

# **Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study Results: Air Quality Data and Source Attribution Analyses Results from the National Park Service / Cooperative Institute for Research in the Atmosphere**

## **Executive Summary**

Big Bend National Park is located in southwestern Texas along the Mexican-Texas border (Figure 1). During the 1990s, the haze at Big Bend and other sites in West Texas and southern New Mexico increased, further obscuring Big Bend's and regions scenic beauty. In response to the increased haze, the Big Bend Regional Aerosol and Visibility Observational (BRAVO) study was conducted. This was an intensive monitoring study sampling aerosol physical, chemical and optical properties, as well atmospheric dispersion using synthetic tracers from July–October 1999. The monitoring was followed by a multi-year assessment of the causes of haze in Big Bend National Park, Texas, with the primary purpose to identify the source regions and source types responsible for the haze at Big Bend. Secondary research objectives of the study were to learn more about the chemical, physical, and optical properties of aerosols responsible for haze. BRAVO study participants include the National Park Service (NPS), the U.S. Environmental Protection Agency (EPA), the Texas Commission on Environmental Quality (TCEQ), and the Electric Power Research Institute (EPRI), among others.

In support of BRAVO, the NPS and Cooperative Institute for Research in the Atmosphere (CIRA) at CSU analyzed the measured aerosol data to better understand the chemical, physical, and optical properties of Big Bend's haze, and conducted a number of complementary qualitative and quantitative haze source apportionment analyses. All source apportionment techniques went through extensive validation and evaluation tests and only those techniques which passed these tests were applied to Big Bend's haze. In addition to the analysis of the BRAVO study data, long-term Big Bend air quality and meteorological data were analyzed to determine the representativeness of the BRAVO time period to other seasons and years.

This Executive Summary summarizes the key findings from the analyses and their implications concerning Big Bend's haze with a focus on the apportionment of particulate sulfate and its contribution to Big Bend's haze. The body of this technical report provides detailed descriptions of the methods, evaluation and validation procedures and results from the multiple analyses employed by the NPS/CIRA group and the reconciliation between all source attribution techniques.

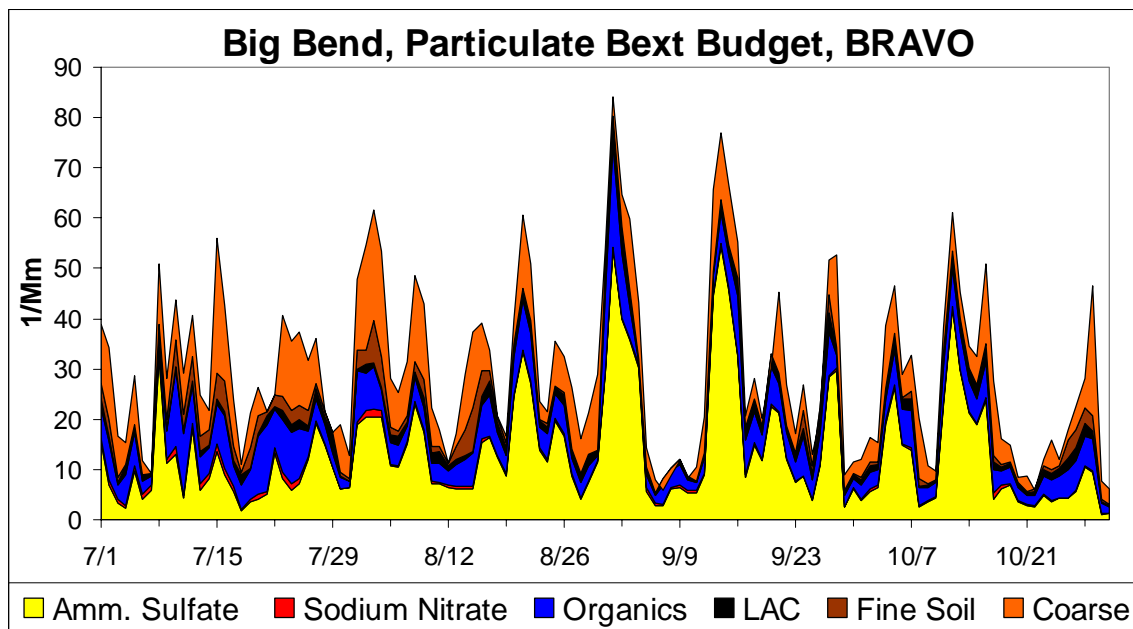


Figure 1. A terrain map of Texas and Mexico as well as some major cities and points of interest to the BRAVO study.

### Characterization of Big Bend’s Haze

Haze is caused by scattering and absorption of light by suspended fine liquid or solid particles in ambient air, known collectively as atmospheric aerosol. The sum of the light scattering and absorption is known as the light extinction and can be thought of as the fraction of light lost per unit of distance. The units of light extinction are inverse distance, e.g., 1/(million meters) or  $\text{Mm}^{-1}$ . Higher light extinction levels correspond to hazier conditions.

Detailed particle size and chemical composition measurements made at Big Bend during the BRAVO study were used to develop advanced estimates for each day’s contributions to light extinction by the major aerosol components. These compare well to direct optical measurements of light scattering and light extinction. Figure 2 shows the daily particulate light extinction (sum of light scattering and absorption) contributions by the major aerosol components. As shown, there is a distinct difference in the particulate extinction budget in the first and second half of the BRAVO study. From July 1–August 15, the light extinction is primarily due to ammoniated sulfates (35%), organics (20%), and coarse mass (30%). In the second half of the study, post-August 15, the ammoniated sulfates account for 50% of the particulate extinction while organics and coarse mass each account for about 20%. On the haziest 1/5<sup>th</sup> of the days, sulfate compounds accounted for about 55% of the particulate  $b_{\text{ext}}$  and organics 15%.

