1. TECHNICAL OVERVIEW

The EPA, NPS, and TCEQ sponsored the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study, with technical support from EPRI. The study was initiated in response to (1) public reports of decreased visibility at Big Bend National Park (BBNP), Texas, confirmed by trends analyses that show increasing haze levels, and (2) the construction of the *Carbón* coal-fired power plants in Mexico approximately 225 km southeast of the Park. The BRAVO Study involved a four-month intensive monitoring period from July through October 1999, followed by a four-year data analysis and modeling effort to assess the causes of haze in Big Bend National Park. The BRAVO Study was specifically designed to use extensive measurements with multiple independent attribution methods to estimate haze contributions from source regions and source types. However, BRAVO was not designed as a regulatory study; and it is beyond the scope of BRAVO to evaluate or to recommend potential control strategies for visibility improvement at the Park.

Visibility at Big Bend National Park is reduced due to haze caused by particles in the atmosphere (particulate haze). Particles contributing to haze originate from numerous sources across various geographic regions. The key points documented in this report concerning the causes of particulate haze at Big Bend National Park are that:

- Sulfate compounds are the largest contributor to particulate haze at Big Bend annually, accounting for about half overall, as well as on the haziest days.
- Dust and carbonaceous compounds comprise the majority of the remaining particulate haze annually.
- Dust or smoke from local and international sources (Mexico and beyond) is the largest contributor on some of the haziest days, particularly during the spring.
- SO_2 emissions from sources in the U.S. and Mexico were estimated to contribute about 26% and 18%, respectively, of the particulate haze on average during the four-month BRAVO Study period. The split among U.S. source regions was Texas – 8%, eastern U.S. – 15%, and western U.S. – 4%.
- SO_2 emissions from sources in the U.S. and Mexico were estimated to contribute about 37% and 17%, respectively, of the particulate haze on the haziest 1/5 of the days during the four-month BRAVO Study period. The split among U.S. source regions was Texas – 11%, eastern U.S. – 22%, and western U.S. – 4%.
- The two *Carbón* power plants in northern Mexico contributed a total of about 9% of the particulate haze on average during the four-month BRAVO Study period, making them the single largest contributing SO_2 emissions facility.
- Throughout the year transport is often from the western U.S. and Mexico on the least hazy days when the appearance of scenic vistas are especially sensitive to small increases in particulate concentrations.

This Technical Overview expands on these points and displays some of the information used to derive them. More complete explanations and justifications are available in the body of the report and the Appendix.

This overview lists several key questions regarding the "state-of-the-knowledge" of haze at Big Bend National Park. The answers to these questions reflect the opinion of the technical participants of the BRAVO Study. This document summarizes several assessments that explored the nature of light extinction and source areas contributing to haze at Big Bend NP during the four-month BRAVO Study. It also includes results of other studies, including long-term aerosol and meteorological monitoring data, in order to place the findings of the BRAVO Study period in perspective relative to haze conditions over an annual cycle and in other years. This context is necessary since conditions vary seasonally and from year to year. The timeframe of the BRAVO study was chosen to coincide with periods that prior analyses have shown to have a high likelihood of airflow from source regions in the eastern U.S. (most frequently in the fall) and northeastern Mexico (most frequent in the non-winter months).

As a Technical Overview, this section does not include sufficiently detailed information for one to judge the credibility of the material presented. This more detailed information is available in the body and Appendix of this report. The goals of the Technical Overview are to clearly inform technically-oriented readers concerning the most important findings of the BRAVO Study and to include appropriate background information to provide interpretive context. The reader should examine the remainder of the report for a more complete understanding of the information that was generated by the BRAVO Study.

Immediately following each question is a short tutorial to provide the reader with background material to better understand the science and to explain how the responses to the questions were developed.

Which are the major aerosol components contributing to haze at Big Bend NP throughout a year?

Haze is caused by scattering and absorption of light by the suspension of fine liquid and 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 Mm^{-1}. Higher light extinction levels correspond to hazier conditions.

Estimates of the contributions to light extinction by the major aerosol components can be made from the measured concentrations of those species. Light scattered by particle-free air, known as Rayleigh scattering, is assumed to be a constant value. Though Rayleigh scattering places a limit on our abilities to see distant scenic features clearly, many do not consider it a haze component since it is a natural and fixed consequence of the earth's atmosphere. Particulate haze refers to the non-Rayleigh portion of the light extinction that is the result of both man-made and naturally occurring particles in the atmosphere. Knowledge of the contributions to the total light extinction (including Rayleigh scattering) is useful for judging the perceptibility of changed conditions, while the contribution to particulate haze is a better way to assess the varying components of haze levels. Figure 1-1 shows the five-year

composite (1998 through 2002) of the light extinction (sum of light scattering and absorption) from measurements made two to three times per week at Big Bend National Park by the IMPROVE Program (IMPROVE, 2004).

- In general, the two haziest periods of the year at Big Bend National Park are in the spring when particulate sulfate and carbonaceous compounds contribute in similar amounts to haze, and in late-summer/fall when particulate sulfate compounds are the largest contributors to haze.
- Particulate sulfate compounds generally 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. 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.

