12. ATTRIBUTION RECONCILIATION, CONCEPTUAL MODEL, AND LESSONS LEARNED

12.1 Introduction

The BRAVO Study attribution analyses estimate the contributions of source areas to particulate sulfate compounds at Big Bend National Park. This emphasis on particulate sulfate is justified by its substantial role in haze at Big Bend (nearly half of the particulate haze) and its being formed almost exclusively from man-made industrial emissions. Our understanding of the important processes that determine the concentrations of particulate sulfate in the atmosphere are well documented and can be simulated reasonably well by available air quality models. The other particulate species contribute less to the annual average haze; though carbonaceous particulate or dust can be dominant during individual episodes. Carbonaceous and dust particles are from a combination of man-made and natural sources, often occur in large concentrations during episodes of extreme emission events, and are currently less reliably simulated by air quality models.

The BRAVO Study approach envisioned the application of multiple independent attribution methods followed by a reconciliation process to compare and evaluate results. The advantages of this approach over use of a single selected "best" method include the use of more of the available data; reduced risk of poor attribution estimates caused by inappropriate assumptions, miscalculation or incorrect input data; and the possibility for enhanced credibility should the results of the multiple methods be comparable. The potential disadvantage is that it takes extra effort to determine which of the estimates are more likely to be reliable.

The BRAVO Study particulate sulfate attribution process consisted of three phases:

- In the first phase, receptor and source modeling methods were tested against the tracer data set, for which the source locations and source strengths are well known. This tracer-screening and evaluation phase resulted in dropping some methods and a number of changes to other attribution methods, including changes to the wind fields, dispersion approaches and other aspects of the various methods to improve their performance.

- In the second phase, the various models that survived the phase I evaluation with tracer data were employed to estimate the source regions responsible for the sulfate measured at Big Bend. This initial application phase produced a matrix of attribution results available for intercomparison and, for the air quality simulation models, comparisons of modeled and measured particulate sulfate and SO_2.

- In the third phase, most of the attribution models were refined. This was done in an attempt to incorporate more information into the attribution approaches in a way that would adjust for potential shortcomings of the original approaches. The refined approaches phase was the genesis of the synthesized REMSAD and

CMAQ-MADRID models and the scaled TrMB and FMBR transport receptor methods.

Each of these phases included components of the reconciliation process.

This chapter will review information generated during the three phases of the BRAVO Study attribution process, in an effort to assess the degree of comparability among attribution results and to make judgments concerning their credibility.

The emphasis of the BRAVO Study on particulate sulfate attribution is reasonable in light of its substantive role in contributing to Big Bend National Park haze. However, the primary goal of the study is to identify source types and source regions responsible for haze at the park. To do this requires that the daily particulate sulfate source attribution results be interpreted in terms of their contributions to daily light extinction. The results of this interpretation are shown and discussed in Section 12.5.

Section 12.6 presents a conceptual model of Big Bend haze that is a plausible story of the influential atmospheric processes and emission sources responsible for changing air quality conditions and associated haze levels. It is a non-quantitative description that is consistent with the available monitoring data, our understanding of atmospheric science, and our knowledge of pollution emission sources and processes. While not a model for predicting haze levels, a conceptual model should be directionally correct, so that a person knowing the conceptual model should be able to predict whether haze levels increase or decrease when any of the influential processes are changed. For example a change in wind direction might be associated with increased likelihood of precipitation that would lower particulate concentrations and improve haze conditions. A conceptual model that is thought to be credible can be used to check the reasonableness of new information (data, model results, etc.), to qualitatively predict the response of haze levels to changes in atmospheric or emission conditions, and to successfully communicate the causes of Big Bend haze to a broad audience.

Attribution methods, whether they are receptor models or air quality models, don't directly produce conceptual models. Whether receptor or air quality simulation model attribution methods are used, additional work is required to assure reasonable results and to build a consistent conceptual model of the important atmospheric processes.

Receptor models generally perform some type of fitting of the measured air quality data set with a characterization of emission source types (e.g., the Chemical Mass Balance approach) or transport from various source locations (via transport regression methods). These are purely mathematical methods applied to optimize relationships among selected data.

Air quality simulation models are computerized mathematical formulations designed to simulate the air quality-related processes that operate on air pollution emissions from the point of emissions to the receptor locations. These computer codes use input data that characterize emissions, atmospheric processes, and geographic information to calculate estimates of the air quality concentrations throughout the model domain. While, in a sense, air quality simulation models numerically summarize our understanding of the air quality processes, they do not in the course of their routine use reveal the important processes related to any particular situation. This is especially true of the more sophisticated full chemistry grid models that are complex computer codes that try to simulate all of the important processes, but are not well understood by many who use the models.

This chapter will describe and offer evidence for a conceptual model of the causes of haze at Big Bend National Park. This conceptual model resulted from the assessment efforts of the BRAVO Study and information from other investigations.

