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Application of the Tracer-Aerosol Gradient Interpretive Technique to Sulfur Attribution for the Big Bend Regional Aerosol and Visibility Observational Study

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ABSTRACT

A simple data analysis method called the Tracer-Aerosol Gradient Interpretive Technique (TAGIT) is used to attribute particulate S and SO_2 at Big Bend National Park in Texas and nearby areas to local and regional sources. Particulate S at Big Bend is of concern because of its effects on atmospheric visibility. The analysis used particulate S, SO_2, and perfluorocarbon tracer data from six 6-hr sampling sites in and near Big Bend National Park. The data were collected in support of the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study; the field portion was conducted from July through October 1999. Perfluorocarbon tracer was released continuously from a tower at Eagle Pass, TX, approximately 25 km northeast of two large coal-fired power plants (Carbon I and II) in Coahuila, Mexico, and approximately 270 km east-southeast of Big Bend National Park.

The perfluorocarbon tracer did not properly represent the location of the emissions from the Carbon power plants for individual 6-hr sampling periods and attributed only 3% of the particulate S and 27% of the SO_2 at the 6-hr sites in and near Big Bend to sources represented by the tracer. An alternative approach using SO_2 to tag "local" sources such as the Carbon plants attributed 10% of the particulate S and 75% of the SO_2 at the 6-hr sites to local sources. Based on these two approaches, most of the regional (65–86%) and a small fraction (19–31%) of the local SO_2 was converted to particulate S. The analysis implies that substantial reductions in particulate S at Big Bend National Park cannot be achieved by only reducing emissions from the Carbon power plants; reduction of emissions from many sources over a regional area would be necessary.

IMPLICATIONS

The Carbon I and Carbon II coal-fired power plants in Coahuila, Mexico, are the largest sources of SO_2 emissions in the area near Big Bend National Park. There has been concern that these plants contribute much of the haze at the park. Our analysis indicates that local sources (such as the Carbon plants) contributed a majority of SO_2, but only a small fraction (approximately 10%) of the particulate SO_4^{2-}, on average, in the vicinity of Big Bend during the BRAVO study. Emissions reductions from more distant regional sources and from the Carbon plants are needed to substantially reduce particulate S and improve visibility at Big Bend National Park.

INTRODUCTION

The Big Bend Regional Aerosol and Visibility Observational (BRAVO) study was designed to understand the long-range transport of visibility-reducing particles from regional sources in the United States and Mexico and to quantify the contributions of specific U.S. and Mexican source regions and source types responsible for poor visibility at Big Bend National Park in Texas.[1] Analyses conducted during the study design phase identified several sources of particular interest: the Carbon I and Carbon II coal-fired power plants located approximately 270 km east-southeast of Big Bend National Park, other urban and industrial sources in northern Mexico, coal-fired power plants along the lignite belt in Texas, which runs from the northeast corner of Texas southwest toward the Carbon I/II facilities in Mexico, and other urban and industrial sources in east Texas. Figure 1 is a map of gridded SO_2 emissions in the study region. The very large and highly variable source in southern Mexico is the Popocatepetl volcano with average SO_2 emissions estimated at an annual rate of approximately 1.7 millions t/yr during the study period. Estimated SO_2 emissions of 240,000 t/yr for the Carbon I/II power plants are shown just south of the U.S./Mexico border approximately 270 km east-southeast of Big Bend National Park.

The field study conducted from July through October 1999 included many gaseous, aerosol, meteorological, and optical measurements. The study also included release of perfluorocarbon tracers at four locations and a network of 37 $PM_{2.5}$ and SO_2 samplers, and 24 tracer-sampling sites collocated with the aerosol sites. Most of the tracer, aerosol, and SO_2 sampling sites collected 24-hr averaged data; however, six 6-hr tracer, $PM_{2.5}$, and SO_2 sites were located along an approximately 300-km-long arc running north-northeast from the Rio Grande River at Big Bend National Park. The 6-hr monitoring sites and tracer release locations are shown in Figure 2. The Monahans Sandhills 6-hr site (the most northerly site) was not used in the Tracer-Aerosol Gradient Interpretive Technique (TAGIT) analysis that follows because it is apparently impacted from time to time by a nearby SO_2 source.

A variation of the TAGIT[2] analysis first used in Project Measurement of Haze and Visual Effects[3] (MOHAVE) was applied to the BRAVO data set to apportion particulate S, SO_2 S, and total (particulate + SO_2) S at the 6-hr sampling sites. In Project MOHAVE, the perfluorocarbon tracer orthoperfluorodimethylcyclohexane (oPDCH) was injected directly into the stack of the Mohave Power Project at a rate proportional to power production and, hence, SO_2 emissions.[4] The tracer oPDCH is 45% ortho-*cis*-perfluorodimethylcyclohexane (ocPDCH), which is detected using electron-capture gas chromatography[5] and is the isomer used for reporting concentrations. In BRAVO, tracer release by injection into the Carbon I and II power plants