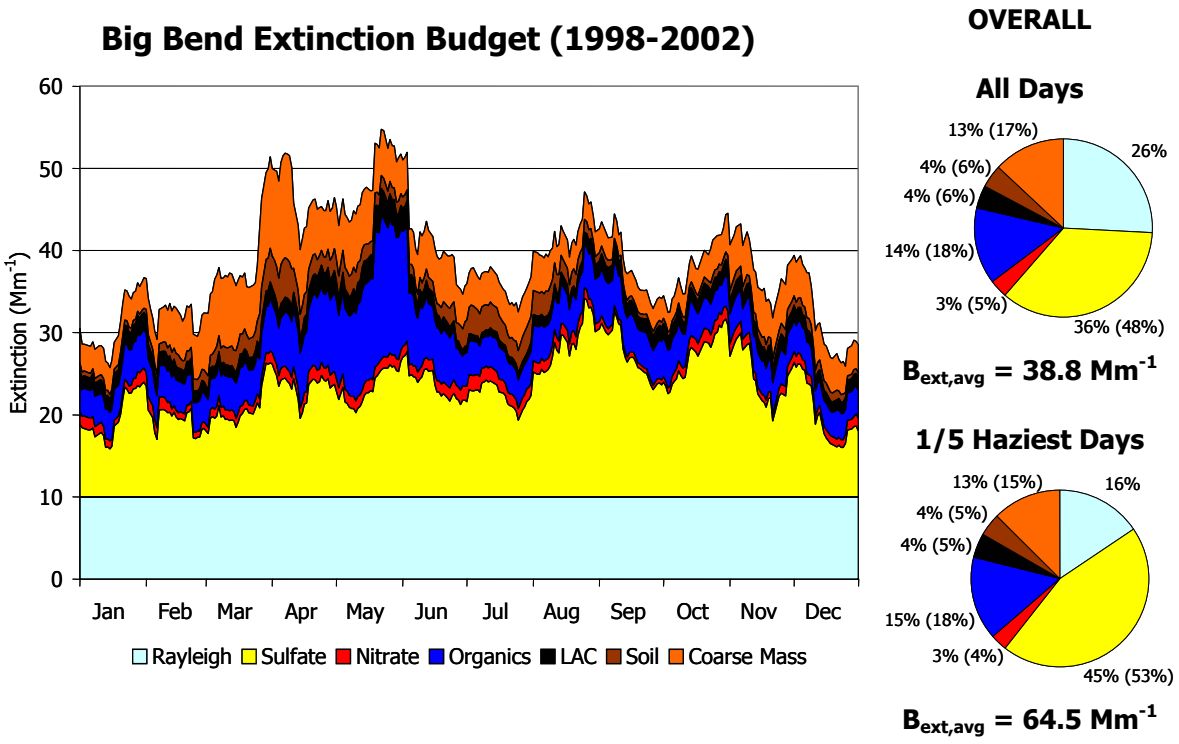

Figure 1-1. *Big Bend National Park five-year composite contributions to haze by components. Time plot uses a 15-day rolling average to smooth the effects of multi-year compositing. Percent contributions to particulate haze (the non-Rayleigh light extinction) are shown in parentheses.*

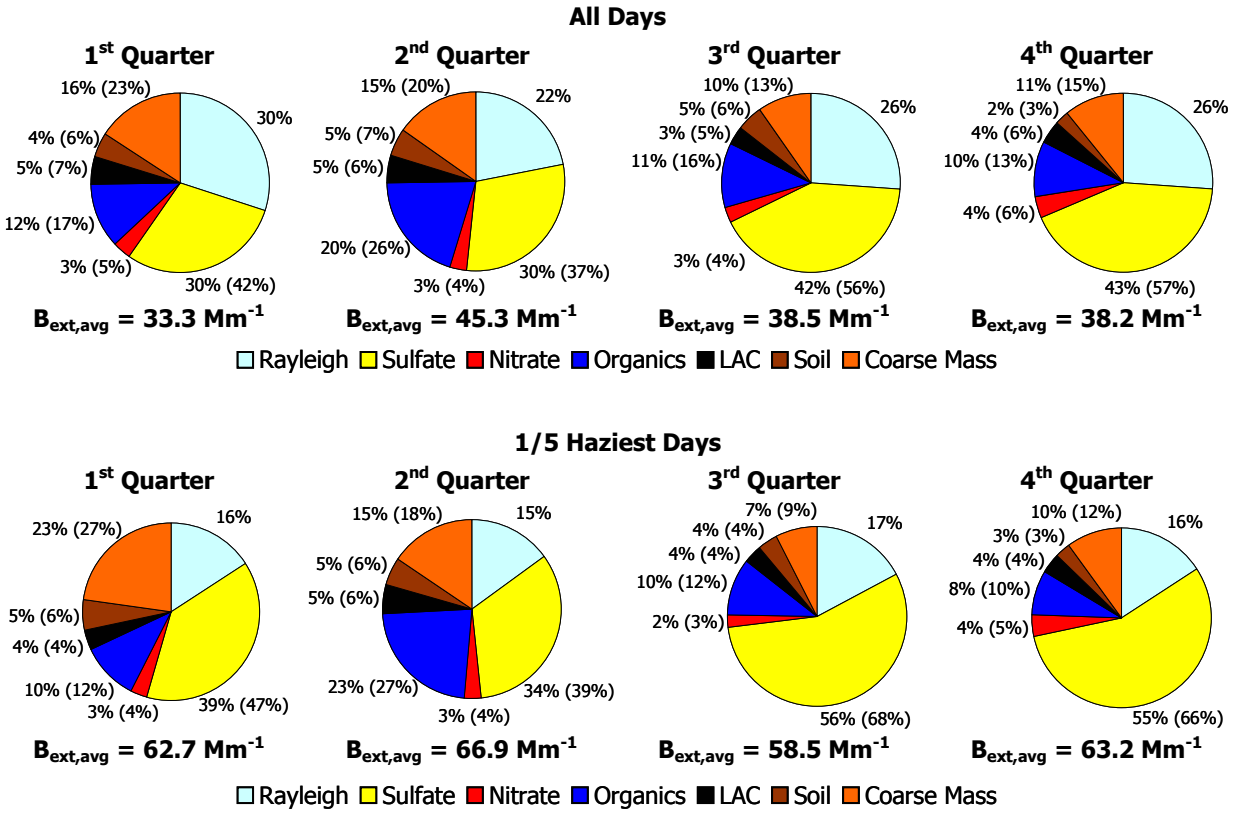

Figure 1-2. *Quarterly aerosol contributions to light extinction averaged over five years (1998 – 2002). Top graphs: all days in each quarter; bottom graphs: annual haziest 1/5 of the days. Percent contributions to particulate haze (the non-Rayleigh light extinction) are shown in parentheses.*

How does the composition of haze vary at Big Bend National Park throughout a year during the haziest days?

Figure 1-2 contains pie diagrams that show the average estimated contributions to light extinction by the various aerosol components and Rayleigh scattering. Separate pie diagrams display the averages allocated by calendar quarter for all days and the 1/5 haziest days of each year for the five-year period from 1998 to 2002. The Rayleigh scattering percent contribution necessarily decreases for the haziest days compared to all days, because its absolute contribution is taken to be constant for all days.

- Quarterly frequencies of annual haziest days for 1998 to 2002 are 1st – 13%; 2nd – 41%; 3rd – 22%; and 4th – 24%.