The final section of this chapter, 12.7, was written to communicate the most important lessons learned and recommendations from the investigators who conducted the BRAVO Study. This section is not as much concerned with the findings of the study as with the planning and implementation of the study. It may be of greatest use by anyone planning a future air quality assessment program.

12.2 Phase I: Tracer Screening and Evaluation

As described in Chapters 3, 5, and 9, four distinct perfluorocarbon compounds were released from four locations in Texas as tracers to uniquely tag the air parcels into which they were released. Tracer concentrations at the surface were monitored at about 40 locations throughout Texas. A primary purpose of the tracer component of the field program was to develop a data set to challenge the source attribution methods used by the BRAVO Study, in a situation where emission rates and release locations were known. The conservative nature of the tracers (i.e., non-depositing and non-reacting) limited the challenge to pollutant transport and dispersion since it could not test the ability of the methods to cope with atmospheric transformation or deposition processes. In spite of this limitation, the ability to simulate transport and dispersion on the scale of the BRAVO Study domain is considered a critical and not necessarily simple task to accomplish.

The performance of the tracer release and monitoring are documented elsewhere in the report. In summary the tracer release worked well at three of the four locations. The tracer release rate at the northeast Texas tracer release location was insufficient to be reliably measured above background levels at some of the west Texas monitoring sites including those near Big Bend. Due to technical difficulties in the tracer analysis system, the number of samples that could be collected and analyzed was reduced substantially from that in the study plan, with most of the data available from just six monitoring sites in a north/south line from Big Bend to Ft. Stockton, Texas. In spite of these limitations the tracer data were of sufficient quality to test the performance of the transport regression and air quality modeling source attribution methods.

Performance statistics for the attribution methods that survived phase I are documented in the report, but performance of those methods that didn't survive is not included in the report. Among them is the application of an earlier version of CMAQ with high spatial resolution for two 10-day episodes (October 5-15 and August 15-25, 1999). The high resolution was accomplished by using a 12-km grid over the heart of the modeling domain and a 4-km grid in regions around the Eagle Pass/*Carbón* power plants and the Big

Bend National Park. These fine grids were nested within the 36-km grid that covered the rest of the modeling domain. The MM5 meteorological modeling that generated the input meteorological fields was similarly constructed for the two episode periods.

Comparison of the high-resolution CMAQ-simulated concentrations against the measured tracer concentrations showed them to be not nearly as good the as the 36-km grid REMSAD-simulated tracer concentrations. This was despite the fact that the 4-km MM5 wind fields compared better to measured winds than did the 36-km MM5 wind fields. This surprising result was the genesis of several months of additional assessments to better understand the causes of the poor performance and how best to cope with them.

Figure 12-1 illustrates the types of problems that were uncovered as a result of these efforts. It shows the distribution of Houston tracer concentrations simulated by REMSAD at 36-km and 12-km grid scales, and by CMAQ at 12-km grid dimensions for October 12th, a date when tracer was measured at the monitoring sites at and near Big Bend. The 12-km spatial resolution CMAQ plume shows less horizontal dispersion than the 12-km REMSAD plume, and both were too far south of Big Bend as compared the 36km REMSAD, which predicted tracer concentrations at Big Bend. It remains unclear why the higher spatial resolution resulted in apparently too little horizontal dispersion and more southerly distribution or why the REMSAD dispersion was broader than that of the CMAQ. However, based on the assessment of these results, the decision was made to apply CMAQ at 36-km resolution and to modify it to use the same dispersion algorithm as used by REMSAD. The computational resource savings by abandoning the high spatial resolution simulations made it possible to run 36–km CMAQ-MADRID for the entire BRAVO Study period instead of just the two 10-day episodes.

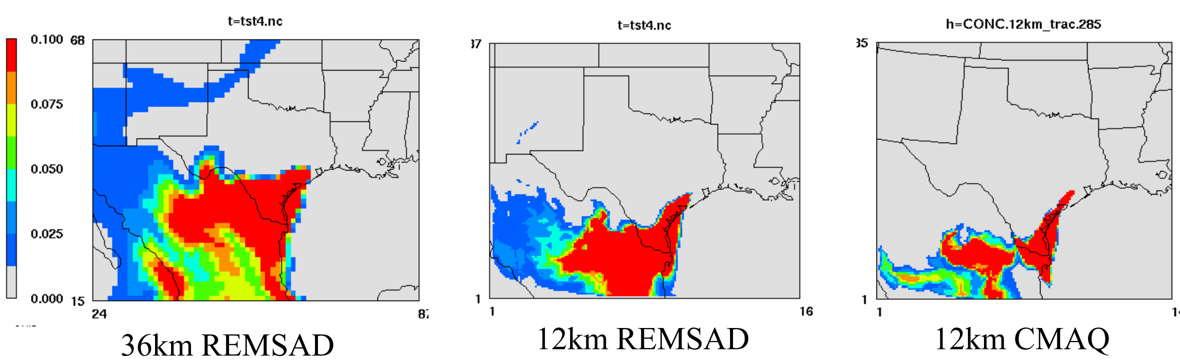


Figure 12-1. *Simulated surface layer PTCH tracer concentrations (released from Houston TX) for October 12th 1999 generated by REMSAD at 36km and 12km and by CMAQ at 12km.*