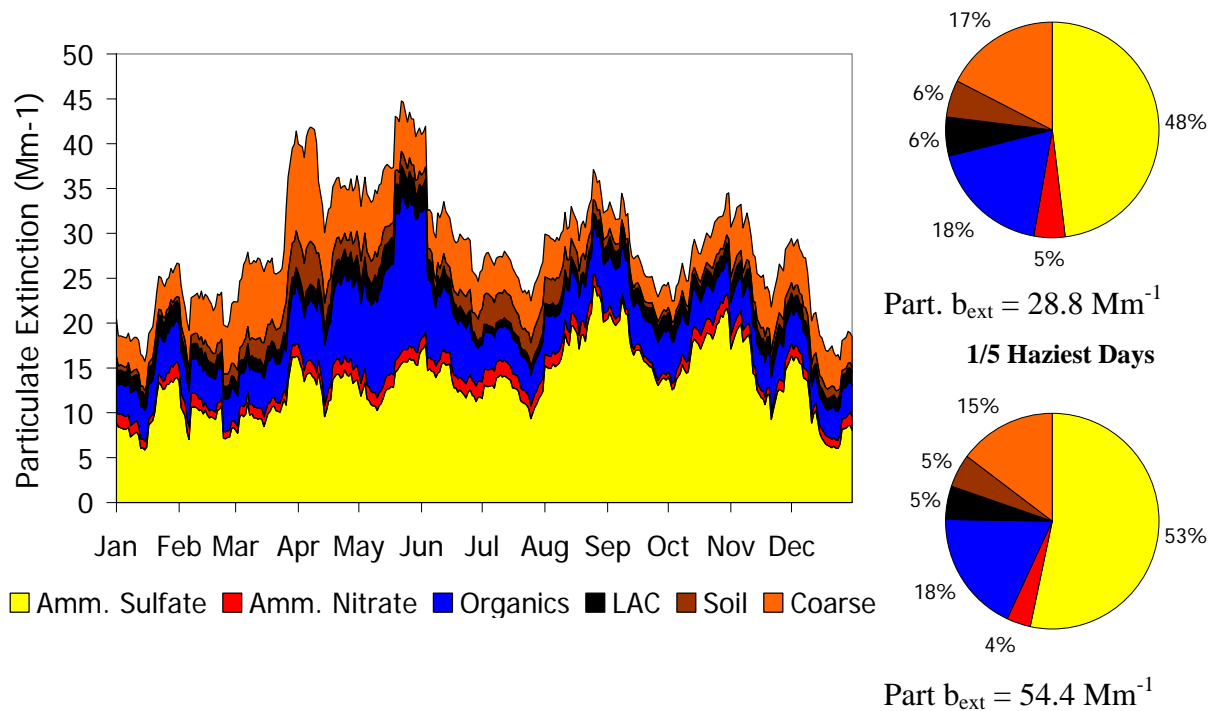


**Figure 2. Big Bend’s particulate light extinction budget during BRAVO.**

The BRAVO period can be put into a larger climatological context by examining Big Bend’s extinction budget over a long time period. Figure 3 shows the five-year (1998 through 2002) light extinction budget from measurements made every three days at Big Bend National Park in the IMPROVE monitoring network. In general, there are two periods of high haze at Big Bend National Park – one in spring when particulate sulfate and carbonaceous compounds contribute in similar amounts to haze and another in late-summer/fall when particulate sulfate compounds are the largest contributors to haze. Similar to the BRAVO period, the particulate sulfate compounds usually contribute more to haze than any other individual aerosol component. Carbonaceous particulate matter – organic compounds and light absorbing carbon (LAC) – generally constitute the second largest individual aerosol component contributing to haze at Big Bend NP and on some days are the single largest contributor to haze. Information from other studies shows that during late spring episodes, concentrations of carbonaceous compounds are increased due to biomass burning in Mexico and Central America. Dust, represented by a combination of fine soil and coarse mass, contributes as much to haze as particulate sulfate compounds during the months of March and April.

On average, sulfate compounds contribute more to light extinction on the haziest days (53%) than for average days (48%). The contribution of carbonaceous (i.e., organic and light absorbing carbon) compounds to light extinction remained the about the same at 23% on average and the haziest days. The coarse mass is also a major contributor to the particulate light extinction accounting for about 17% of the particulate light extinction on average and 15% on the haziest days. Since the sulfates accounted for more than half of the particulate extinction on the highest haze days, the lower contribution of organics and the fact that they have a potentially large contribution from smoke and other natural sources lead us to concentrate on understanding the source attribution of sulfate.

## Big Bend Extinction Budget (1998-2002)

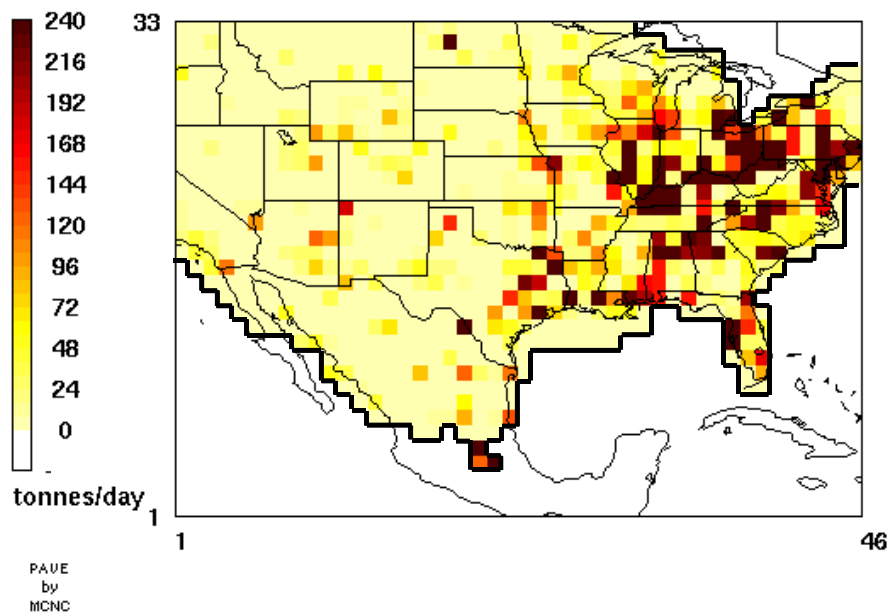


**Figure 3. Big Bend National Park five-year light extinction budget. All days with that fall on the same day of the year were averaged together, then the data were smoothed using a 15-day moving average.**

### Apportionment of Big Bend's Sulfate Haze

Ambient particulate sulfate compounds result from direct emissions of sulfate (primary sulfate) or are produced by chemical transformation (oxidation) of  $\text{SO}_2$  emissions in the atmosphere (secondary sulfate). Secondary sulfates constitute most of the particulate sulfate compounds measured at ambient monitoring sites, such as Big Bend National Park. The extent of the oxidation of  $\text{SO}_2$  to secondary sulfate depends on the oxidative capacity of the atmosphere, which is influenced in large part by nitrogen oxides ( $\text{NO}_x$ ) and volatile organic carbon emissions. Oxidation of  $\text{SO}_2$  to sulfate can be slow, often requiring one to two days to convert about half of the  $\text{SO}_2$  to particulate sulfate compounds. However, this extent of transformation can occur much more rapidly, from a few hours to several minutes, in the presence of mists, fogs, and clouds. Meanwhile, atmospheric dispersion and deposition processes are reducing the ambient  $\text{SO}_2$  and sulfate concentrations during transport from emission sources to distant monitoring locations. Consequently, it is typically challenging to establish causal relationships between measured ambient particulate sulfate concentrations and  $\text{SO}_2$  emissions sources.