- Particulate sulfate compounds contribute more to light extinction for the haziest days in each quarter than for all days during the five-year period.
- The five-year percent contribution from sulfate compounds to light extinction increases from 36% on all days to 45% on the haziest days (corresponding to 48% and 53% of particulate haze, respectively, as shown in Figure 1-1).
- The five-year percent contribution from carbonaceous compounds (organics and light-absorbing carbon) is 18% on all days and 19% on the haziest days. Carbonaceous compounds account for 14–17% of the extinction in the 1st, 3rd, and 4th quarters and 25% in the 2nd quarter. The percent contribution to extinction by carbonaceous compounds on the haziest days increases only in the 2nd quarter (28%).
- With the exception of coarse mass in the first quarter, there are little, if any, differences in the quarterly percent contributions to light extinction from the other particulate components when comparing all days to the haziest days per quarter.

How does airflow to Big Bend National Park vary throughout the year?

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.

Hourly five-day-long trajectories of air that arrived at Big Bend National Park were calculated for a five-year period (1998 to 2002). Each trajectory gives estimates of the locations of air parcels every hour of the five days prior to their being transported to Big Bend. Residence time analysis uses these trajectories for selected periods of time (e.g., a month) or selected receptor site conditions (e.g., haziest days at Big Bend) to estimate the frequency of air parcel transport and its duration over various potential source regions prior to arriving at Big Bend.

Figure 1-3 displays examples of the geographic distribution of trajectory residence times for individual months. Histograms of the monthly residence times for different discrete potential source regions in the U.S. and Mexico are shown in Figure 1-4.

- Transport patterns to Big Bend vary considerably throughout the year as shown in Figures 1-3 and 1-4:
  - Upwind regions during the months from November through March are primarily to the west of Big Bend.
  - April and May flows are frequently from regions to the southeast and west.
  - June and July are characterized by airflow from regions to the southeast.
  - August through October is the only time of year with much flow from regions to the east and northeast, in addition to the more common flow from regions to the southeast.

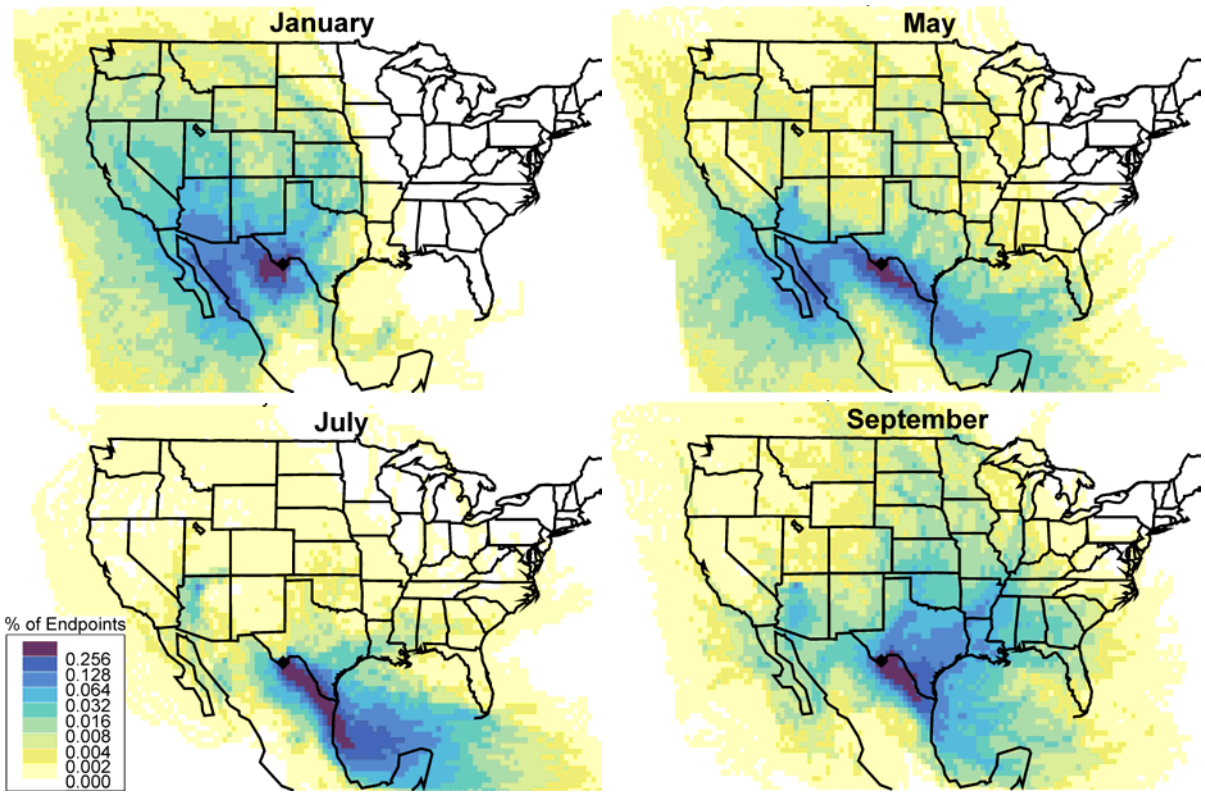

Figure 1-3. *Examples of geographic distribution of the fraction of time that air parcels spend during the five days prior to arriving at Big Bend National Park for the months of January, May, July and September based upon a five-year analysis period (1998 to 2002).*

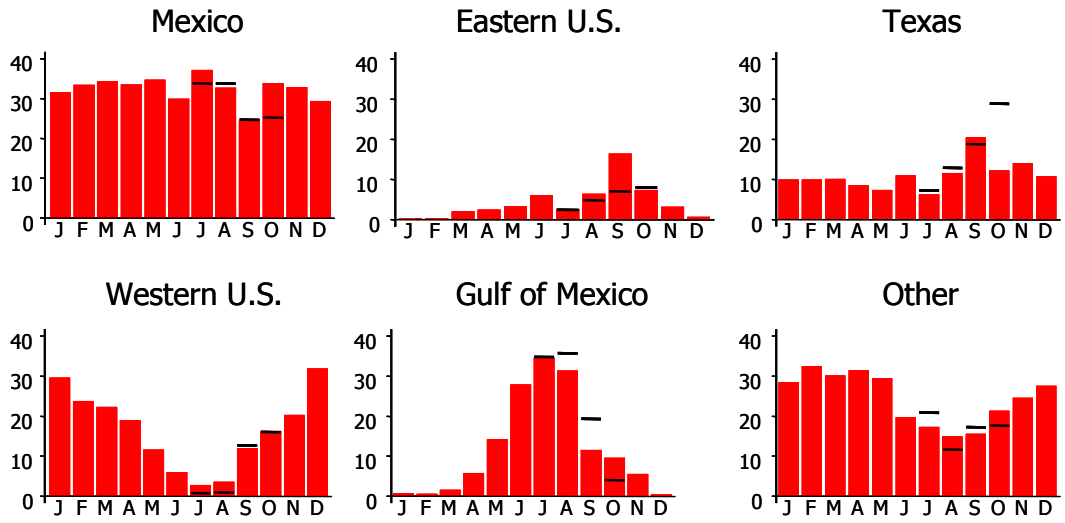

Figure 1-4. *Monthly fractions of time that air parcels spend in a region prior to arrival at Big Bend, based on five-day back trajectory calculations for the five-year period from 1998 to 2002. The lines shown over the months of July through October correspond to the values during the BRAVO Study period in 1999. The plot labeled "Other" represents locations beyond the other five regions.*