Several months after the decision was made to abandon the high resolution CMAQ modeling, the U.S. EPA announced that the MCIP meteorological processor that was used for the CMAQ simulations of the BRAVO Study tracers contained a major error. Using an updated MCIP processor that corrected the error, the 36-km tracer simulations demonstrated improved performance compared to simulations made with the flawed processor. (See Pun et al., 2004 in the Appendix for details.) To what extent this improved performance would have carried over to the finer grid resolution simulations is unknown since there was insufficient time and resources to evaluate this as part of the BRAVO Study. However, this question is being independently explored outside the BRAVO Study framework (Pun, personal communication).

Prior to discovering the inconsistencies in the comparison of simulated and measured tracer concentrations, there was every reason to believe that the application of CMAQ at high spatial resolution should have produced the best simulations of pollution fields throughout the domain and the most reliable source attribution results. The high spatial resolution CMAQ outperformed REMSAD in predicting the measured particulate sulfate concentrations for the two 10-day episodes, which would have been interpreted as further evidence of its superiority. Thus, the high spatial resolution CMAQ results might have been considered the standard against which REMSAD and the receptor modeling methods were to be judged. Under the circumstances of this BRAVO Study evaluation, however, the availability of the tracer data led to a different (and, under the circumstances, more appropriate) conclusion. While the resulting changes that were made to CMAQ do not guarantee reliable attribution results, they do demonstrate one of the ways that the credibility of the results was improved by the testing done in the BRAVO Study.

Other attribution methods that were affected by their performance in predicting tracer were several of the numerous combinations of trajectory methods and wind fields discussed in Chapter 9. Evaluation of these transport receptor models with tracer data was done in two ways. First the methods were used to identify the emission source areas for each of the individual tracer materials. Good performance in this test demonstrated that the wind fields were adequate for identifying the source locations. In the second series of tests, the receptor site concentrations of the tracer compounds from the various release locations were summed and the transport receptor methods were challenged to sort out how much came from the three emission source areas. This more rigorous test demonstrated that the successful methods were able to treat multiple sources and correctly estimate their individual contributions.

Tracer comparisons were not solely responsible for a decision to abandon some of the trajectory/wind field methods. Poor performance in simulating the REMSAD produced virtual atmosphere (see Section 12.4 below) was also considered in the decision to withdraw more than half of the trajectory/wind field methods. The removal of methods that performed poorly in tracer evaluations increases the credibility of the suite of attribution methods that remained, and it incidentally improved the overall consistency among the various surviving attribution results.

12.3 Phase II: Initial Application

Application of the attribution methods for Big Bend particulate sulfate afforded a number of opportunities for assessing the reasonableness of the results. Study period-averaged, monthly-averaged, and episode-specific estimates from each of the methods were intercompared. REMSAD and CMAQ-MADRID[1] modeled particulate sulfate and SO_2 were compared to corresponding measurements at Big Bend and at the numerous monitoring sites throughout the modeling domain. Spatial patterns across Texas of source attribution results by source region were also examined for the air quality simulation models to assess their reasonableness. Detailed descriptions and discussions of these various comparisons are in Chapter 9, and in the CIRA/NPS report (Barna et al., 2004) and the EPRI report (Pun et al., 2004), both of which are in the Appendix. This section consists of an overview of the comparisons that focuses on attribution method performance insights.

Table 12-1 contains the study period-averaged attribution results for the six methods that permit attribution by source region. One of the most striking differences among the methods is that both air quality simulation models agree that the eastern U.S. is the number one contributor to particulate sulfate at Big Bend over the study period, in contrast with the transport receptor models that indicate Mexico source contributions (including the *Carbón* plants) are the greatest contributors. The differences between the receptor and air quality models for these two source regions are about a factor of two. Also notice that REMSAD attributes much less to the *Carbón* power plants than the transport receptor methods. Aside from these differences the study period-averaged attribution results agree well across the various methods.

Table 12-1. Estimates of Big Bend's relative sulfate source attributions (in percent) by the various air quality and receptor modeling techniques. The relative contributions for each method are the average concentrations attributable to each source region divided by the average estimated concentration at Big Bend during the entire BRAVO period. (Note that the Mexico contribution estimates include contributions of the *Carbón* power plants.)