## 1999 BRAVO SO<sub>2</sub> Emissions Inventory



**Figure 4. (Left) SO<sub>2</sub> emissions based on the 1999 BRAVO emissions inventory used in the REMSAD and CMAQ-MADRID modeling. No emissions were included beyond the black outline shown in the figure. Mexico City and Popocatepetl volcano emissions are located in the three most southern emission grid cells.**

Figure 4 presents the SO<sub>2</sub> emission inventory used in the BRAVO study. As noted on the map the BRAVO study emission inventory did not include sources in southern Mexico (except for Mexico City and the Popocatepetl volcano), Cuba, or other Caribbean islands. Effects of sources outside of the modeling domain, beyond the frames of Figure 4, were accounted for in BRAVO study modeling by use of four-month average boundary conditions obtained from global model simulations. The largest SO<sub>2</sub> emissions are in the eastern U.S. where about 14 million tonnes /year are emitted. In Texas approximately 1 million tonnes of SO<sub>2</sub> are emitted each year, almost all in eastern Texas, and the western U.S. emissions are about 1.7 million tonnes /year. In Mexico, SO<sub>2</sub> emissions are estimated to be about 2.5 million tonnes /year with 1.5 million tonnes/year from the Popocatepetl volcano. There are a few high emitting locations in northern Mexico, including the Carbón I & II coal-fired power plants located about 200 km east-southeast of Big Bend and at urban and industrial areas near Monterrey in northeastern Mexico.

U.S. SO<sub>2</sub> emission inventories have been in development for over 30 years and in the 1990s continuous emission monitors were placed into the largest SO<sub>2</sub> point sources. Therefore the U.S. SO<sub>2</sub> emission inventory is considered to be of a high quality. However, less information was available about the Mexican SO<sub>2</sub> emissions and significant uncertainties in the inventory remain. For example, a recently produced emission inventory for Mexico differs from the BRAVO emissions inventory for SO<sub>2</sub> emissions, with emissions by as much as a factor of two larger in some regions. In addition, uncertainties in Carbón SO<sub>2</sub> emissions exist and emissions of 154,000 and 245,000 tonnes/year were used.

The Popocatepetl volcano in central Mexico near Mexico City has been active for a number of years including during the BRAVO study period and is the largest single SO<sub>2</sub> emissions source in North America. Limited modeling of the flow of its emissions indicated that it likely had little effect on Big Bend haze during the BRAVO study period. The effects of emissions from southern Mexico, Cuba, and other areas outside of the BRAVO study emissions inventory are also thought to be small at Big Bend.

### **Spatial Patterns of Aerosol Components**

Examination of the spatial and temporal patterns in several fine particulate species, including sulfate, measured during BRAVO suggests that there are unique sources for different aerosol types and that transport patterns are seasonal with more transport from Mexico to southern Texas during the summer than during the fall and conversely more transport from the eastern U.S. during the fall than during the summer. These findings are consistent with the back trajectory analyses. Sulfate concentrations at Big Bend were highest during four episodes, September 1 and 2, 14 and 15, October 12, and August 22. The four episodes were characterized by different trace element concentrations and different spatial patterns in sulfate indicating differing contributions from different source types for each episode. Sulfate concentrations measured within a few hundred km are generally highly correlated in time, but measurements in southwestern Texas were not highly correlated with measurements in northeast Texas, and different regions of the state also had different seasonal patterns in sulfate concentrations indicating they are influenced by different sources. Highest sulfate concentrations measured during BRAVO were in northeast Texas during the summer while highest concentrations at Big Bend were during the fall. Spatial patterns in sulfate concentrations show influence from the Carbón I & II power plants, especially north and west of the plants, though the contribution is not quantifiable by these analyses.

Spatial and temporal patterns in the iron concentrations and the abrupt drop in Al/Ca ratios from summer to fall are evidence of Saharan dust episodes during the summer.

The trace element most associated with sulfur at Big Bend is selenium which is usually associated with coal combustion. Selenium concentrations were highest in northeast Texas with evidence of selenium sources within the state, at the Carbón I & II plants, and possibly entering Texas from the east.

### **Airmass Transport to Big Bend during BRAVO Days with High and Low Particulate Sulfate Concentrations**

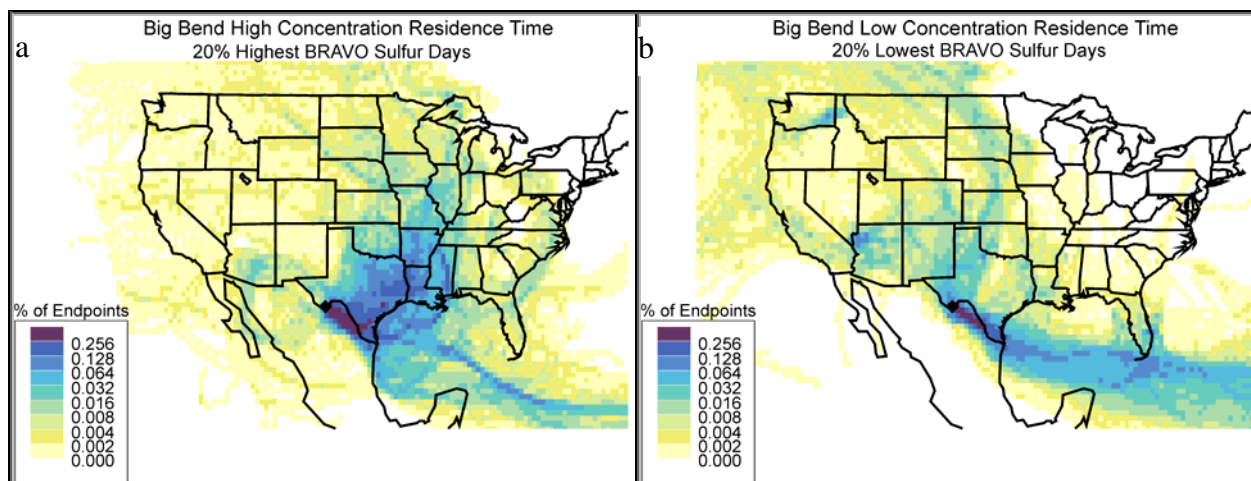
All other things being the same, a source region's potential to contribute to haze at Big Bend increases for time periods when air parcels frequently pass over and spend more time over the source region prior to transport to Big Bend. These airmass transport characteristics can be estimated from trajectories, where a trajectory gives the estimated location of air parcels every hour prior to their being transported to Big Bend. Residence time analysis is used to aggregate the number of air parcels that resided over an area for selected periods of time at Big Bend (e.g., a month) or selected receptor site conditions (e.g., haziest days at Big Bend). This is related to the aggregate of time all trajectories resided over a given area. While the residence time is dependent on airmass transport frequency from a given region to Big Bend and the time it spends over the region, it has been shown that the difference in the residence time from one region to another is primarily dependent on different transport frequencies.