- Throughout the year air masses en route to Big Bend frequently reside over Mexico, in particular northern Mexico.
- As shown in Figure 1-2, the second quarter (April-June) has both the highest frequency of hazy days and the highest haze levels of any quarter during the five-year period from 1998-2002. Flows during these months are frequently from the southeast and can become influenced by biomass burning in Mexico and Central America.
- Airflow from the western U.S. to Big Bend is greatest in the winter months when haze levels at the park are lowest.
- Eastern U.S. airflow to Big Bend is infrequent during most of the year, with almost no flow except during a few summer and fall months.
- During September, a month with among the highest contribution to haze by particulate sulfate compounds, both Texas and the eastern U.S. have their largest frequencies of airflow to Big Bend.

Where are emission sources that may cause particulate sulfate compounds that contribute to Big Bend haze?

Ambient particulate sulfate compounds result from direct emissions of sulfate (i.e., primary sulfate) or are produced by chemical transformation (oxidation) of SO_2 emissions in the atmosphere (i.e., 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 SO_2 to secondary sulfate depends on the oxidative capacity of the atmosphere, which is influenced in large part by nitrogen oxides (NO_x) and volatile organic compound emissions. Oxidation of SO_2 to sulfate can be slow, often requiring one to two days to convert about half of the SO_2 to particulate sulfate compounds. However, this extent of transformation can occur much more rapidly, in 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 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 SO_2 emissions sources.

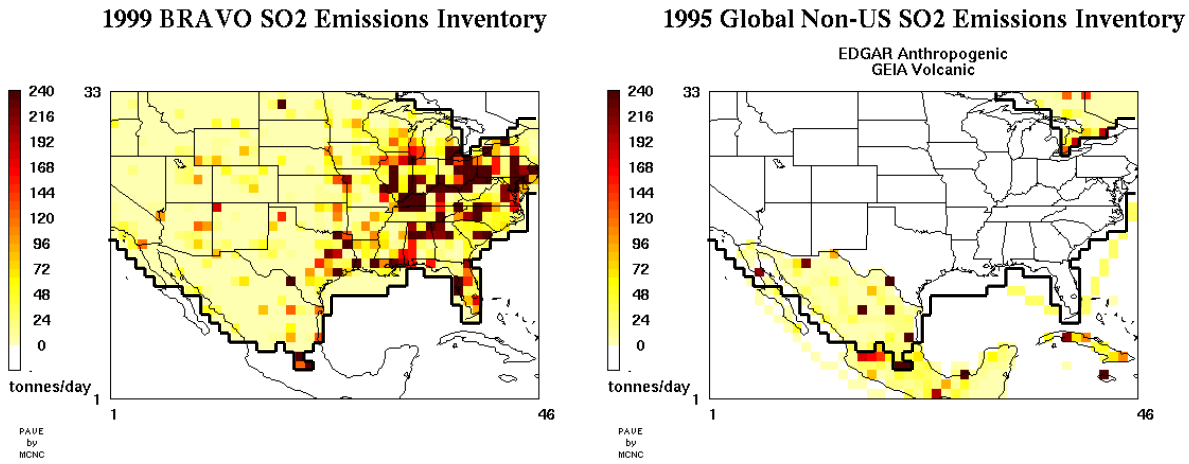

Figure 1-5. *(Left) SO_2 emissions based on the 1999 BRAVO emissions inventory used in the REMSAD and CMAQ-MADRID modeling. No emissions were included beyond the black outline shown in the figure. (Right) SO_2 emissions outside of the United States based on 1995 global emission inventories used by climate models.*

BRAVO Study data analysts and air quality modelers developed source attribution estimates for Big Bend particulate sulfate compounds using the locations and magnitudes of emission sources and airflow information. To the left in Figure 1-5 is a map of the estimated magnitudes and locations of SO_2 emissions sources that were 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 1-5, were accounted for in BRAVO Study modeling by use of four-month average boundary conditions obtained from global model simulations. The map to the right in Figure 1-5 (displaying non-US SO_2 emissions in the BRAVO domain, based on 1995 global emissions inventories used by climate models) provides an estimate of the magnitudes and locations of SO_2 emissions not included in the BRAVO inventory. These emissions inventories were obtained from the Emission Database for Global Atmospheric Research (EDGAR) and the Global Emissions Inventory Activity (GEIA) database.

- SO_2 emissions are much greater in the eastern U.S. than in the rest of the BRAVO Study modeling domain.
- Eastern Texas emits more SO_2 than the rest of Texas.
- SO_2 emissions are high at a few locations in northern Mexico, including the *Carbón* coal-fired power plants in Mexico located about 225 km east-southeast of Big Bend and at urban and industrial areas near Monterrey in northeastern Mexico.
- The Popocatepetl volcano in central Mexico near Mexico City, which has been active for a number of years including during the BRAVO Study period, is the

largest single SO_2 emissions source in North America. Limited modeling of the flow of its emissions indicated that they traveled far to the west of and likely had little effect on Big Bend during the BRAVO Study period.

- A recently produced emission inventory for Mexico differs from the BRAVO emissions inventory for SO_2 emissions, by as much as a factor of two higher or lower depending on the region, which indicates that there remain significant uncertainties in Mexican emissions information.
- The effects of emissions from southern Mexico, Cuba, and other areas outside of the BRAVO Study emissions inventory are thought to be small at Big Bend, but their absence contributes to modeling uncertainties.

? How does the composition of haze vary at Big Bend National Park during the four-month BRAVO Study period?

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 1-6 shows the daily light extinction (sum of light scattering and absorption) contributions by the major aerosol components in a format similar to that of Figure 1-1.