Source Region	CMAQ-MADRID	REMSAD	FMBR - MM5	FMBR - EDAS/FNL	TrMB - MM5	TrMB – EDAS/FNL	Range
Mexico	32	23	55 ± 14	52 ± 14	45 ± 20	48 ± 20	23-55
Carbón	-	14	26 ± 6	20 ± 7	23 ± 12	22 ± 12	14-26
Texas	19	16	24 ± 8	24 ± 12	19 ± 13	30 ± 20	16-30
Eastern U.S.	39	42	20 ± 10	24 ± 10	23 ± 9	16 ± 14	16-43
Western U.S.	6	9	0 ± 5	0 ± 9	14 ± 15	6 ± 17	0-14
Outside of domain	5	7					5-7

Examination of time plots of simulated and measured particulate sulfate for Big Bend provides some clues that might help explain why the air quality models indicate much less attribution to Mexico than the receptor methods. The air quality models tend to underestimate the particulate sulfate at Big Bend during the first two months when the flow is from Mexico. This is also true for other study sites that are near to the Mexico border, but

[1] As described in Chapter 8, the model that was used for the 36-km simulations of aerosol for the BRAVO Study differed from configurations of the CMAQ model provided by the U.S. EPA and used in the tracer simulations. It used a different diffusion algorithm (the Smagorinsky scheme) and the MADRID aerosol module.

not true of sites in eastern Texas. The shortfall in estimating the measured sulfate seems to be associated with flow from Mexico, suggesting that it may result from an underestimation of sulfate contributed by sources in Mexico.

A number of factors could cause this underestimation, including underestimated Mexican SO_2 emissions in the emissions inventory, a tendency for underestimated SO_2 to sulfate conversion or for overestimated deposition of either SO_2 or sulfate associated with flow from Mexico. Mexico emissions sensitivity analyses were conducted with CMAQ-MADRID to test whether the model would better estimate the measured sulfate when using twice the non-*Carbón* SO_2 emissions from the CMAQ-MADRID domain portion of Mexico and the upper limit of the estimated range for *Carbón* SO_2 emissions (about 1.6 times the lower emissions rate estimate). These higher emissions produced a better fit to the observations, though they did not remove the tendency for underestimation in the early months of the study for sites near Mexico. However the model performance was sufficiently improved by use of these higher emissions, in combination with scaling of boundary conditions as discussed below, that they were adopted for the CMAQ-MADRID attribution analyses summarized in Table 12-1. This may explain in part why the CMAQ-MADRID attribution for Mexico is slightly higher than the REMSAD estimate.

Comparisons of the spatial patterns of air quality model estimates of SO_2 to measured SO_2 provide another possible explanation for the tendency of air quality models to attribute more of the particulate sulfate to the eastern U.S. than the receptor models. REMSAD tends to overestimate the SO_2 throughout Texas by a factor of about 2, but sites on the far eastern edge have a much higher SO_2 over-prediction (e.g., at Big Thicket it's a factor of seven). REMSAD-estimated SO_2 compared to the CASTNet measured values throughout the eastern U.S. show an overestimation of about a factor of 2.5. On the other hand, comparisons of estimated to measured particulate sulfate in the BRAVO Study network and with CASTNet show the models performing much better with only minor overestimations (e.g., less than 20%).

The only reasonable explanation for having a substantial overestimation of SO_2, while having a pretty close estimate of sulfate, is some combination of compensating errors. For example, perhaps the model's SO_2 deposition rate and its SO_2 to sulfate conversion rate are both smaller than the true rates. Whatever the reason, the models estimated more eastern U.S. SO_2 on the eastern edge of Texas than was truly there. During periods with airflow from the east the model transports and converts some of this overestimated eastern U.S. particulate sulfate to Big Bend. This could explain why the air quality models occasionally overestimated sulfate levels when air parcels from the eastern U.S. reached the park.

The CMAQ-MADRID modeling domain is much smaller than the REMSAD domain. The plan was to have CMAQ-MADRID use the REMSAD air quality predictions at the domain edges as its boundary conditions, which in essence results in a one-way nesting of the two models. However, due to the large overestimation of the SO_2 at the boundary, REMSAD-modeled SO_2 and sulfate concentrations were adjusted by scaling to observations of SO_2 and particulate sulfate prior to their use as CMAQ-MADRID boundary conditions. This use by CMAQ-MADRID of measurement data to scale the boundary conditions should mitigate the magnitude of any over attribution of Big Bend particulate sulfate from the eastern U.S. Nevertheless, CMAQ-MADRID also exhibited an overestimation of SO_2 that was more pronounced towards the eastern edge of its domain.

The transport receptor models are not subject to the same issues that could have caused problems for the air quality models, since they don't use emissions data nor do they explicitly account for chemical conversion or deposition. However, they too can produce biased attribution results. If transport to the receptor location through one of the source area is often associated with transport through some other source area (referred to as collinearity), the statistical regression method can mistakenly attribute some of one area's contribution to the collinear other area.

The regression method can also have difficulties treating contributions that are so small that they are similar in magnitude to the sulfate measurement uncertainty. This would affect more distant source regions, which are also subject to greater uncertainty in predicted transport. To mitigate these problems the sizes of the more distant source areas were designed to be larger compared to the sizes of nearby source areas.