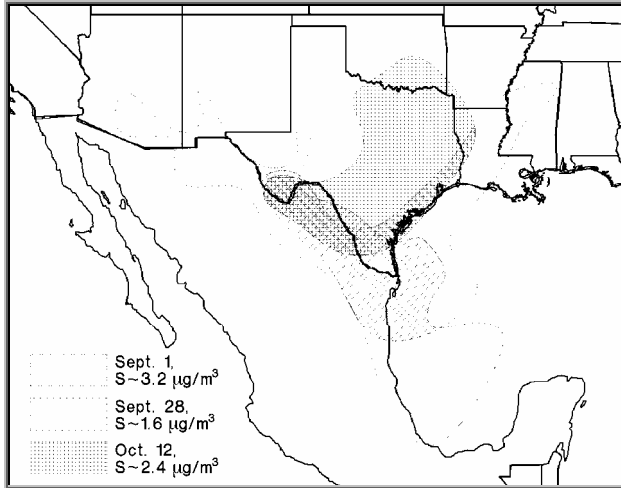
On days with the 20% highest particulate sulfur concentrations during the BRAVO study, air parcels were most likely to have previously resided over northern Mexico, Texas, and the eastern U.S. (Figure 5a). These tended to be low level and low speed air parcels which are conducive to the accumulation of pollutants from sources. In contrast, on days with the 20% lowest particulate sulfate concentrations, air parcels were most often previously over northern Mexico and the Gulf of Mexico as well as over the western U.S. and infrequently over eastern Texas or the eastern U.S. (Figure 5b). The transport over Mexico tended to be low level but high speed which is not conducive to the accumulation of emissions into the air parcels.

The examination of transport pathways during individual particulate sulfate episodes showed that there were three common pathways associated with elevated sulfate at Big Bend, from eastern Texas, the southeastern U.S., and northeastern Mexico (Figure 6). The largest concentrations occurred when transport over several of these regions occurred. For example, the September 1 episode had transport over all three regions and had the highest concentrations during the BRAVO study. Elevated sulfate was also associated with prior transport over the Midwest (Missouri, Kentucky, and Tennessee), though this was infrequent and airmasses tended to be elevated and had higher speeds relative to the other three regions.

These results show that the transport from eastern Texas and the southeastern U.S. is associated with elevated sulfate concentrations at Big Bend and is not associated with low sulfate concentrations. These results, combined with the fact that eastern Texas and the Southeast have high sulfur dioxide emissions, support the notion that these areas contribute to the sulfate concentrations and haze at Big Bend. Northeastern Mexico appears to be a common transport pathway during both high and low sulfate days. However, the time airmasses spend over northern Mexico prior to reaching Big Bend is greater on the high sulfate days than the low sulfate days. The increased time allows for potentially greater accumulation of SO<sub>2</sub> emissions and time for transformation to sulfate.



**Figure 5. Fraction of time that air parcels spent during ten-day trajectories for periods with the a) 20% highest concentrations of particulate sulfate compounds and b) for the periods with the 20% lowest concentrations of particulate sulfate during the BRAVO study period July through October 1999.**



**Figure 6. Airmass transport patterns to Big Bend, TX, during three sulfate episodes. Each isopleth shows the most likely pathway the air mass traversed prior to impacting Big Bend.**

### **Quantitative Source Apportionment of Big Bend’s Sulfate Haze**

NPS/CIRA employed numerous methods to identify the source types (e.g., power plants) or source regions (e.g., Texas, the eastern U.S., the western U.S., and Mexico) that contribute to the particulate sulfate compounds that influence Big Bend haze and to estimate the magnitude of their contributions. The techniques fall into three categories, receptor-oriented modeling, source-oriented modeling and hybrid modeling combining features from both source and receptor modeling.

**Airmass History Based Receptor Models:** Several airmass history based receptor analysis methods were used for source attribution. These methods developed statistical relationships between the Big Bend particulate sulfate concentrations and airflow prior to reaching Big Bend. Variations of the trajectory methods included the use of two methods of estimating wind over North America (EDAS from the National Weather Service and MM5 applied specifically for the BRAVO study) and the use of back-trajectories from Big Bend employed in Trajectory Mass Balance (TrMB), and forward transport and dispersion from all potential source regions used in Forward Mass Balance Regression (FMBR).

Extensive testing of TrMB and FMBR applied to both sets of wind information showed adequate overall performance when used to attribute artificial tracer released as part of the BRAVO study. Additional evaluations showed that these airmass history regression models were accurate within their stated precision when applied to synthetic sulfate concentration with known attribution results. Only the combination of airmass history model and meteorological data inputs that passed these evaluations was used for attribution of measured sulfate.

An inherent characteristic of these techniques is the estimation of the average relationship between air transport from an area and that area’s contribution to sulfate. Therefore, these techniques were used only for estimating average attributions. These techniques are subjected to increased uncertainties due to collinearity of transport from multiple source regions. For example, transport from the eastern U.S. typically traversed Texas in route to Big Bend. In addition, other issues can bias the results. For example, it was found that FMBR tended to enhance attributions to nearby source regions and reduced attribution from more distant source regions.



**Regional Air Quality Source Oriented Models:** The REMSAD regional air quality model was used to estimate the effects of transport, dispersion, chemical transformation, and deposition on emissions, and thereby to predict particulate sulfate concentrations throughout the modeling domain, including at Big Bend. The difference in predicted concentrations between air quality model prediction with all emissions (base case) and those with emissions for a specific source or source region set to zero (emissions sensitivity case) is interpreted as the particulate sulfate attributed to the specific source or source region. The CMAQ-MADRID air quality model was also operated by EPRI and Atmospheric and Environmental Research (AER).

Eulerian air quality models are limited by the soundness of emissions and meteorological data, as well as the accuracy of transformation, deposition, dispersion, and other numerical algorithms. Biases and uncertainties identified in any of these processes can adversely affect their source attribution estimates. The Eulerian models were tested against the BRAVO tracer data to evaluate their capability of simulating dispersion in Texas where it was found that they could reproduce the tracer concentrations within the inherent uncertainty of the tracer data. Also, the simulated sulfate and SO<sub>2</sub> concentrations and sulfate apportionments were extensively compared to measured data. It was found that both models tended to underestimate particulate sulfate compound concentrations in the first half of the BRAVO study period when sources in Mexico were determined to have the largest contribution. Both models also tended to overestimate particulate sulfate concentrations when flow was from the eastern U.S.

