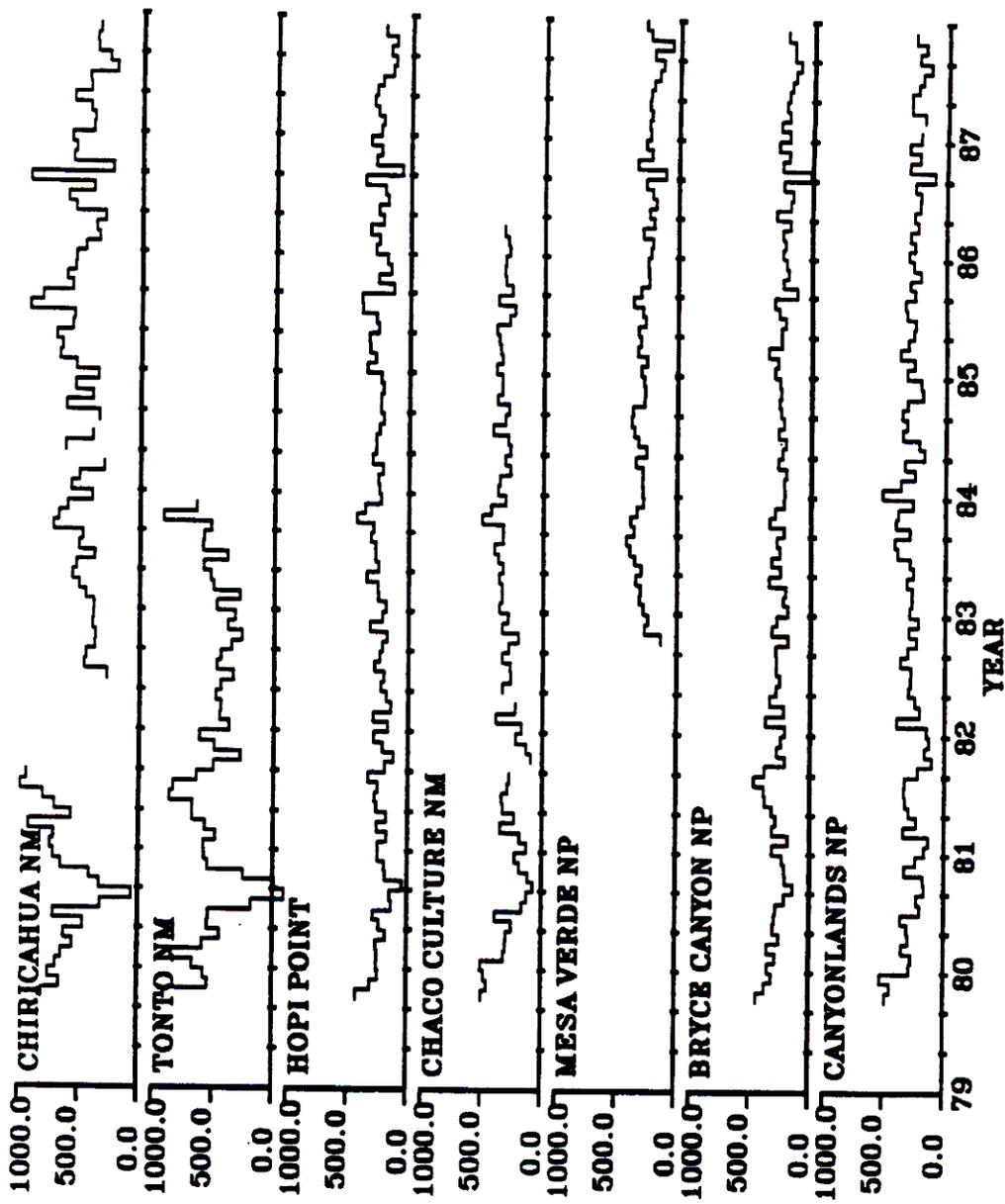Figure 3. Temporal history of monthly elemental sulfur concentrations (ng/m^3) at the Hopi Point monitoring site.