Transport regression methods tend to positively bias the attribution to the source areas with the least transport uncertainties (often those associated with the nearby sources) at the expense of the source areas with greater uncertainty, those from smaller or more distant sources. In other words the transport receptor models could over estimate the attribution of sulfate from Mexico's sources, which is a nearby source region in a frequent transport pathway, by mistakenly attributing some of the contributions of the more distant eastern U.S. emissions to Mexico during periods when transport pathways were over both source regions.

To summarize, at this point in the attribution process results were available from six methods that are from two broadly different categories of attribution approaches. The results were similar except for the important issue of which source region contributed the greatest to the particulate sulfate at Big Bend during the BRAVO Study period. The air quality models indicate that sources in the eastern U.S. are the greatest contributors, while the transport receptor models indicated that sources in Mexico are the greatest contributors. Reasonable explanations of possible biases for both approaches that could explain the attribution differences were developed, but these were qualitative so there was no basis to select one approach over another, or to justify a selection of any attribution result within the range of results from the six approaches.

12.4 Refined Attribution Approaches

Two innovative methods were developed specifically to provide a quantitative assessment of the possible biases in the BRAVO Study application of air quality modeling and transport receptor attribution approaches for particulate sulfate.

Synthesized air quality modeling is a hybrid method that starts with the attribution results from an air quality model and uses a statistical approach to identify multiplicative adjustment coefficients for each source region's attribution that would result in a best fit to the measured data. If the modeling was perfect the coefficients would all equal unity and the synthesized model would not change the results from the original model. The synthesized approach uses the type of information that originally identified the biases in the air quality model prediction in an objective way to quantitatively adjust the attribution results. For example the particulate sulfate underestimation when airflow was from Mexico resulted in coefficients greater than one for the attribution from sources from Mexico. This approach provides no explanation for biases; it only adjusts for them in an objective manner (Enting, 2002).

Unlike the transport receptor approach, which determines the best coefficients to fit the measurements at the receptor site, the synthesized approach uses measurement data from all of the sites over a several day period to determine a set of source area coefficients. Another difference between the transport receptor attribution approach and the synthesized approach is that the former explicitly incorporates only the temporal variations in transport while the synthesized approach, by starting with air quality model results, explicitly accounts for predicted variations in conversion chemistry and deposition. These differences should give the synthesized approach better fidelity (i.e., the ability to match temporal variations) than the transport receptor methods, not only with respect to matching ambient concentrations, but also with regard to characterizing temporally varying attribution by the various source regions. More complete descriptions of the synthesized REMSAD and CMAQ-MADRID attribution methods, their performance and results are available in Chapters 8, 9, and 11, and in the CIRA/NPS report (Barna et al., 2004), which is included in the Appendix.

Scaled transport receptor models are the second approach developed to assess attribution biases. In the case of transport receptor methods, the concerns were that attribution to certain source areas would be subject to large uncertainties because they were collinear with other source areas, or because they were responsible for small and variable contributions, or because of increased transport uncertainty for the more distant source areas.

The genesis for the scaled transport receptor methods was the desire to conduct a test of these concerns that would be specific to the BRAVO Study application of these methods. The test involved application of the various transport regression methods to the virtual conditions generated by the REMSAD model application for the BRAVO Study. In essence the REMSAD model can be thought of as a self-consistent virtual atmosphere where the fate of emissions from each source region is known in time and space. Using the same MM5 wind fields used by REMSAD, the transport receptor models were challenged to reproduce the source area attribution results of REMSAD when applied to the REMSAD-predicted concentrations at Big Bend. The underlying assumption is that the transport receptor approaches are subject to the same types of attribution biases in application to this virtual or predicted particulate sulfate data set as when applied to the measured particulate data set in the real world. Comparisons of the transport receptor model attribution results at Big Bend to the corresponding REMSAD results gave a measure of the average attribution biases for each source region, though just as in the synthesized air quality model, the causes of the biases are not a product of this testing.

The results of the testing became the basis for what are known as the scaled transport receptor attribution methods. This was done by simply multiplying the original daily transport receptor attribution results at Big Bend for each source region by the corresponding bias value for that source region (i.e., ratio of REMSAD attribution for a source region to the transport receptor attribution estimate for that source region when applied to the REMSAD virtual conditions). More detailed information about the scaled transport receptor attribution methods is in Chapter 9 and in the CIRA/NPS report (Barna et al., 2004), which is in the Appendix.

Clearly both of the refined attribution approaches (i.e., synthesized air quality modeling and scaled transport receptor methods) incorporate more information than the original methods from which they were derived. They do this in ways that were designed to improve the estimates by addressing possible deficiencies in the design and performance of the original approaches. In other words, these two approaches are expected to yield better attribution results than the original approaches.

However, both refined approaches incorporate much of the same information, which though it is included in different ways, nonetheless make the methods less independent than the original air quality modeling and transport receptor models. Therefore it's reasonable to expect that the two approaches will yield similar attribution results and no great amount of additional credibility should be given to the results if they are similar, though legitimate credibility questions may be raised if their results are dissimilar.