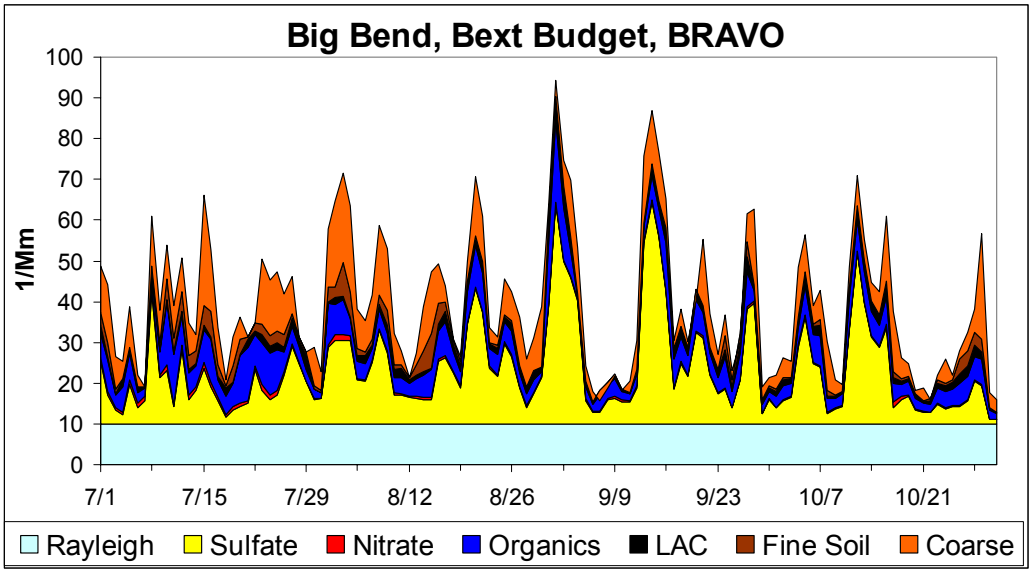

Figure 1-6. *Contributions to haze by components during the BRAVO Study period. (LAC is light absorbing carbon.)*

- Particulate sulfate compounds constituted the largest individual contribution to the haze, accounting for about 35% of the light extinction.
- Rayleigh scattering caused by particle-free air is the second largest contributor (~25%), followed by coarse particles (~18%) and organic carbon compounds (~13%). The remaining particulate compounds comprised about 9% of the light extinction.
- The relative contribution of particulate sulfate compounds to light extinction was less in the first two months of the study period than during the second two months (~30% compared to ~39%). This is due to the greater combined contributions to light extinction by fine soil and coarse particles in the first two months (~27%) compared to the second two months (~17%), much of which is thought to be transported to Big Bend from sources in Africa.

How did different source regions contribute to particulate sulfate compounds affecting haze levels at Big Bend National Park during the BRAVO Study period?

BRAVO Study participants employed numerous methods to identify source types (e.g., power plants) or source regions (e.g., Texas, Eastern U.S., Western U.S. and Mexico) contributing to the particulate sulfate compounds that influence Big Bend haze and to estimate the magnitudes of their contributions.

Spatial Analysis: The methods include a relatively simple spatial analysis method (named TAGIT) to separate sulfate from nearby SO_2 emissions sources from sulfate from more distant sources by subtracting the sulfate levels from nearby background sites from those sites where elevated concentrations of SO_2 show a local source impact. TAGIT was used to infer the particulate sulfate contributions by the largest sources of SO_2 in the region surrounding Big Bend, the *Carbón* power plants.

The only input data required for TAGIT is particulate sulfate and SO_2 concentration data, which are considered to be of good quality. For TAGIT to yield reliable values, two assumptions need to be applicable: that background particulate sulfate levels are uniform near the receptor location, and that local sources are not contributing to the particulate sulfate levels at background sites. The first assumption is likely to be true on average, though not for every sample period, so it should not affect the four-month average attribution, while the second assumption could lead to underestimation of the attribution to local sources.

Transport Regression Receptor Models: Several transport regression 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. Two methods were used to estimate winds over North America (EDAS from the National Weather Service and MM5 applied specifically for the BRAVO Study) and two methods for determining transport were employed. Backward trajectories from Big Bend were employed in Tracer Mass Balance (TrMB) and forward transport and dispersion

from all potential source regions were used in Forward Mass Balance Regression (FMBR). Testing of the TrMB and FMBR methods involved reproducing measured tracer concentrations and simulated sulfate concentrations from a deterministic model using both sets of wind information. Approaches that passed these evaluations were used for attribution of measured sulfate.

An inherent feature of these techniques is estimation of a mean relationship between air transport from an area and that area's contribution to sulfate. Since time-varying dispersion, deposition, and transformation are not calculated and do vary from the mean, these techniques were used only for estimates of the mean attributions. Statistical uncertainties for these techniques were quantified and are documented elsewhere in the report. In addition, collinearity, caused since air tends to often arrive from two or more regions simultaneously, is a potential problem. Discussion and quantitative assessments of collinearity are included in Chapter 9 and Appendix 8.

Regional Air Quality Models: Two regional air quality models (REMSAD and CMAQ-MADRID) were used to estimate the effects of transport, dispersion, chemical transformation and deposition on emissions; and thereby to simulate particulate sulfate concentrations throughout the modeling domain, including at Big Bend. The difference in simulated concentrations between a case with all emissions (base case) and one 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.

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 in any of these processes can adversely affect their source attribution estimates. 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.

Synthesis Inversion Analysis of Air Quality Models: Concerns about possible systematic biases that could be the result of Mexico's SO_2 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.

This 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 contributions that may have been improperly attributed to small distant sources by the Eulerian model runs were most likely attributed to source regions near Big Bend in the synthesized method. The technique also systematically underestimated the measured sulfate concentrations. It is not known if this underestimation impacts one source region more than another.