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Figure 4. Temporal history of de-seasonalized elemental sulfur concentrations (ng/m^3) for seven national Park monitoring sites.
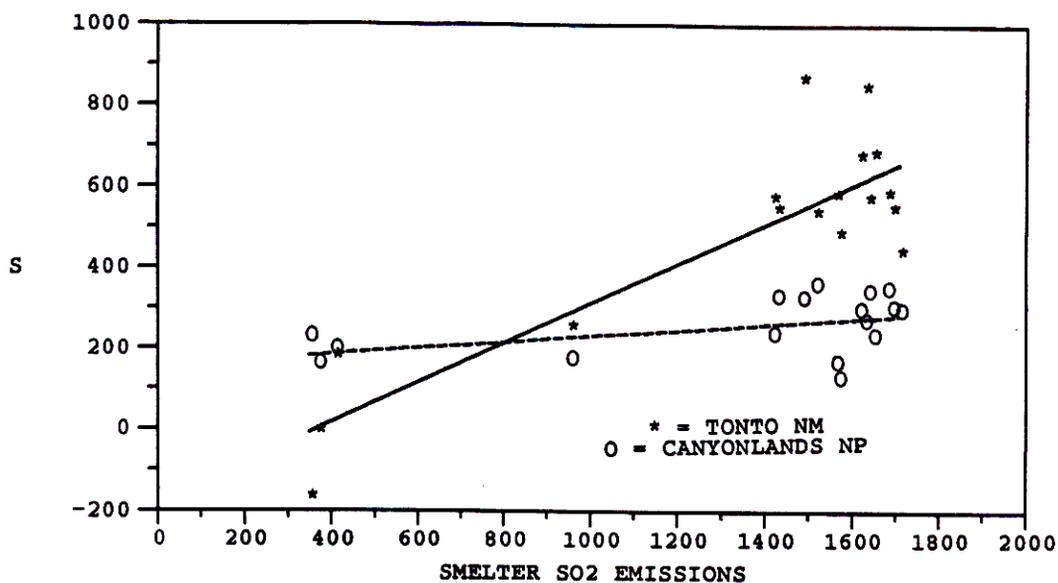
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Figure 5. Scatterplots of de-seasonalized sulfur concentrations (ng/m^3) vs smelter emissions (tons/day) for Tonto NM and Canyonlands NP during the strike period.