Table 12-2 contains the attribution results of the refined approaches. The methods do agree more closely than the attribution results from the original methods (see Table 12-1) with all methods now showing Mexico to be the largest contributor of particulate sulfate during the BRAVO Study period and the eastern U.S. being the second largest contributor.

Table 12-2. Estimates of Big Bend's relative sulfate source attributions (in percent) by the refined approaches. The source attribution results by the various air quality and receptor modeling techniques have been adjusted to correct for identifiable biases. The relative contributions for each method are the ratios of the average source attributions to the average estimated concentration at Big Bend during the entire BRAVO period. (Note that the Mexico contribution estimates include contributions of the *Carbón* power plants.)

Source Region	Synthesized CMAQ-MADRID	Synthesized REMSAD	Scaled FMBR – MM5	Scaled TrMB – MM5	Range
Mexico	38 ± 1.7	39 ± 2.3	43	34	34-43
Carbón	-	23 ± 1.8	22	23	22-23
Texas	17 ± 1.3	16 ± 1.2	17	16	16-17
Eastern U.S.	30 ± 1.2	32 ± 0.5	24	25	24-32
Western U.S.	8.5 ± 1	6 ± 1		11	6-11
Outside of domain	6.4 ± 1	7 ± 1			6-7
***Unaccounted Mass**			17	14	

* The Unaccounted Mass is the difference between the scaled source attribution results and 100%. For the scaled FMBR this is primarily due to contributions from the boundary conditions and western U.S., for TrMB this is primarily due to contributions from the boundary conditions.

Attribution results from the refined approaches for each of the source regions were all within the range defined by the results of the original methods for the corresponding source regions (shown in the last column of Table 12-1). Assuming that the refined approach results are better estimates of the true attributions, the range of results from the original approaches bracketed the true attribution. Had there been no refinement phase of the attribution process, the best estimates available would have been the range of results from the tracer-tested air quality and transport receptor methods. The refinement improved the certainty of the particulate sulfate attribution results by narrowing the range of the best estimates.

Given the narrow range of results from the refined approaches, there is little reason to select a single value within the range as the best estimate for the study period averaged attribution results. However, for purposes of examining higher time resolution attribution results, a best method was selected. The synthesized CMAQ-MADRID method was selected as the method with the best chance of having good fidelity with respect to its source attribution. There are several reasons for making this selection. The transport receptor approaches were not thought to be a good choice for high time resolution attribution because they apply a best-fit average coefficient to each day's transport. The scaled transport regression uses only a single bias adjustment for each source region so it too cannot be expected to match the attribution fidelity of the air quality models. Among the air quality models, CMAQ-MADRID has more sophisticated chemistry and produced better model performance statistics, both in its initial application and as refined, than did REMSAD. In the BRAVO Study application of CMAQ-MADRID, measurement data were used to improve boundary conditions. Since the CMAQ-MADRID domain is smaller than the REMSAD domain, these measurement-scaled boundary values are closer to Big Bend, so CMAQ-MADRID simulations are expected to be less biased compared to REMSAD simulations.

CMAQ-MADRID simulations did not separate the particulate sulfate attribution for the *Carbón* power plants from their estimates for Mexico. In order to examine higher time resolution attribution that included estimates for the *Carbón* power plant, the daily synthesized REMSAD-determined *Carbón* fraction of Mexico's contribution was used to subdivide the corresponding synthesized CMAQ-MADRID estimated contributions for Mexico. The attribution results of synthesized CMAQ-MADRID modified in this way to include attribution estimates for the *Carbón* power plants are referred to as the "BRAVO Estimates."

Figure 12-2 is a smoothed time plot of measured and BRAVO Estimates of particulate sulfate for Big Bend that indicates the BRAVO Estimates of source region attribution. There are a number of features of this plot that are relevant to the topic of attribution uncertainty. Notice the attribution variability on a cycle of just a day or two. Any one of the six source regions may be the greatest contributor on a particular day. Some of the source regions infrequently contribute substantially to Big Bend particulate sulfate (e.g., western U.S.), while other source areas more frequently contribute substantially (e.g., Mexico and *Carbón*). Also there seems to be a tendency for the largest peaks to include substantial contributions by the eastern U.S. and/or Texas.

It is reasonable to assume that these highly variable attribution patterns are typical of the sulfate attribution for Big Bend during the late summer and early fall time period (see discussion of haze and source influence variations in Section 12.6). That being the case, then any four-month average attribution result is sensitive to the specific period of time selected. If the BRAVO Study period were shifted by several days in either direction or shortened (or lengthened) by several days, the average contributions would change. The same four months in another year are also likely to have a somewhat different attribution pattern than in 1999. The range of attribution that is associated with selection of alternate late summer and early fall time periods (i.e., either the same period for a different year or a changed period in 1999) are likely to be much greater than the BRAVO Estimates attribution uncertainties for the BRAVO Study period. Assuming that the purpose of the BRAVO Study assessment is to determine how much the various source areas are contributing to Big Bend particulate sulfate in a typical or average late summer and early fall time period, even perfect attribution results for any particular period (e.g., the BRAVO Study period) would be an uncertain estimate of a multi-year averaged result. In that sense, the uncertainties associated with the BRAVO Estimates are thought to be modest when compared with the apparent magnitude of source contribution temporal variations.