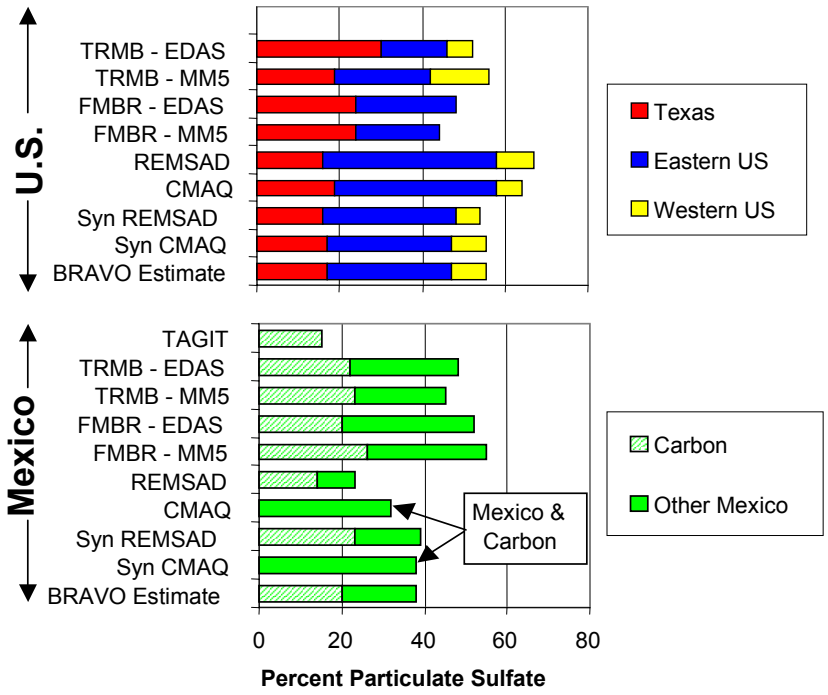

Figure 1-7. *Estimates by several data analysis and modeling methods of the study-period averaged percent contributions to particulate sulfate at Big Bend by U.S. and Mexico sources. TAGIT only attributed the* Carbón *power plants, while CMAQ and Synthesized CMAQ attribution did not distinguish* Carbón *from the rest of Mexico.*

The technical participants of the BRAVO Study 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 1-7 shows the study period-averaged attribution results for nine methods as well as the BRAVO Estimate results. TAGIT attribution was only for *Carbón* power plants, while CMAQ-MADRID and Synthesized CMAQ-MADRID attribution did not delineate the *Carbón* power plants. Figure 1-8 shows a smoothed daily attribution using the BRAVO Estimate method. The top plot in Figure 1-8 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.

- U.S. sources contributed about 55% (BRAVO Estimate) of the particulate sulfate at Big Bend during the BRAVO Study period, with a range among methods of 44% to 67%.
- Mexico sources contributed about 38% (BRAVO Estimate) of the particulate sulfate at Big Bend during the BRAVO Study period, with a range among methods of 23% to 55%.

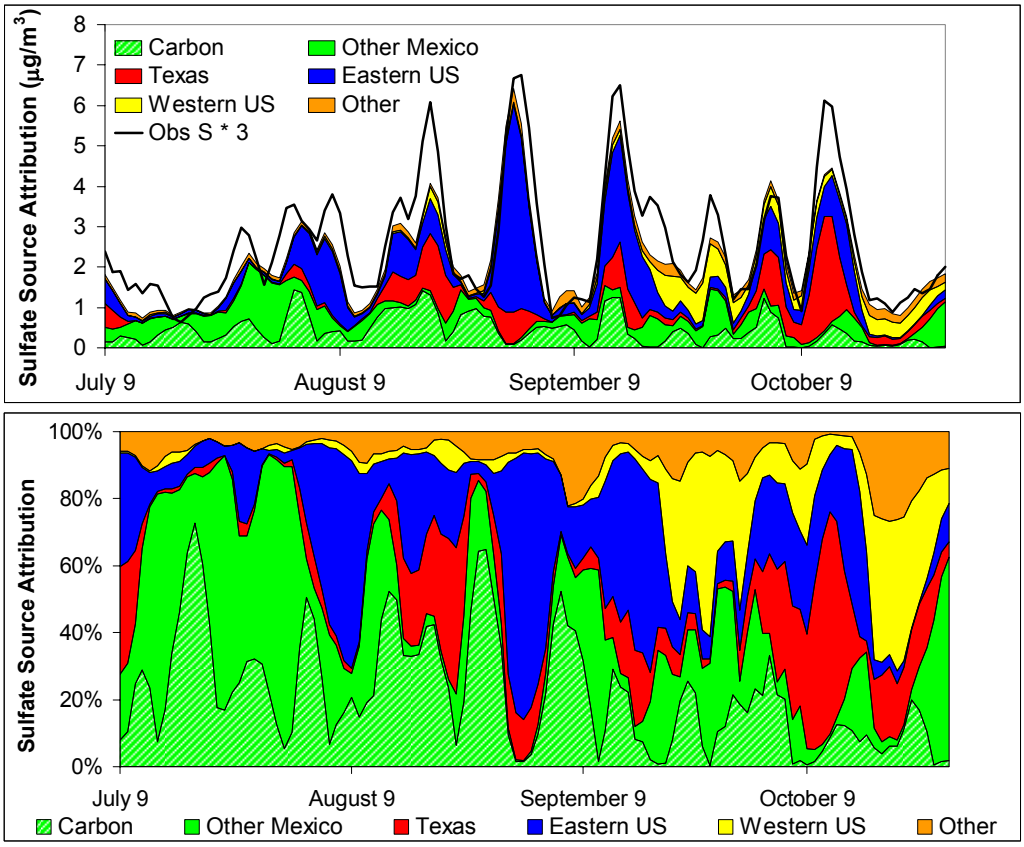

Figure 1-8. *Smoothed daily estimates by source regions to particulate sulfate concentration (top plot) and fraction of total predicted particulate sulfate (bottom plot) at Big Bend during the study period.*

- Eastern U.S., Texas, and western U.S. sources contributed about 30%, 17%, and 9%, respectively (BRAVO Estimate), of the particulate sulfate at Big Bend during the BRAVO Study period, with ranges among the methods of 16% to 42%, 16% to 30%, and 0% to 14%, respectively.
- The *Carbón* power plants contributed about 20% (BRAVO Estimate) of the particulate sulfate at Big Bend during the BRAVO Study period, more than any other single SO_2 emissions facility, with a range among the methods of 14% to 26%.
- 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 µg/m^3 every day. During the largest peak in late July, sources in Mexico contributed about 2 µg/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 µg/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 $\mu g/m^3$. During two episodes in October, sources in Texas had peak contributions of about 1.2 to 2.8 $\mu g/m^3$ of particulate sulfate and constituted 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 $\mu g/m^3$. The largest of these contributions is greater than 5 $\mu g/m^3$ and constitutes about 80% of the largest peak particulate sulfate measured during the BRAVO Study period.

How did different source regions contribute to haze levels at Big Bend National Park during the BRAVO Study period?