**Hybrid Modeling - Synthesis Inversion Analysis of Air Quality Models:** Concerns about possible systematic biases that could be the result of Mexico's SO<sub>2</sub> emissions and/or transformation chemistry biases resulted in the development of a hybrid modeling approach. This approach entailed the development of statistical relationships between the daily source attribution results from REMSAD and CMAQ-MADRID and the measured particulate sulfate concentrations in and around Big Bend.

The synthesis inversion technique was unable to resolve distant source regions with small source contributions. To minimize problems caused by this behavior, attribution results for these sources were held close to their originally modeled values. Thus, any sulfate that may have been improperly attributed to small distant sources by the Eulerian models runs was most likely attributed to source regions near Big Bend in the synthesized method. The technique also systematically underestimated the measured sulfate data. It is not known if this underestimation impacts one source region more than another.

It was determined that Synthesized CMAQ-MADRID combined with the attribution of Carbón power plants from Synthesized REMSAD provided the best available estimates of the source attribution for particulate sulfate at Big Bend during the BRAVO study period, henceforth referred to as the BRAVO Estimate.

Figure 7 shows the study period-averaged attribution results for nine methods as well as the BRAVO Estimate results. CMAQ-MADRID and Synthesized CMAQ-MADRID attribution did not include the Carbón power plants. TAGIT was a source attribution technique employed by the Desert Research Institute (DRI) to attribute Carbón power plants' contribution to Big Bend's sulfate.

As shown in Figure 7, during the BRAVO study period U.S. sources contributed to about 55% (BRAVO Estimate) of the particulate sulfate at Big Bend, with a range among methods of 44% to 67%. The Mexico sources contributed about 38% of Big Bend's particulate sulfate, with

a range among methods of 23% to 55%. The eastern U.S. was the largest U.S. contributor at ~30%, followed by Texas at ~17% and the western U.S. at ~9%, with ranges among the methods of 16% to 42%, 16% to 30%, and 0% to 14%, respectively. The Carbón power plants in Mexico contributed to about 20% of the particulate sulfate at Big Bend, more than any other single SO<sub>2</sub> emissions facility, with a range among the methods of 14% to 26%.

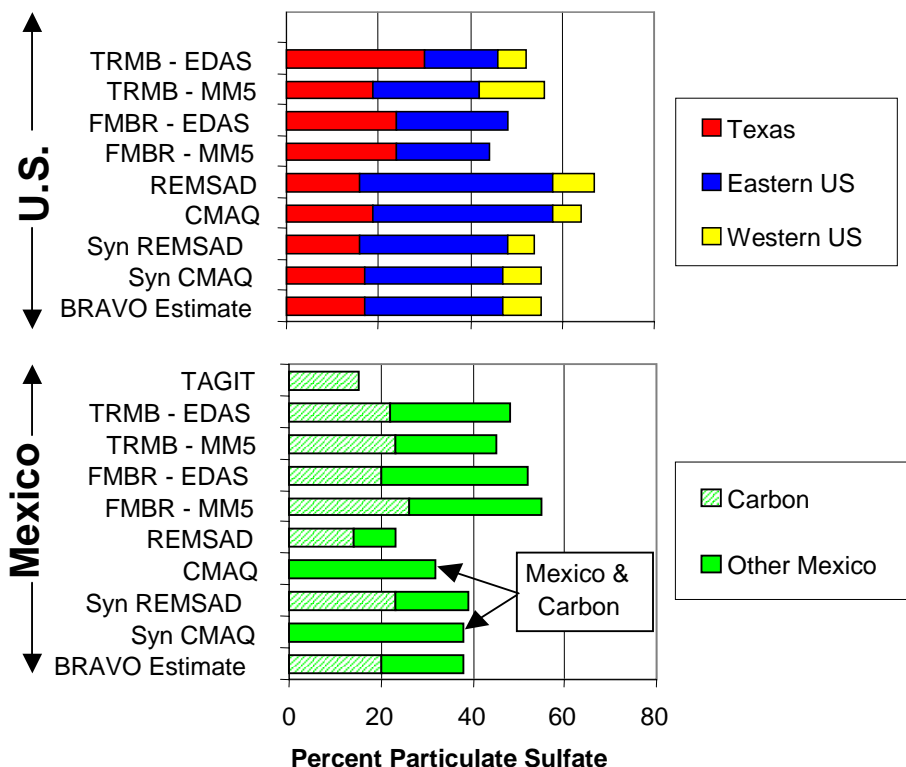
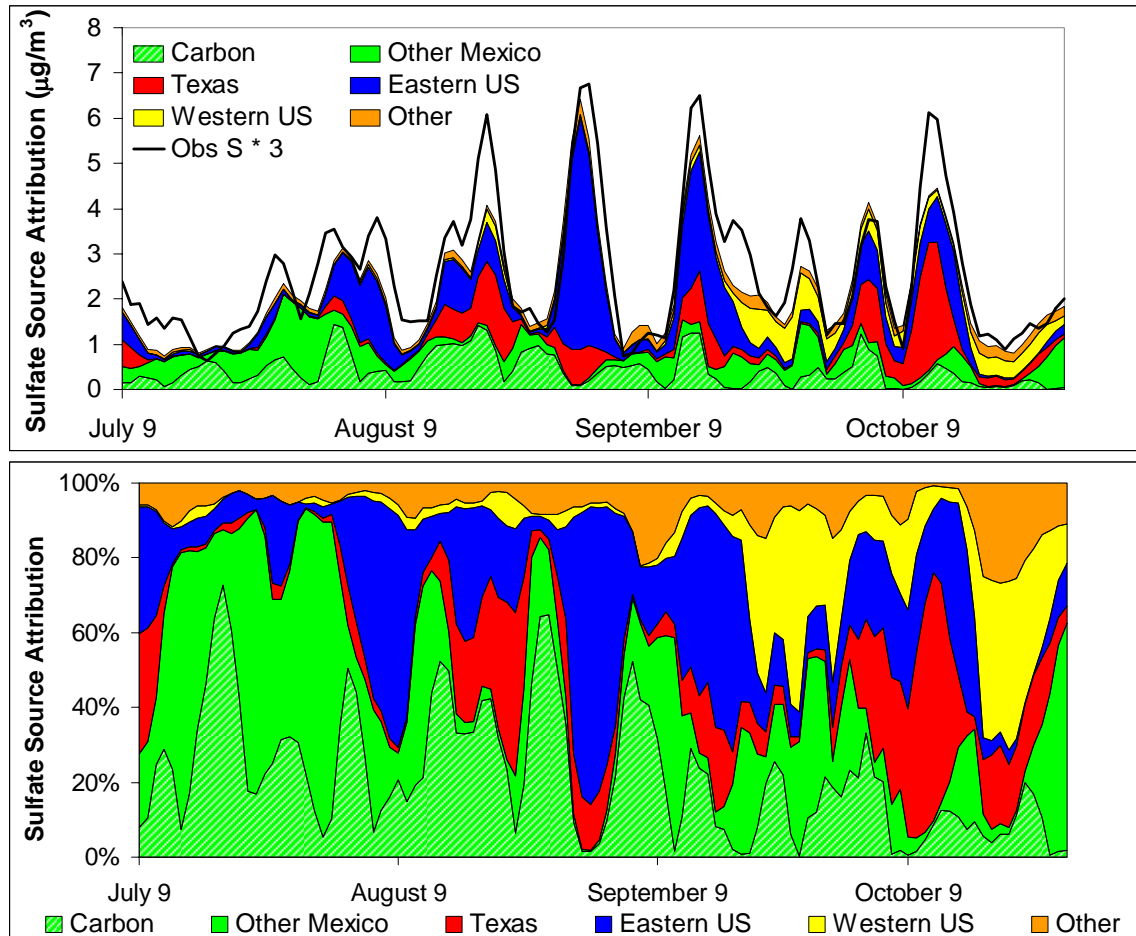