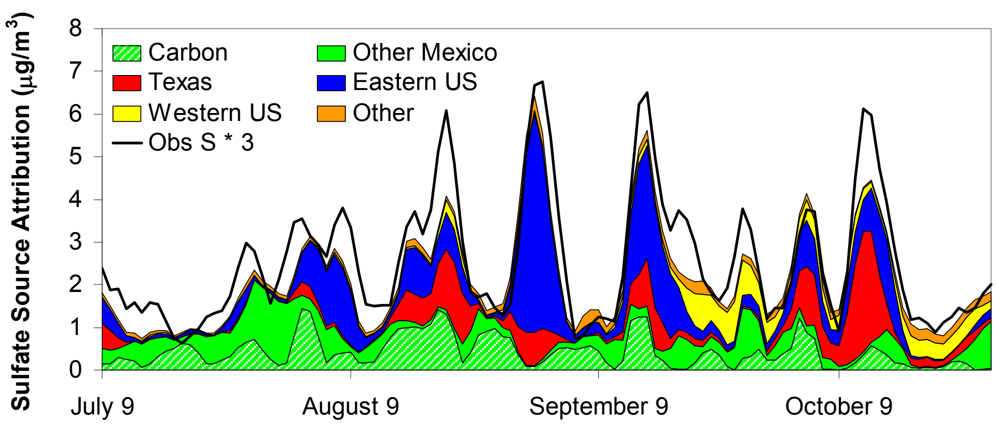


Figure 12-2. *Smoothed daily BRAVO Estimates of contributions to Big Bend particulate sulfate by source region.*

12.5 Haze Source Attribution

While particulate sulfate compounds are major contributors to Big Bend haze, they are not the only contributors and their relative contributions vary over time, as discussed in Section 6.3. Particulate sulfate attribution results also vary over time, as shown in Figure 12-2. To estimate the particulate sulfate source regions' contributions to the haze, each day's BRAVO Estimates were applied to apportion the light extinction associated with that day's measured sulfate concentration. Figure 12-3 shows the absolute and percent contributions by particulate sulfate source regions to haze at Big Bend during the BRAVO Study period. Rayleigh scattering, light scattered by particle-free air, is shown as a constant 10 Mm^{-1} in the top figure. The contributions by the other non-sulfate particulate matter are combined in these time plots.

According to the BRAVO Estimates, SO_2 sources in Mexico generally contributed between 5 Mm^{-1} and 15 Mm^{-1} of the light extinction, corresponding to less than 20% of the total on most days during the study period. However, during some of the smaller haze episodes in July and August their relative contributions were 30% to 40% of the average light extinction. SO_2 sources in Texas contributed less than 5 Mm^{-1} on most days of the study period, but during one of the periods of higher contribution Texas was responsible for nearly 30 Mm^{-1}, or about 40% of the light extinction on the haziest day in October. SO_2 sources in the eastern U.S. also contributed less than 5 Mm^{-1} on most days of the study period, but during the two haziest episodes its sources contributed about 50 Mm^{-1} and about 30 Mm^{-1}, respectively, corresponding to about 50% and 30% of the total light extinction.