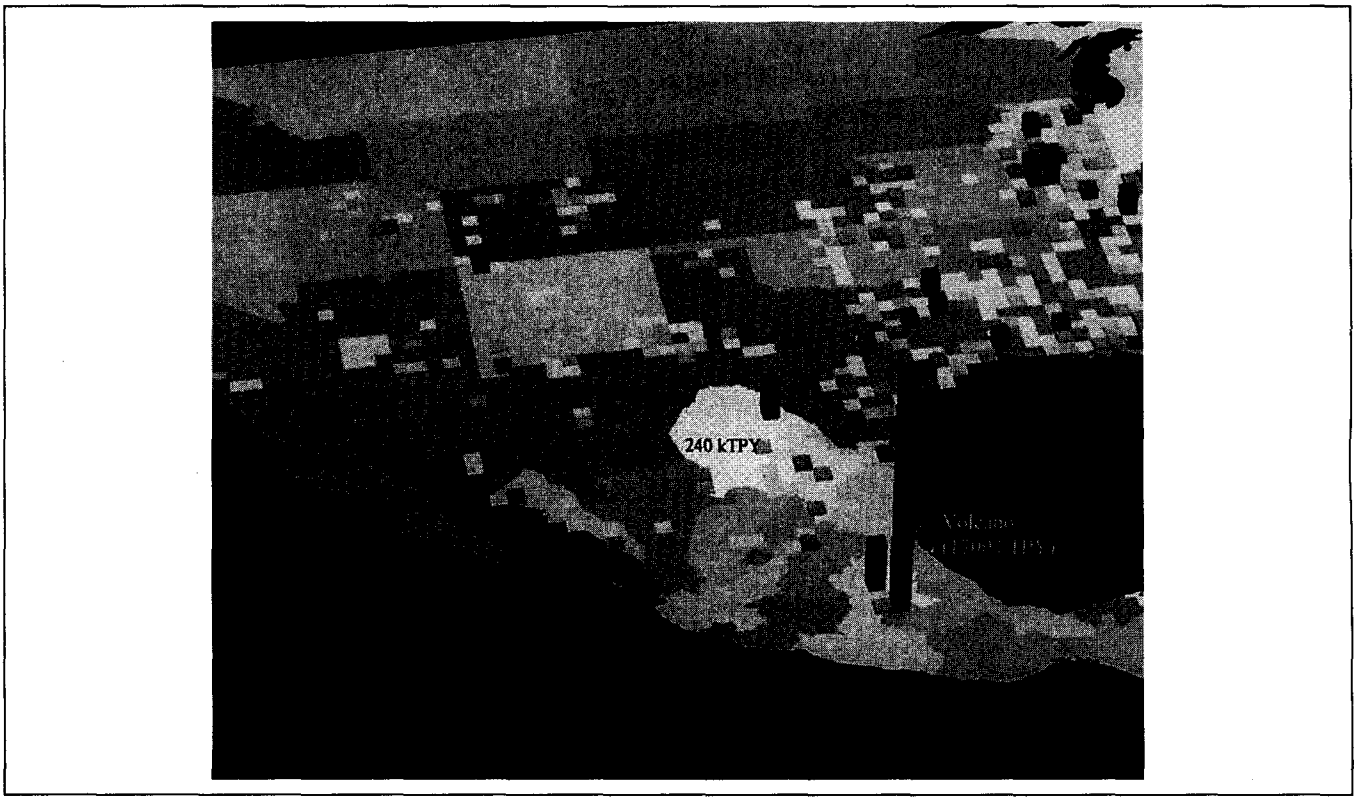

Figure 1. Gridded 1999 SO_2 emissions in the study region. Big Bend National Park is the small black area near the center of the figure.

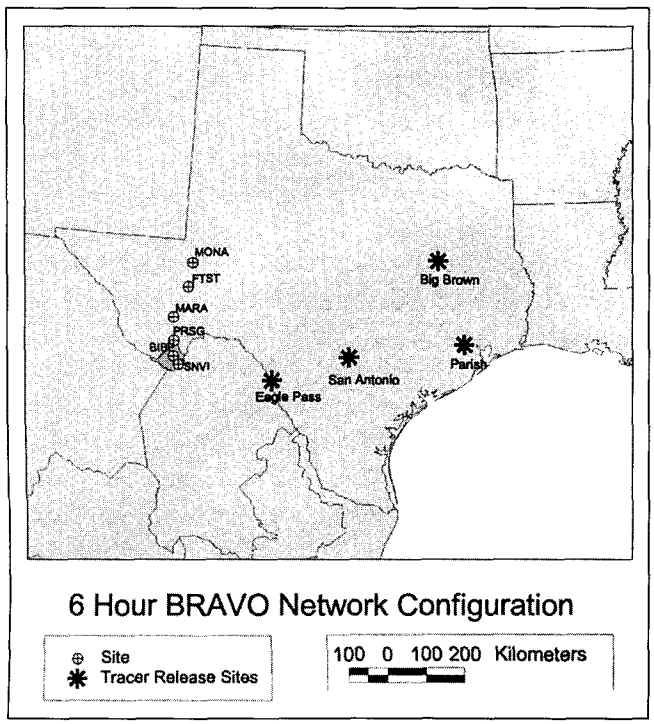

Figure 2. Six-hr monitoring sites and tracer release locations. Six-hr sites include Monahan Sandhills (MONA), Fort Stockton (FTST), Marathon (MARA), Persimmon Gap (PRSG), Big Bend (BIBE), and San Vicente (SNVI). Only data from the Eagle Pass tracer release are used for this analysis. The Carbon power plants are located 25 km southwest of Eagle Pass.

was not possible, so oPDCH was released continuously from Eagle Pass, TX, at a nearly constant rate (nominally 43 mg/sec) from July 5 until November 1. The release was intended to approximate the plumes from the Carbon I and Carbon II power plants in the state of Coahuila, Mexico, and approximately 25 km southwest of the Eagle Pass release location. The release was from the top of a 107-m-tall tower. Details of releases for all artificial tracers used in the study are described elsewhere.[1,6] Carbon I has a capacity of 1200 MW and Carbon II has a capacity of 1400 MW. Stack heights for the plants are 120 m. The SO_2 and particulate S samples were collected using Interagency Monitoring of Protected Visual Environments (IMPROVE) samplers and analyzed at the University of

Table 1. Correlation coefficients between SO_2 and ocPDCH at 6-hr sites.