Figure 7. Estimates by several data analysis and modeling methods of the study-period averaged percent contributions to particulate sulfate at Big Bend by U.S. and Mexico sources. TAGIT only attributed the Carbón power plants, while CMAQ and Synthesized CMAQ attribution did not distinguish Carbón from Mexico.

Figure 8 presents a smoothed daily attribution using the BRAVO Estimate method. The top plot in Figure 8 shows attribution in absolute concentrations for direct comparison to the measured particulate sulfate concentrations, while the bottom plot shows the percent fraction of the predicted amount by each source region. As shown, each source region's contribution to Big Bend particulate sulfate had unique characteristics over the BRAVO study period. Sources in Mexico were the largest contributors to sulfate in July and August, contributing from 0.5 to 1.5  $\mu\text{g}/\text{m}^3$  every day. During the largest peak in late July, sources in Mexico contributed to about 2  $\mu\text{g}/\text{m}^3$ , constituting about 90% of the modeled particulate sulfate. In September and October contributions by sources in Mexico decreased to roughly less than 1  $\mu\text{g}/\text{m}^3$ . Sources in Texas contributed very little to sulfate concentrations in July, with three episodes in the middle months of the study period having peak values from about 0.8 to 1.5  $\mu\text{g}/\text{m}^3$ . During two episodes in October, sources in Texas had peak contributions of about 1.2 to 2.8  $\mu\text{g}/\text{m}^3$  of particulate sulfate and constituted to over 60% of the largest peak in October. Sources in the eastern U.S. contributed to sulfate concentrations mostly in the middle two months of the study period with

several peak contributions exceeding  $1 \mu\text{g}/\text{m}^3$ . The largest of these contributions is greater than  $5 \mu\text{g}/\text{m}^3$  and constitutes about 80% of the largest peak particulate sulfate measured during the BRAVO study period.



**Figure 8.** Smoothed daily estimates by source regions to particulate sulfate concentration (top plot) and fraction of total predicted particulate sulfate (bottom plot) at Big Bend during the study period.

### The Contribution of Sulfur Source Regions to Particulate Haze Levels at Big Bend National Park during the BRAVO Study Period

Both the fraction of light extinction associated with particulate sulfate (see Figure 2) and the fraction of particulate sulfate attributed to each source region (see Figure 8) varied considerably throughout the BRAVO study period. This information was combined to show variation in the absolute and percent fractional contribution by sulfur source regions to Big Bend light extinction (shown in the top and bottom plots of Figure 9, respectively). Pie diagrams are shown in Figure 10 to illustrate the differences in particulate sulfate contributions by various source regions to light extinction for the study period 20% haziest days compared to the study period 20% least hazy days. The numbers of 20% haziest days during each month of the BRAVO study from July through October are 1, 8, 10, and 4, respectively, while the numbers per month for the 20 least hazy days were 3, 1, 10, and 9, respectively.