Both the fraction of light extinction associated with particulate sulfate (see Figure 1-6) and the fraction of particulate sulfate attributed to each source region (see Figure 1-8) varied considerably throughout the BRAVO Study period. This information can be 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 1-9 respectively). Pie diagrams are shown in Figure 1-10 to illustrate the differences in particulate sulfate contributions by various source regions to light extinction for the study period's 1/5 haziest days compared to the study period's 1/5 least hazy days. The numbers of 1/5 haziest days during each month of BRAVO Study from July through October are 1, 8, 10, and 4, respectively; while the numbers of days per month for the 1/5 least hazy days are 3, 1, 10, and 9, respectively.

- SO_2 sources in Mexico generally contributed to 5 Mm^{-1} to 15 Mm^{-1} 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 30% to 40% of the average light extinction.
- SO_2 sources in Texas contributed to less than 5 Mm^{-1} on most days during the study period, but during one of the few periods of higher contribution these sources contributed to nearly 30 Mm^{-1}, corresponding to about 40% of the light extinction on the haziest day in October.
- SO_2 sources in the eastern U.S. contributed to less than 5 Mm^{-1} on most days during the study period, but during the two haziest episodes of the study period these sources contributed to about 50 Mm^{-1} and about 30 Mm^{-1}, respectively, corresponding to about 50% and 30% of the light extinction.
- Particulate sulfate contributions to light extinction were more than a factor of 2 higher on the haziest days compared to the least hazy days (47% compared to 21%).
- Non-sulfate haze contributions to light extinction were somewhat greater on the haziest days compared to the least hazy days (38% compared to 32%).

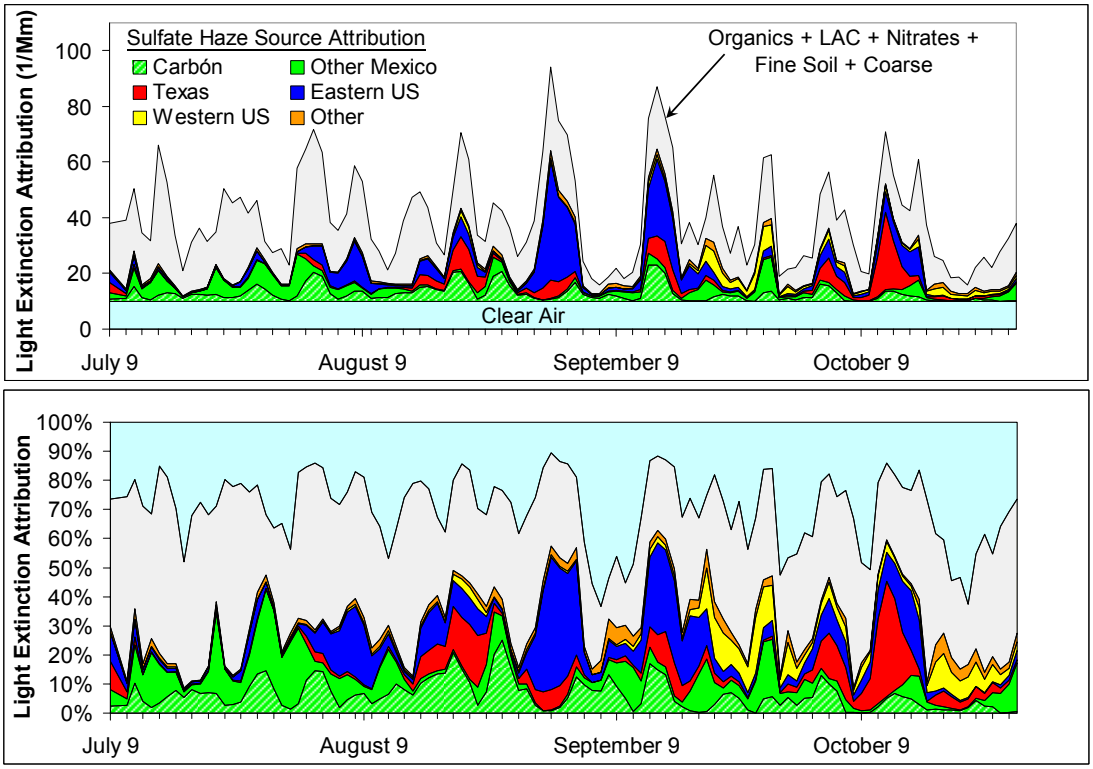

Figure 1-9. *Estimated contributions to light extinction by various particulate sulfate source regions. The top plot shows the absolute haze contributions by the various particulate sulfate sources as well as the total light extinction level (black line) and Rayleigh or clear air light scattering. The bottom plot shows the fractional contribution to light extinction by the various particulate sulfate sources and by Rayleigh light scatter (top-most on the plot), which is relatively more important on the clearest days. The contributions to light extinction by particle free air (i.e., Rayleigh scattering) are shown explicitly since they represent a natural limit that cannot be improved upon.*

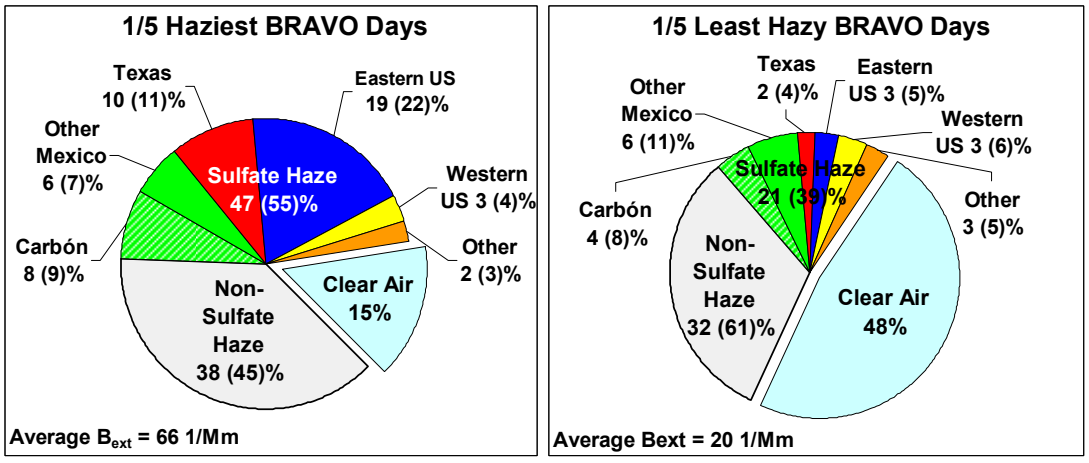

Figure 1-10*. Estimated contributions by particulate sulfate source regions to Big Bend light extinction levels for the 1/5 haziest days and the 1/5 least hazy days of the BRAVO Study period. Percent contributions to particulate haze (non-Rayleigh light extinction) are shown parenthetically.*

- Compared to the least hazy days, the haziest days had a higher relative contribution to light extinction by coarse particles (20% compared to 11%) and a lower relative contribution by carbonaceous particles (15% compared to 21%).
- The relative contributions to light extinction at Big Bend by Texas and eastern U.S. SO_2 sources increased from 2% to 10% and from 3% to 19%, respectively, on the haziest days of the BRAVO Study period compared to the least hazy days.
- The *Carbón* power plants' contributions to light extinction at Big Bend increased from 4% on the least hazy days to 8% on the haziest days. The relative contributions to light extinction of other SO_2 sources in Mexico were about the same for the haziest and least hazy days.
- SO_2 sources in the western U.S. had similar low contributions to light extinction on both least hazy and haziest days at Big Bend during the BRAVO Study period.