	BIBE SO_2	FTST SO_2	MARA SO_2	PRSG SO_2	SNVI SO_2
BIBE ocPDCH	0.09	0.02	−0.09	−0.07	0.20
FTST ocPDCH	0.15	0.12	0.40	0.41	0.16
MARA ocPDCH	0.03	−0.01	0.07	0.13	0.11
PRSG ocPDCH	0.03	0.06	−0.02	−0.02	0.07
SNVI ocPDCH	0.14	−0.13	−0.11	−0.14	0.34

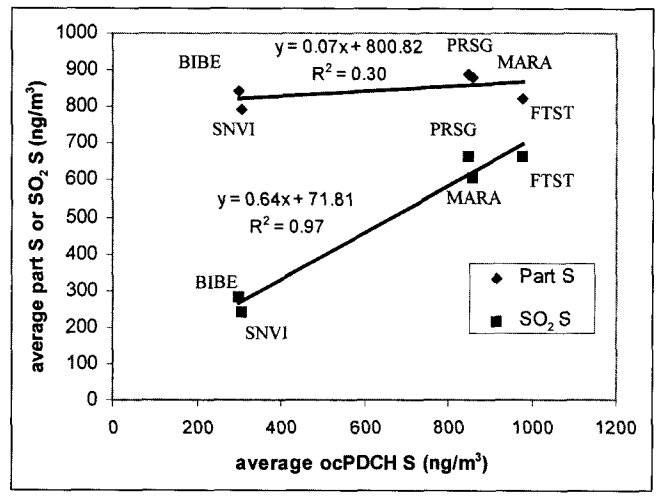

Figure 3. Relationship between average SO_2 S, particulate S, and ocPDCH-equivalent S at five 6-hr sites. The ocPDCH S is calculated by multiplying the ocPDCH concentration by the ratio of the estimated SO_2 S emissions rate from the Carbon plants to the ocPDCH emissions rate from Eagle Pass. Data include periods when SO_2, S, and ocPDCH are generally available; not included is the period before August 5, when SO_2 was not available.

California at Davis using the standard IMPROVE methodology.[7]

TAGIT is a receptor model that can attribute primary or secondary species associated with the source "tagged" by tracer release or other surrogate. The approach is simple. For each sample period, the background concentration of the species, such as particulate S, is determined by averaging the concentrations of the species at nearby sites that do not have elevated tracer concentrations that are significantly above background (for ocPDCH, defined as greater than twice the uncertainty of the measurement above global background). This background for each sample period is then subtracted from the concentration of the species of interest at impacted receptor sites for

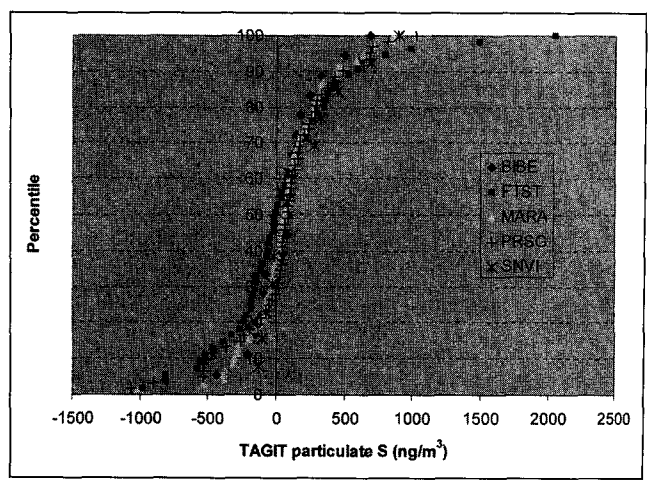

Figure 4. Cumulative frequency distribution of TAGIT attribution of particulate S, by site.

Table 2. Average TAGIT-attributed particulate S (ng/m^3) at each site for periods with elevated tracer concentrations. Also shown are the average particulate S, percentage of S at the sites attributed by TAGIT, and the percentage of observations with tracer above background.

	BIBE (n = 16)	FTST (n = 55)	MARA (n = 41)	PRSG (n = 45)	SNVI (n = 12)	ALL (n = 169)
Average TAGIT-Attributed S	86 ± 65	66 ± 69	75 ± 37	75 ± 48	189 ± 90	80 ± 26
Average S for TAGIT Assessment Periods	899	1038	942	954	803	958
% S Attributed for Impact Periods	9.6 ± 7.2	6.4 ± 6.6	8.0 ± 3.9	7.9 ± 5.0	23.5 ± 11.2	8.4 ± 2.7
% of Periods with ocPDCH > Background	22	50	48	37	16	35

corresponding sample periods. The difference is the concentration attributable to the tagged source.

The 24-hr sites were not used in the analysis for two reasons: (1) the sites were spread over a large geographic area, and thus were likely to have significantly varying background S concentrations; and (2) the 24-hr network was shut down for much of the study because of delays in development of the electron capture gas chromatography system needed to analyze samples promptly so that the sampling tubes could be cleaned and reused.

The use of a constant release rate for BRAVO compared with a rate proportional to SO_2 emissions as was done for Project MOHAVE does not affect the use of TAGIT in any fundamental manner. It is possible that releasing tracer at a constant rate for BRAVO could result in significant tracer concentrations even during periods when the Carbon power plants were shut down; however, the TAGIT attribution should give zero S attribution to these plants for these periods because there would have been no SO_2 emissions from these sources.