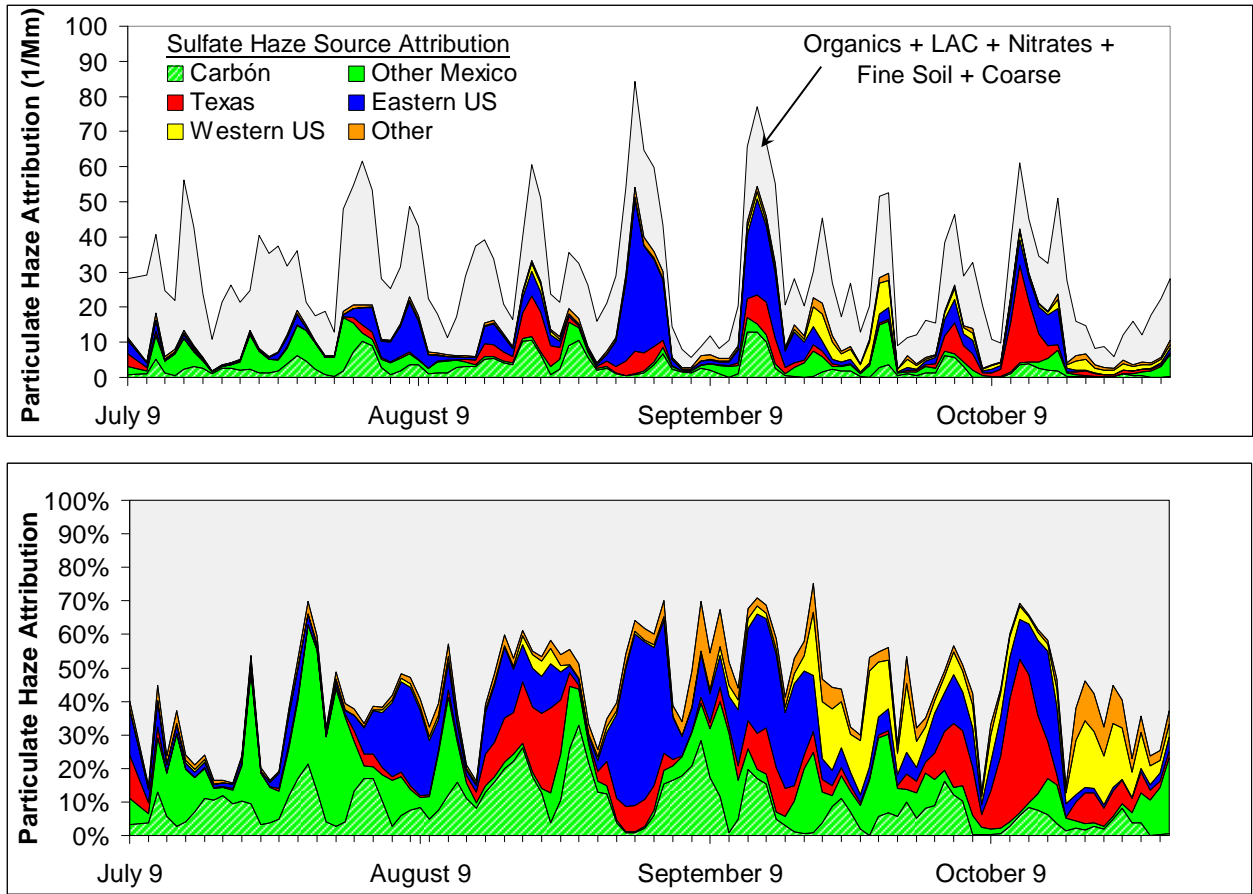


Figure 9. Estimated contributions to particulate haze by various particulate sulfate source regions. The top plot shows the absolute haze contributions by the various particulate sulfate sources as well as the total particulate haze level (black line). The bottom plot shows the fractional contribution to haze by the various sources.

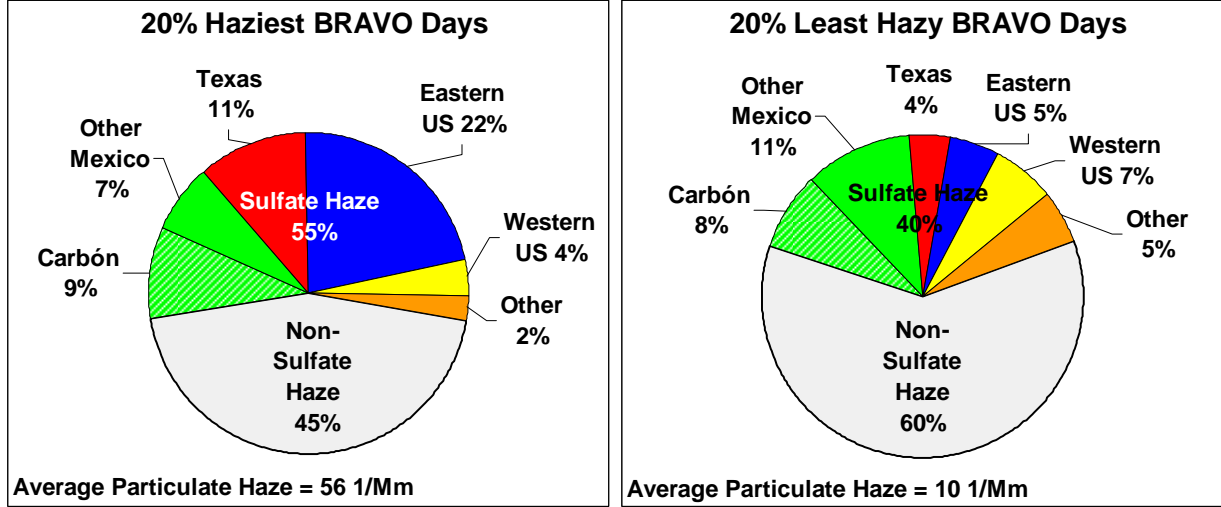


Figure 10. Estimated contributions by particulate sulfate source regions to Big Bend particulate haze levels for the 20% haziest days and the 20% least hazy days of the BRAVO study period.

The SO<sub>2</sub> sources in Mexico generally contributed a moderate 5 Mm<sup>-1</sup> to 15 Mm<sup>-1</sup> of the light extinction on most days during the study period, but during some of the minor haze episodes in July and August their relative contributions were 40% to 60% of the average particulate light extinction. SO<sub>2</sub> sources in Texas contributed to less than 5 Mm<sup>-1</sup> on most days during the study period, but during one of the few periods of higher contribution these sources contributed to nearly 30 Mm<sup>-1</sup>, corresponding to about 50% of the particulate light extinction on the haziest day in October. SO<sub>2</sub> sources in the eastern U.S. also contributed to less than 5 Mm<sup>-1</sup> on most days during the study period, but during the two haziest episodes of the study period these sources contributed to about 50 Mm<sup>-1</sup> and about 30 Mm<sup>-1</sup> respectively, corresponding to about 50% and 30% of the light extinction.

The sulfate contribution to particulate light extinction is higher on the haziest days compared to the least hazy days (55% compared to 40%). This increase in the sulfate contribution on the haziest days compared to the least hazy days is driven by increased relative contributions from the eastern U.S. and Texas. The relative contribution of sulfate on the haziest days from Texas increased by about a factor of 3 (4% to 11%), and from the eastern U.S. it increased by about a factor of 4 (5% to 22%) compared to the least hazy days. In contrast, the relative contributions for the Carbón I & II power plants remained about the same at 8% to 9% and the contribution of other sources in Mexico decreased from 11% on the least hazy days to 7% on the haziest days. The relative contribution of sulfate sources in the western U.S. to Big Bend's sulfate haze also decreased from 7% on the least hazy days to 4% on the haziest days. These results are consistent with the observation that the Texas and eastern U.S. sources had their largest sulfate contributions during the highest sulfate episodes.

The non-sulfate haze is primarily due to dust (fine soil and coarse particles) and carbonaceous (organic and carbon) compounds. Compared to the least hazy days, the haziest days have a higher relative contribution to light extinction by dust (25% compared to 19%) and a lower relative contribution by carbonaceous particles (19% compared to 39%).

### **Application of the Source Attribution Results to Other Months and Years**

In order to assess the applicability of haze attribution results for the BRAVO study to other years or other times of year, it is necessary to compare the four-month study period with the same months in other years and with other months of the year. Emissions and meteorology are the two most important factors that influence haze levels. Between 1999 and the present the annual emissions responsible for particulate sulfate concentrations in North America have not appreciably changed (U.S. emissions have decreased about 15%, but less is known about emission trends in Mexico). Seasonal variations in SO<sub>2</sub> emissions and in the SO<sub>2</sub> to particulate sulfate oxidation rate make extrapolations of the BRAVO study results to other months of the year prone to additional uncertainty. One of the most influential meteorological processes affecting the haze at Big Bend is the airflow patterns that determine which potential source regions are upwind of Big Bend. In spite of the uncertainties inherent in such a simple approach, comparisons of the meteorological flow patterns from the residence time analysis were used alone in an attempt to assess the applicability of BRAVO study results to other years and times of year.