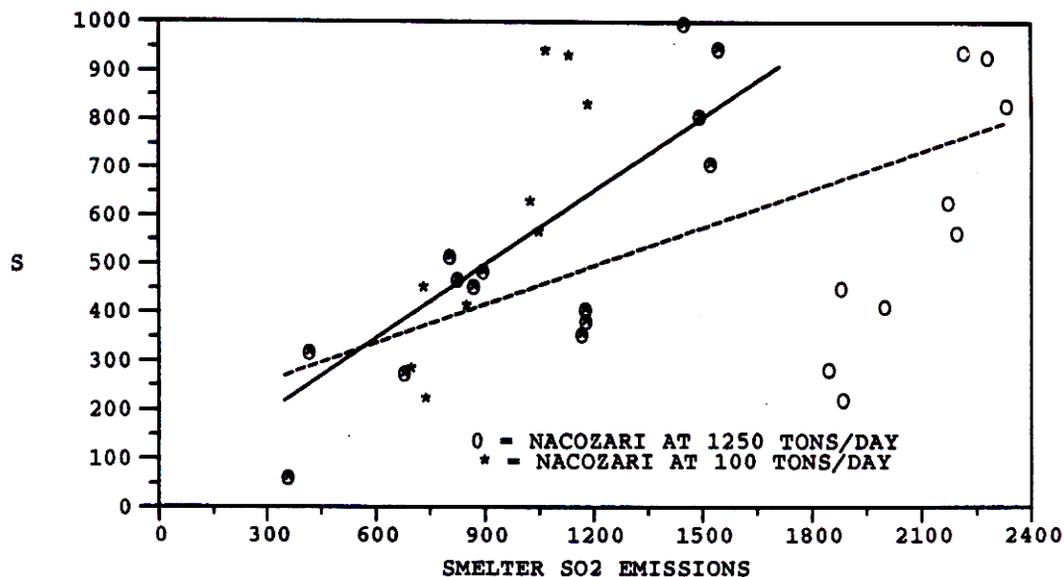
Figure 6. Scatterplots of summer season de-seasonalized sulfur concentrations (ng/m^3) against total SO_2 emissions (tons per day) for monthly data and two constant levels of Nacozari SO_2 emissions at Chiricahua.
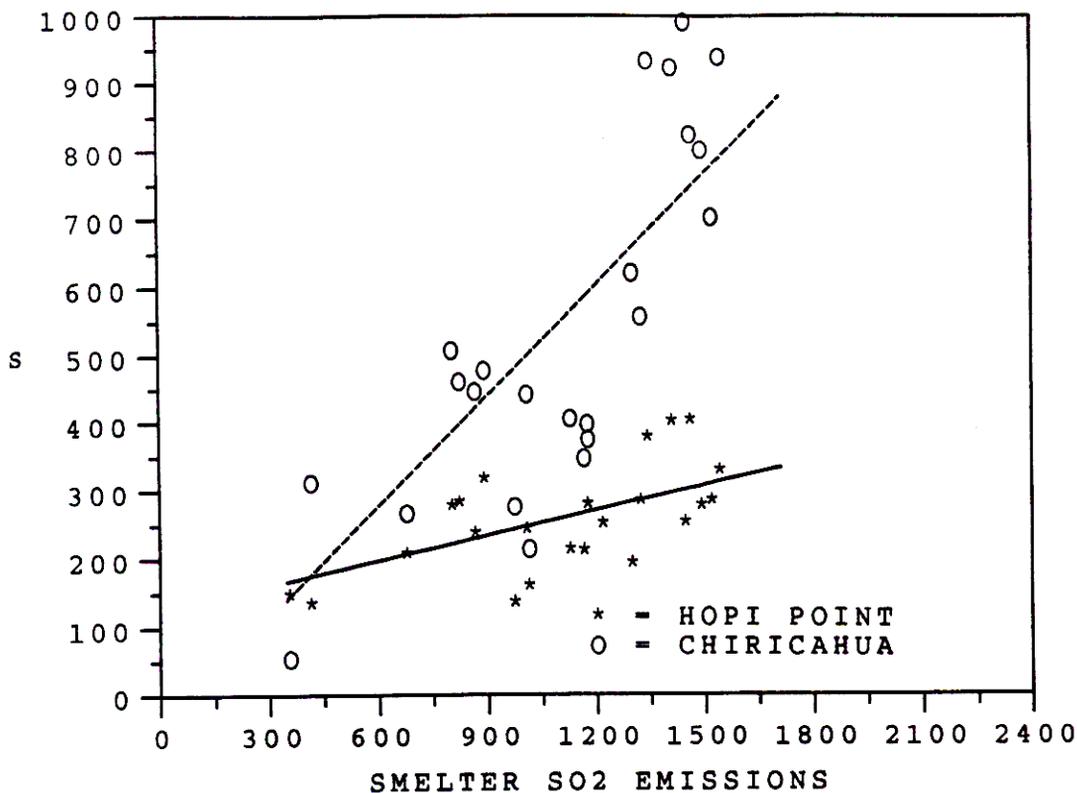
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Figure 7. Scatterplots of summer season de-seasonalized sulfur concentrations (ng/m^3) vs smelter emissions (tons/day) for monthly data at Hopi Point and Chiricahua NM and Nacozari emissions at 380 tons/day.