It should be noted that the mass concentration data of the species of interest are normalized to a common atmospheric density for all sites. This eliminates the component of spatial gradients that are a function of air density but would be equivalent in terms of volumetric ratios (e.g., ppb). The sites ranged in elevation from 549 to 1280 m mean sea level. Atmospheric pressure, temperature, and relative humidity measurements at the Big Bend National Park monitoring site (BIBE) were used to directly calculate density at that site on an hourly basis, which was then averaged over the entire study period. Average density at the other sites was estimated by using the average virtual temperature and pressure at Big Bend and integrating the hydrostatic equation with an assumed virtual temperature lapse rate of 6.5 °C/km to calculate average pressure and virtual temperature at the other sites. All particulate S, SO_2, and total S mass concentrations were standardized to the average atmospheric density at the BIBE site of 1.042 kg/m^3 that was obtained from National Oceanic and Atmospheric Administration (NOAA) meteorological measurements at K-Bar Ranch in Big Bend National Park by multiplication by the ratio of the BIBE density to the site density.

Uncertainties in the attribution method arise from the assumptions that variations in the background concentrations can be ignored and that there is no impact from the tagged source if the tracer concentration is less than the level considered to be "significantly" above its background. Uncertainty associated with both of these assumptions can be quantified. Unless background concentrations of the species vary systematically in space (as they may well do), the first type of uncertainty is random, rather than a systematic bias. The second uncertainty mentioned, assuming no impact from the tagged source when the tracer is not statistically above background, would lead to an underestimation of attribution. This is because uncertainty in the tracer concentration can result in sites being designated background though they are impacted by the tagged source. Its species concentrations are then used when computing the average background to be subtracted from the concentration at the receptor sites.

Table 3. Correlation matrix for particulate S at 6-hr sites.

	BIBE S	FTST S	MARA S	PRSG S	SNVI S
BIBE S	1.00				
FTST S	0.75	1.00			
MARA S	0.78	0.87	1.00		
PRSG S	0.87	0.82	0.90	1.00	
SNVI S	0.94	0.75	0.78	0.84	1.00

Table 4. Correlation matrix for SO_2 at 6-hr sites.

	BIBE SO_2	FTST SO_2	MARA SO_2	PRSG SO_2	SNVI SO_2
BIBE SO_2	1.00				
FTST SO_2	−0.04	1.00			
MARA SO_2	0.04	0.47	1.00		
PRSG SO_2	0.24	0.29	0.58	1.00	
SNVI SO_2	0.78	−0.04	0.11	0.20	1.00

Table 5. Correlation matrix for ocPDCH at 6-hr sites.

	BIBE ocPDCH	FTST ocPDCH	MARA ocPDCH	PRSG ocPDCH	SNVI ocPDCH
BIBE oc	1.00				
FTST oc	0.28	1.00			
MARA oc	0.36	0.53	1.00		
PRSG oc	0.42	0.44	0.41	1.00	
SNVI oc	0.76	0.34	0.32	0.32	1.00

TAGIT computes attribution on a sample-period-by-sample-period basis. Some periods will have a negative concentration attributed to the tagged source; in Project MOHAVE, these negative values were generally within the calculated uncertainty of 0. The results are most meaningful when averaged over a number of sampling periods, such as the average over the field study. The assumptions, uncertainties, and limitations of TAGIT are discussed in detail elsewhere.[2]

METHODOLOGY

In the BRAVO Study, TAGIT was first used for attribution of particulate S, SO_2, and total S (particulate S + SO_2 S) associated with the Eagle Pass artificial tracer release. (Later in this paper we describe using SO_2 rather than an artificial tracer as a surrogate for "local" emissions.) The TAGIT attribution was done for the 6-hr sites only; these sites have by far the greatest number of tracer samples. Sites were determined to be at background for sample periods where the measured ocPDCH concentrations are less than twice the concentration uncertainty above global background for the tracer, as reported by Brookhaven National Laboratory. The concentration needed to be significantly above background was usually approximately 0.13 femtoliters per L (fL/L) or parts per quadrillion. This tracer concentration corresponds to approximately 330 ng/m^3 of SO_2 S from the Carbon power plants if the assumed SO_2 emission rate of 240,000 t/yr (6900 g/sec) is correct.

Attribution was calculated for each 6-hr site and sample period with an ocPDCH concentration greater than twice the uncertainty above background, provided at least one of the other four sites used had ocPDCH concentrations not significantly above background. Of the 337 periods with two or more sites having valid particulate S and tracer data, 32 periods (9.5%) had no sites with tracer at background (all tracer sites above background). For these periods, attribution calculations could not be performed.

A significant limitation to the use of TAGIT for BRAVO is that the ocPDCH tracer was not released from the stacks of the Carbon power plants. The release from a tower versus a stack with buoyant emissions likely leads to vertical as well as horizontal displacement of the tracer and Carbon power plant plumes and decreased initial dispersion of the tracer compared with power plant emissions. The buoyant emissions would be at higher levels, particularly at night when vertical mixing is limited. Systematic shear in vertical wind speed and direction in the lowest 400 or so meters has been noted nearby at the Del Rio radiosonde site.[1] Daytime tracer release and transport might be expected to more closely mimic power plant emissions; however, the typical transport time of 12–15 hr from the Eagle Pass tracer release site to the 6-hr monitoring sites[8] means that most samples will show a combination of daytime and nighttime release and transport.