How applicable are the particulate sulfate attribution results for the BRAVO Study period to other years or times of year?

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, U.S. emissions have decreased about 15% but less is known about emission trends in Mexico. Seasonal variations in SO_2 emissions and in the SO_2 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 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. There are seasonal differences in airflow as shown in Figures 1-3 and 1-4. Separate analyses have shown that most of the information conveyed in these figures is due to the variations in flow frequency over regions as opposed to duration variations. That means, for example, that 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, as opposed to doubling its contribution during any particular episode. 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 double. Of course, when comparing different time periods, whether it's the same month in other years or different months in any year, other influential atmospheric processes that can change deposition or SO_2 oxidation rates may be different, such as precipitation or cloud cover. Only airflow

pattern differences are considered in responding to this question, which necessarily means that the responses are more speculative than those to other questions.

Residence time analysis was applied to the BRAVO Study period to examine the difference in transport patterns compared to the five-year average (Figure 1-4) and for the highest 20% particulate sulfate compound concentrations compared to the transport patterns for the lowest 20% particulate sulfate compounds for five-day trajectories (see Figure 1-11).

- During the BRAVO Study period, airflow to Big Bend was similar to the airflow conditions during the five-year period (Figure 1-4) except for:
  - September 1999, when there was 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;
  - October 1999, when there was more flow over Texas, implying that its average haze contributions for that month may be over estimated by the BRAVO Study result; and
  - October 1999, when there was less flow over Mexico, implying that its average contributions for that month may be underestimated.

However, though the estimated average contributions by these source regions may change as indicated above, the magnitudes of the short-term peak contributions in these cases are probably not much affected by the atypical frequency of flow.

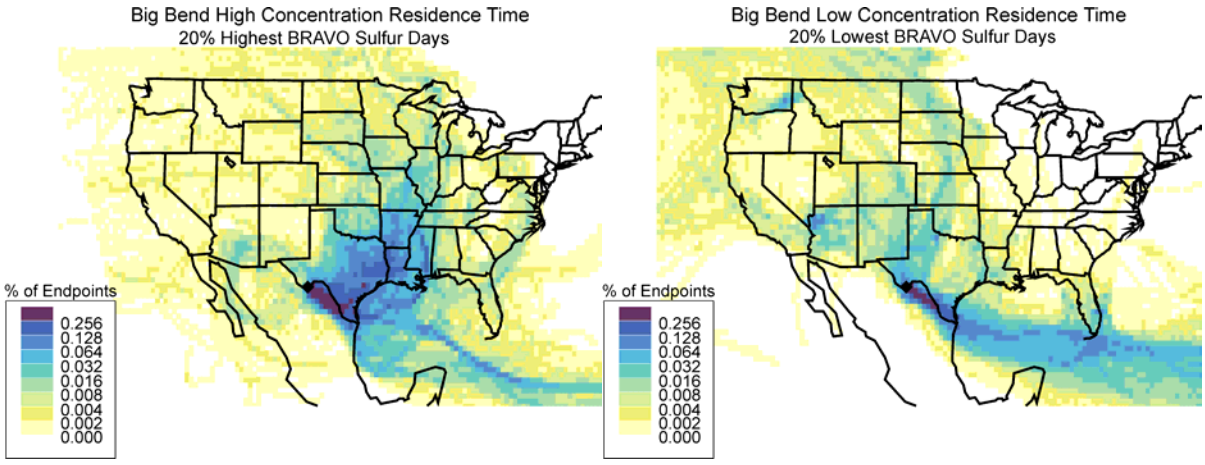

Figure 1-11. *Fractions of time that air parcels spent during five-day trajectories for periods with the 20% highest concentrations of particulate sulfate compounds and for the periods with the 20% lowest concentrations of particulate sulfate compounds during the BRAVO Study period July through October 1999.*

- Comparing the airflow patterns for the BRAVO Study period to those of the other months of the year (Figure 1-3):
  - Sources in Mexico are likely to be contributing less in the months of November to March (represented by January in Figure 1-3) because airflow across Mexico occurs less frequently in general and is over lower emission density regions of Mexico to the west of Big Bend (Figure 1-5). SO_2 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 comparably to its contributions the BRAVO Study July and August months.
  - 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, because the airflow during those months is not frequently over the high emissions regions of east Texas, just as was the case during July 1999.
  - Sources in the eastern U.S. are very 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 to sulfate haze a modest amount, comparable to that estimated for July and early August.
- Airflow to Big Bend for days with the 20% lowest particulate sulfate days during the BRAVO Study period was most often over northern Mexico and the Gulf of Mexico, with little or no flow from the eastern U.S. (see Figure 1-11).
- Airflow to Big Bend for days with the 20% highest particulate sulfate periods was also over northern Mexico, but also included parts of Texas and other States to the east and north.

The remainder of this report describes the BRAVO Study activities, including the study design, monitoring program, and emissions inventory (Chapter 2 through 4); monitoring results and an assessment of the extent to which the study periods fits into the longer term record for Big Bend (Chapters 5 through 7); descriptions and performance assessments of the data analyses and modeling attribution approaches (Chapters 8 and 9); particulate sulfate attribution results (Chapters 10 and 11); and in the final chapter, a synthesis featuring an attribution reconciliation assessment, a conceptual model of the causes of Big Bend haze, and a compilation of lessons learned (Chapter 12). The Appendix includes a wealth of more detailed information, which is not readily available elsewhere, and which forms the basis of much of the material presented in the report. For those with limited time, an alternative approach to reading the report sequentially would be to skip from here to the beginning of Chapter 12 (excluding the lessons learned section), then select other chapters and the Appendix as time and interest permit.