Table I. Descriptive statistics for SO_2 emissions (tons per day) for the 7 Arizona smelters.

site	no. of obs	std dev	max	75th prcntl	mean	med	25th prcntl	min
NEW CORNELIA	132	30.270	122.00	56.00	28.52	27.00	0.00	0.000
MORENCI	132	98.322	310.00	191.25	109.45	108.50	0.00	0.000
MAGMA	132	75.310	453.00	288.00	240.63	255.00	194.00	0.000
KENNECOTT/HAYDEN	132	24.392	122.00	32.25	17.32	0.00	0.00	0.000
INSPIRATION	128	30.538	165.00	56.75	39.77	34.50	17.00	0.000
DOUGLAS	132	168.982	557.00	416.25	291.48	340.00	179.75	0.000
ASARCO/HAYDEN	132	70.980	278.00	157.00	94.82	106.50	26.00	0.000

Table II. Descriptive statistics of the seasonal component in sulfur concentrations at 7 NPS aerosol monitoring sites.

site	seasonal components (ng/m^3)			
	mean	maximum	minimum	range
Chiricahua NM	531 ± 240	808	370	438
Tonto NM	524 ± 264	735	335	400
Hopi Point	246 ± 124	375	136	239
Chaco Culture NM	320 ± 137	478	211	267
Mesa Verde NP	267 ± 51	345	191	154
Bryce Canyon NP	253 ± 84	426	141	285
Canyonlands NP	282 ± 40	356	239	117

Table III. Stike period regression results of de-seasonalized sulfur concentrations (ng/m^3) against total SO₂ emissions ($tons/day$).

site	intercept ng/m^3	slope $(ng/m^3)/(tons/day)$	non-smelter contribution	p-value	r²
Chiricahua NM	115 ± 97	$0.345 \pm .068$	20%	0.0001	0.63
Tonto NM	-180 ± 101	$0.492 \pm .071$	0%	0.0001	0.76
Hopi Point	77 ± 31	$0.097 \pm .022$	37%	0.0004	0.57
Chaco Culture NM	53 ± 51	$0.134 \pm .036$	23%	0.0022	0.48
Bryce Canyon NP	169 ± 40	$0.071 \pm .028$	64%	0.0251	0.29
Canyonlands NP	155 ± 48	$0.075 \pm .034$	61%	0.0453	0.24

Table IV. Summer season regression results of monthly de-seasonalized sulfur concentrations (ng/m^3) against total SO_2 emissions ($tons/day$).

site	intercept ng/m^3	slope $(ng/m^3)/(tons/day)$	r^2
Nacozari = 100 tons/day			
Chiricahua NM	39.9 ± 115	$0.509 \pm .102$	0.49
Hopi Point	145 ± 39	$0.112 \pm .038$	0.27
Nacozari = 380 tons/day			
Chiricahua NM	-49.7 ± 115	$0.543 \pm .102$	0.56
Hopi Point	124 ± 41	$0.122 \pm .036$	0.33
Nacozari = 700 tons/day			
Chiricahua NM	202 ± 148	$0.407 \pm .118$	0.35
Hopi Point	140 ± 40	$0.096 \pm .032$	0.28
Nacozari = 1250 tons/day			
Chiricahua NM	177 ± 118	$0.265 \pm .082$	0.32
Hopi Point	174 ± 37	$0.06 \pm .026$	0.19

Table V. Summer season regression results of monthly and seasonly averaged de-seasonalized sulfur concentrations (ng/m^3) against total SO_2 emissions ($tons/day$) at Hopi Point, Tonto NM and Chiricahua NM.

site	intercept ng/m^3	slope $(ng/m^3)/(tons/day)$	r^2
monthly			
Hopi Point	124 ± 42	$0.122 \pm .037$	0.33
Chiricahua NM	-49 ± 115	$0.543 \pm .102$	0.56
Tonto NM	-50 ± 119	$0.562 \pm .109$	0.68
seasonaly averaged			
Hopi Point	146 ± 67	$0.098 \pm .059$	0.28
Chiricahua NM	-37 ± 201	$0.511 \pm .177$	0.54
Tonto NM	-219 ± 160	$0.746 \pm .143$	0.90