If the tracer and power plant emission plumes are substantially separated, then sites that are considered to be at background, based upon tracer concentrations, may actually be impacted by the source. This would have the effect of improperly elevating background for subtraction and systematically underestimates the true impact of the source. Because the Carbon plants are large isolated emitters of SO_2, a good correlation between SO_2 and ocPDCH would indicate that the tracer is doing a good job of representing the power plant emissions. Correlation coefficients between SO_2 and ocPDCH at the 6-hr monitoring sites shown in Table 1 are low, indicating that the tracer released from Eagle Pass is not doing a good job at tagging the plumes from the Carbon plants, at least for individual 6-hr sample periods.

The highest correlations occur between ocPDCH at Ft. Stockton, TX, and SO_2 at its two neighboring sites to the south, Marathon and Persimmon Gap. While for individual sites and 6-hr periods, tracer and SO_2 are not well related, on average, both SO_2 and ocPDCH are higher at the northern sites compared with the southern sites, as shown in Figure 3. Figure 3 indicates that the tracer and SO_2 are being transported to similar areas on average. The

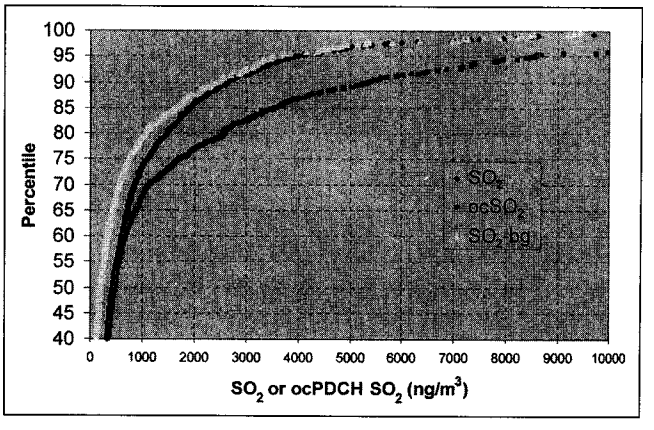

Figure 5. Cumulative frequency distribution of SO_2, ocPDCH-related SO_2, and SO_2 above background for the 6-hr sites. The background is insignificant at high concentration levels but is a significant fraction of the concentration at lower levels.

Table 6. Use of TAGIT SO_2 method for attribution of particulate S.

	BIBE	FTST	MARA	PRSG	SNVI	ALL
Average Attribution (ng/m^3)	136 ± 18	38 ± 21	95 ± 21	138 ± 20	42 ± 21	91 ± 9
% of Particulate S	14.4 ± 1.9	4.3 ± 2.4	10.1 ± 2.2	14.0 ± 2.0	4.6 ± 2.4	9.8 ± 1.0

good relationship between SO_2 and tracer, on average, but lack of a strong relationship between particulate S and tracer suggest that impacts of the Carbon power plants to particulate S may be relatively small at these sites. This assumes that elevated SO_2 is a good indicator of the potential impact area from the Carbon plants (by far the dominant SO_2 source within 300 km of the sites) and that if sites that are frequently impacted by the Carbon emissions compared with neighboring sites do not have significantly higher particulate S than their neighbors then the impact from the Carbon plants on particulate S must be small. This also assumes that the background (non-Carbon plant) particulate S is similar among the sites.

RESULTS

TAGIT Using ocPDCH Tracer

Because some displacement between the Carbon emissions and the tracer is expected on a sample-by-sample basis, it is most meaningful to consider results averaged over the entire study period. However, it should be recognized that the method would tend to underestimate attribution to the Carbon plants for reasons explained previously. The cumulative frequency distribution of TAGIT particulate S attribution for each site is shown in Figure 4. This includes only those sampling periods where the site had tracer significantly above background, at least one site had tracer at background levels, and valid particulate S data were available. Although tracer release started July 5, the particulate sampling did not begin until approximately July 22 at the 6-hr sites.

It can be seen that many values are below 0. It is also apparent that the frequency distribution among sites is similar, except for San Vicente, which did not have any large negative attributions. Table 2 summarizes the results for each site and the average for the five sites. Over all sites, the average attribution of particulate S was 80 ng/m^3, with a standard error of the mean of 26 ng/m^3. On average, 8.4% of the particulate S was attributed for periods with elevated tracer concentrations (35% of all periods).

The TAGIT analysis was also performed for SO_2. The average SO_2 attributed (all sites) for periods with tracer above background was 350 ± 144 ng/m^3 out of an average SO_2 concentration of 1293 ng/m^3. Thus, 27 ± 11% of the SO_2 was attributed for the impact periods. For total S (particulate and SO_2 S), an average of 258 ± 90 ng/m^3 of S out of an average of 1579 ng/m^3 S was attributed by TAGIT. This is 16 ± 6% of the total S for periods of elevated tracer.

DISCUSSION

The method does not attribute substantial fractions of the particulate S to the Carbon plants. Considering that the tracer is above background on average approximately 35% of the 6-hr periods and that the attributed particulate S during these periods is only approximately 8% of the total measured particulate S, then an estimate of study period particulate S attributed by TAGIT is only approximately 3%. However, as mentioned previously, because the Carbon and tracer emissions were not collocated, the method systematically underestimates the impact from the Carbon plants. While significant SO_2 gradients exist across the area, and average values are higher where average ocPDCH is higher, the particulate S is more regional in nature, as indicated by the correlation matrices shown in Tables 3–5. This suggests that much of the SO_2 from the Carbon plants has not been converted to particulate S before arriving at the sampling sites. Tracer data showed that the most common transport time from Eagle Pass to the monitoring sites is on the order of 15–18 hr.[8,9] Except for periods with in-cloud conversion, not more than approximately 20% of the SO_2 is likely to convert, based on an assumed conversion of 2%/hr for 12 daytime transport hours. Wilson and McMurry[10] calculated a conversion rate of 1.9 ± 0.8%/hr for another power plant in a desert environment, the Navajo Generating Station in Arizona,

Table 7. Use of TAGIT SO_2 method for attribution of SO_2 S (SO_2/2).