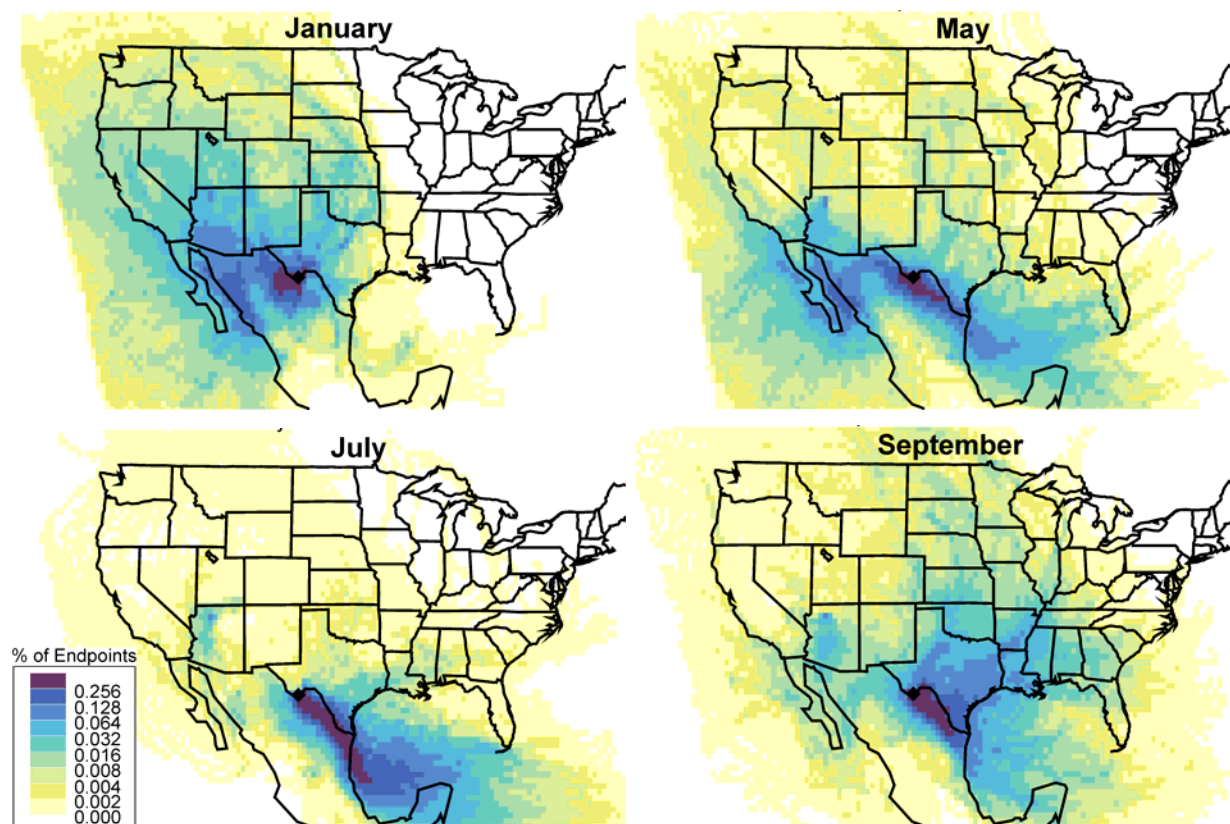
Residence time plots convey information about both the frequency of transport over potential source regions and its duration over the regions. However, it was shown that the residence time transport patterns are primarily driven by the variations in transport frequency

over regions as opposed to duration variations. Consequently, a change that doubles the residence time over a source region for a specific month can be thought of as doubling the probability of influence of that source region during that month. In this example the monthly averaged contribution would likely double because the numbers of impacting periods would about double, but the amount of the peak impact is not expected to change much.

During the BRAVO study period airflow to Big Bend was mostly similar to the airflow conditions during the five-year period. However, in September 1999 there was typically less flow over the eastern U.S. than for the five-year average, implying that the BRAVO results may underestimate the average haze contributions by that region's sources. In addition, during October 1999 there was typically more flow over Texas and less flow over Mexico, implying that the average October BRAVO haze contributions may be overestimated for Texas and underestimated for Mexico compared to the five-year average. While the estimated average contributions by these source regions may change, the peak contributions are likely not affected by the atypical frequency of flow.

Comparing the airflow patterns for the BRAVO study period to that of the other months of the year (Figure 11) it is evident that SO<sub>2</sub> sources in Mexico are likely to contribute less from November through March. This is because airflow across Mexico is less in general and is over lower emission density regions of Mexico to the west of Big Bend. SO<sub>2</sub> sources in Mexico are likely to be contributing to the particulate sulfate portion of the Big Bend haze during the months of April through June comparable to their contributions for the BRAVO study months of July and August. Sources in Texas are likely to contribute little to the particulate sulfate portion of the Big Bend haze for the months from November through June since the airflow is not frequently over the high emissions regions of east Texas, similar to July 1999. Eastern U.S. sources are unlikely to contribute to Big Bend haze during the months from November through March since airflow to Big Bend is rarely over that region during those months. During the months from April to June, the eastern U.S. sources may contribute a modest amount to sulfate haze, comparable to that estimated for July and early August.





**Figure 11.** Examples of geographic distribution of the fraction of time that air parcels spend during the five days prior to arriving at Big Bend National Park for the months of January, May, July, and September based upon a five-year analysis period (1998 to 2002).

### Implications

There is no single answer to the question of what sources are responsible for the haze at Big Bend National Park; sources in both the U.S. and Mexico are responsible. Mexican SO<sub>2</sub> emissions contribute to the sulfate haze most frequently, but to generate the haziest events that occur in the late summer and fall, contributions from Texas and the eastern U.S. must occur. The greatest individual contribution to haze is the Carbón I & II power plant in northern Mexico. Substantial changes of that facility's emissions would likely result in small but noticeable changes in haze levels on many days, but it would not make much difference to the worst haze episodes during late summer and early fall. To substantially affect all of the haze episodes during the late summer and fall where U.S. contributions are large at Big Bend will require SO<sub>2</sub> emission changes in both Texas and the eastern U.S. Because of the high frequency of air transported to Big Bend from the southeast along a corridor on both sides of the Rio Grande River, emission changes there have a potential to affect haze levels at Big Bend especially during June through September when transport from this region is most frequent.

The clearest days at Big Bend also had low sulfate concentrations. The visual scene on a clear day is more sensitive to small changes in haze than a hazy or moderately hazy day. On these clear days, the Carbón I & II power plants and other sources in northeast Mexico were the largest contributors to Big Bend's sulfate. Reduction in emissions from Carbón would likely result in creating more clear days. On the other hand, growth along this border region will likely further reduce the number of clear days.