	BIBE	FTST	MARA	PRSG	SNVI	ALL
Average Attribution (ng/m^3)	273 ± 38	518 ± 40	434 ± 39	531 ± 53	179 ± 29	397 ± 19
% of SO_2 S	68 ± 10	76 ± 6	76 ± 7	79 ± 8	61 ± 10	75 ± 4

Table 8. Use of TAGIT SO_2 method for attribution of total S.

	BIBE	FTST	MARA	PRSG	SNVI	ALL
Average Attribution (ng/m^3)	408 ± 50	556 ± 51	529 ± 52	669 ± 65	221 ± 41	488 ± 24
% of total S	31 ± 4	36 ± 3	35 ± 3	40 ± 4	19 ± 3	33 ± 2

at noon in July. A diurnal average of 0.9 ± 0.4%/hr was calculated.

It is also worth noting that the analysis did attribute approximately 27% of the SO_2, on the average, compared with 8% of the particulate S. Because the Carbon plants are the largest in the area, the 27% may be low; however there are other smaller nearby SO_2 sources in the area that may be contributing significantly to SO_2 at individual sites during some sample periods. The TAGIT attribution of SO_2 to Carbon is underestimated for the same reason as the particulate S attribution because of the horizontal and vertical displacement of the Carbon emissions and the oPDCH release.

To assess the reasonableness of the TAGIT attribution of total S from the Carbon I and II power plants, the maximum total S possible from the Carbon plants was estimated from the measured tracer concentration. This is done by multiplying the tracer-derived dispersion factors by the assumed emissions rate of SO_2 from the plants (240,000 t/yr) and assumes no loss by deposition of S emitted from the plants. By this method, the site-averaged maximum percent of total S that could be attributed to the power plants for periods when there are tracer, SO_2, and particulate S is shown here for each site.

BIBE	FTST	MARA	PRSG	SNVI	Average
33%	70%	58%	56%	50%	54%

The average maximum possible impact of 54% of total S is in contrast with the TAGIT analysis, which suggests an attribution of approximately 6% of total S over the study period (16% when impacted by 35% frequency of impact). Of course, the real impact would be considerably less than the tracer-predicted maximum because of dry and wet deposition of SO_2 and particulate S. If half of the total S is removed via deposition, that would still leave approximately 27% of the total S caused by the power plants, based on this analysis, still far higher than the TAGIT results. It is quite possible that the nominal emission rates used for the Carbon plants are too high; this would cause the tracer maximum total S estimates to be too high. For periods with high SO_2, most of the SO_2 might be expected to come from the Carbon plants.

Figure 5 shows the cumulative frequency distribution of measured SO_2 and tracer-derived SO_2. Also shown is the SO_2 concentration minus an estimated background SO_2 concentration (the lowest of the SO_2 values at the five sites). It can be seen that the ocPDCH SO_2 is approximately twice the measured SO_2 at the higher percentile ranges. It is also approximately twice at lower percentile ranges if the background is subtracted out. Although there would certainly be some deposition of SO_2 between the source and receptor, as well as some conversion of SO_2 to particulate S, loss of one-half over a typical 15–18 hr transport time seems excessive. It is possible for dispersion factors for the power plant emissions to be greater than those for the tower release from Eagle Pass, but it seems unlikely that they would be a factor of 2 higher over the approximately 270 km transport distances. This suggests

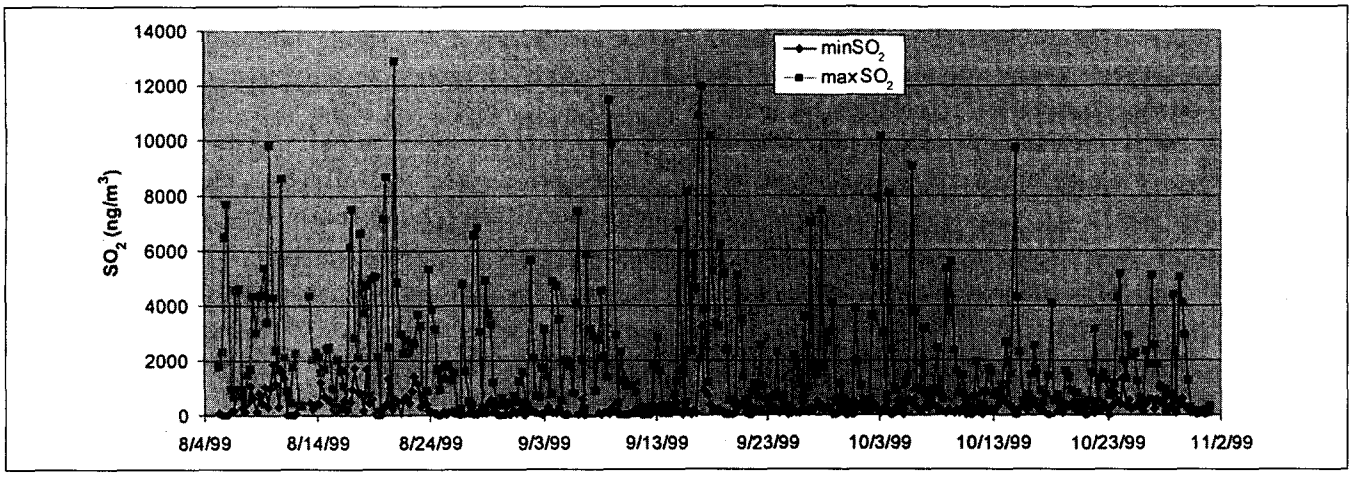

Figure 6. Maximum and minimum SO_2 at 6-hr sites (excepting Monahans).

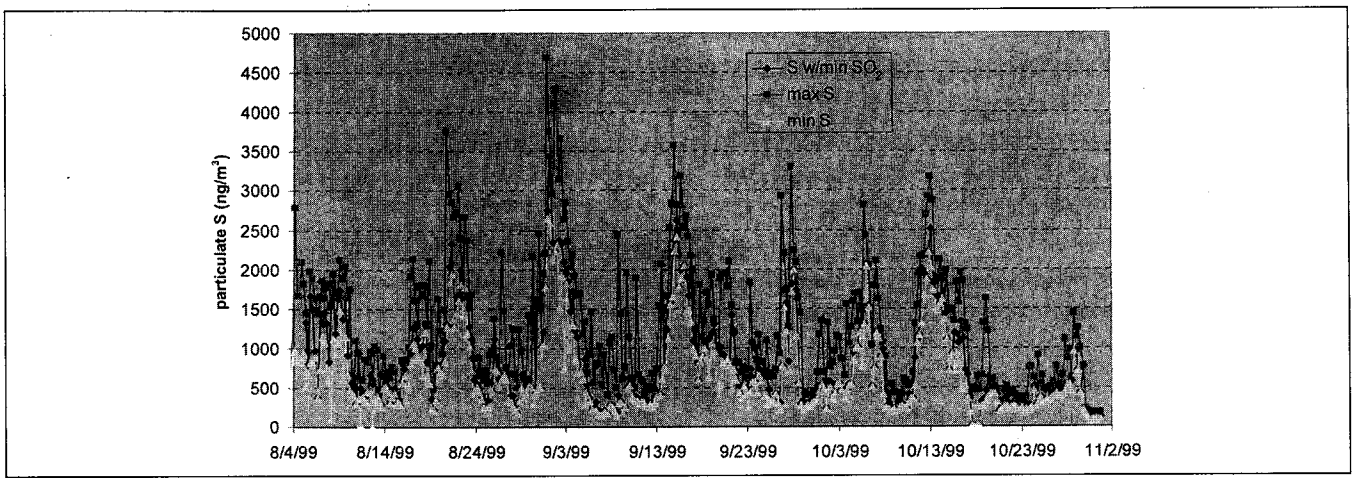

Figure 7. Maximum and minimum particulate S, and particulate S at site with lowest SO_2 (designated background site).

that the emissions estimate of 240,000 t/yr from the Carbon power plants is too high, at least for the study period. For this estimate, it was assumed that local coal is used to fuel the plants. The plants actually use a mixture of local coal and lower S, higher energy content coal from Wyoming that results in lower SO_2 emissions. Recent information obtained from the government of Mexico (Secretaria de Energia) reports the average SO_2 emission rate for the Carbon plants as 152,000 t/yr, which is more consistent with this analysis.

Use of SO_2 as a Tracer

Because the ocPDCH was not released from the Carbon power plants, elevated concentrations of SO_2 may be a better indicator of the Carbon emissions. A TAGIT-type analysis was done using SO_2 instead of ocPDCH for the same five monitoring sites. A difficulty lies in the definition of a background SO_2 value. The Carbon plume is not likely to be impacting all five sites simultaneously very often; this assumption is supported by the occurrence of elevated tracer at all five sites simultaneously for only five 6-hour periods. The site with the lowest SO_2 was defined as the background site. The particulate S for this site was then set as the background particulate S and attribution was determined by subtracting this background from the particulate S at each of the other sites. The results are shown in Table 6. Tables 7 and 8 show the attribution of SO_2 S (SO_2 concentration multiplied by the molecular weight of S divided by the molecular weight of SO_2, which is $SO_2 \times 32/64$ or $SO_2/2$) and total S.

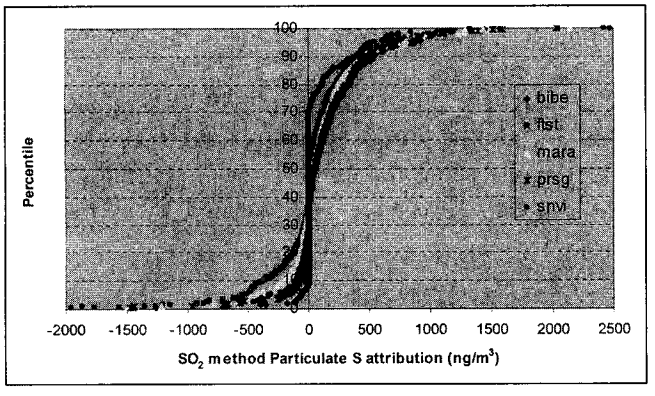

Figure 8. Cumulative frequency distribution of particulate S attribution at each site from the TAGIT SO_2 method.

Table 6 indicates an average attribution over all sampling periods of approximately 10% for particulate S. This indicates higher attribution than the tracer attribution method average of 8.4% for the 35% of sampling periods with elevated tracer concentrations (see Table 2). Table 7 shows that most of the SO_2 is attributed, averaging 75%, while Table 8 shows that 33% of the total S is attributed. The high percentages for SO_2 attribution demonstrate SO_2 concentrations are not regionally uniform. The 75% average attribution means that, on average, the concentration at the lowest site is one-fourth of the concentration averaged over the other sites.

Figure 6 is a time series plot of the lowest and highest 6-hr averaged SO_2 at the five sites. Figure 6 shows that there is nearly always a large difference between the highest and lowest SO_2 concentrations. Figure 7 is a time plot of the particulate S for the highest site, the site with lowest SO_2 (used as background), and the lowest site. Figure 7 shows that there is less difference between the particulate S concentrations than the SO_2 concentrations; during the major episodes, all sites have elevated concentrations.

Figure 8 shows the cumulative frequency distribution of particulate S attribution at each site. San Vicente had many 0 values for attribution because it often served as the background site. Figure 9 is a time series plot comparing attributed particulate S and total particulate S at the

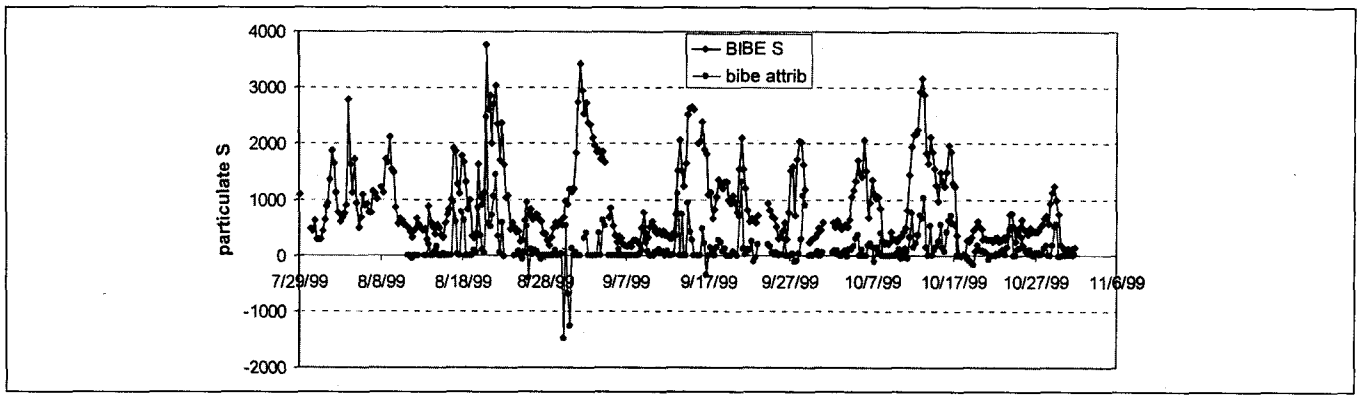

Figure 9. Time series plot of particulate S attribution by TAGIT using SO_2 and total particulate S at BIBE.

BIBE site in Big Bend National Park. The plot shows that the attributed particulate S is usually much less than the total but is sometimes a significant portion of the total, such as for the episodes near August 20 and October 12.

The use of SO_2 for attribution may be considered to represent attribution from all subregional scale sources, so it tends to set an upper limit to the contributions from the Carbon power plants. It is possible that the designated background site for SO_2 could have been impacted from Carbon and had low SO_2 because of high conversion to particulate S in clouds, and so on. This would give a high particulate S background concentration that would then be subtracted from the concentrations measured at the other sites. This is not expected to be a concern, because if impacts were high from Carbon, we would still expect to see significant SO_2 and would not expect to see near-complete conversion at one site and not at the others. Also, simultaneous impacts of SO_2 from Carbon at all sites cannot be ruled out, although, as discussed previously, the tracer data indicate that this is rare. Also, the typically large difference between the lowest and average SO_2 concentration among sites usually indicates that one or more sites has low SO_2 concentrations and thus is not likely to be significantly impacted by the Carbon plants.

CONCLUSIONS

The Carbon power plants were significant contributors to SO_2 concentrations during the 4-month BRAVO Study, but contributed a small fraction of the particulate S at the five 6-hr sites in and around Big Bend National Park. Average contributions to particulate S range from approximately 3% using the ocPDCH tracer (8% when tracer is significantly above background) to approximatley 10% using the SO_2 method (all periods). The TAGIT tracer method probably underestimates Carbon impacts, while the TAGIT SO_2 method probably overestimates Carbon impacts. SO_2 attribution ranges from 27% when tracer is above background (35% of samples) using the tracer method to 75% using the SO_2 method (all periods). Again, the TAGIT tracer method underestimates and the TAGIT SO_2 method overestimates Carbon impacts.

Sulfur was segregated into local and regional components, gaseous and particulate. Local is defined as TAGIT-attributed; regional is the remainder. From the partitioned regional and local particulate and gaseous concentrations, it is simple to calculate the particulate fraction of local and regional S. The particulate fraction of local S is $S_{Lp}/(S_{Lp} + S_{Lg})$ where S = sulfur, l = local, p = particulate, and g = gas. Similarly, the particulate fraction of regional S is $S_{Rp}/(S_{Rp} + S_{Rg})$, where r = regional. For the TAGIT tracer method, the particulate fraction of local S is 31% and the particulate fraction of regional S is 65%. For the TAGIT SO_2 method, 19% of the local and 86% of the regional S is particulate. Because the tracer was not injected into the Carbon stack, the regional SO_2 and particulate S is overestimated using the tracer method, but the SO_2 is overestimated more so because of relatively low conversion. As a consequence, the regional particulate S fraction of 65% using the tracer method is underestimated. Thus, most of the regional (65–86%) but a relatively small fraction (19–31%) of the local SO_2 has been converted to particulate form.

A general conclusion is that sources on a relatively large spatial scale need to be considered because local sources (i.e., including the Carbon power plants) contribute a relatively minor amount of the particulate S. However, for some short time periods, a significant fraction of the particulate S is attributable to local sources. Another significant finding is that, based upon the tracer and SO_2 data, it appears that the Carbon power plant SO_2 emissions initially assumed are overestimated, by up to a factor of 2.

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