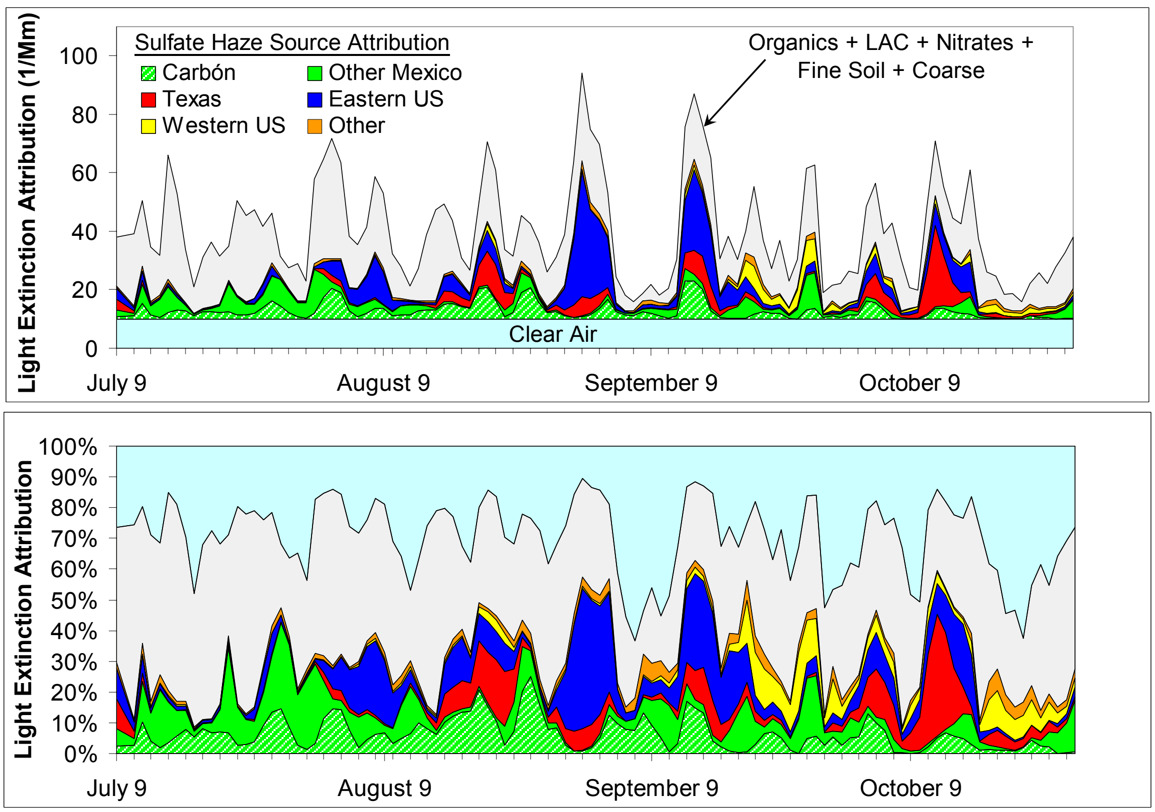


Figure 12-3. *Estimated contributions to light extinction by various particulate sulfate source regions. The top plot shows the absolute haze contributions by the various particulate sulfate sources as well as the total light extinction level (black line) and Rayleigh or clear air light scattering. The 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.*

The pie diagrams in Figure 12-4 illustrate the particulate sulfate contributions by various source regions to light extinction for the study period's haziest days compared to the study period's least hazy days. The numbers of 1/5 haziest days per month of the BRAVO study from July 9th through October are 1, 8, 10, and 4; while the numbers per month for the 1/5 least hazy days are 3, 1, 10, and 9, respectively.

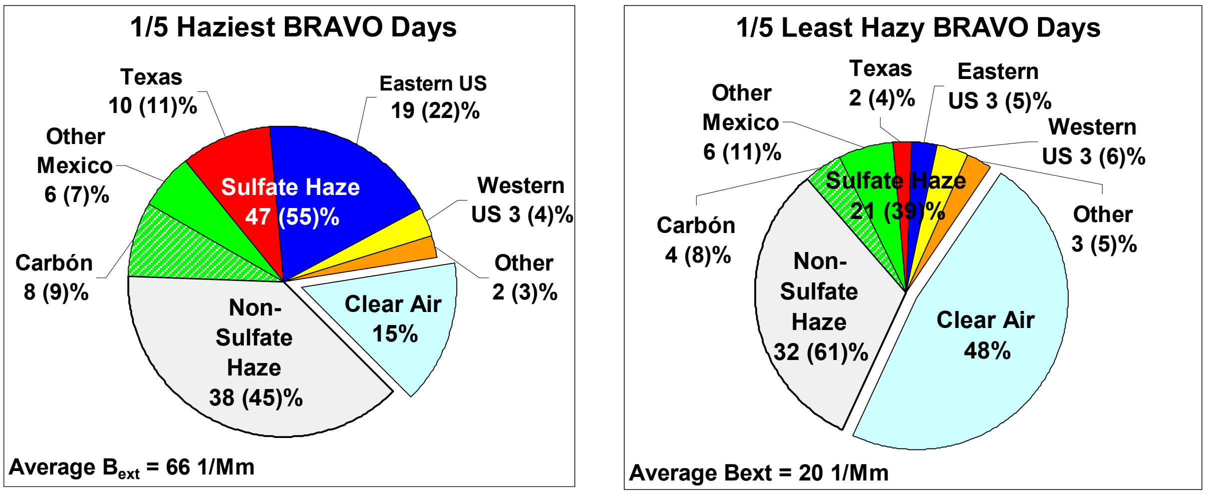


Figure 12-4. *BRAVO Estimates of contributions by particulate sulfate source regions to Big Bend light extinction levels for the 1/5 haziest days and the 1/5 least hazy days of the BRAVO Study period. Percent contributions to particulate haze (non-Rayleigh light extinction) are shown parenthetically.*

As shown, particulate sulfate contributions to light extinction were about twice as high 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%). 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 compared to the least hazy days. The *Carbón* power plants' contributions to light extinction at Big Bend also increased on the haziest days compared to the least hazy days (8% compared to 4%). However, the relative contributions of the other SO_2 sources in Mexico and the sources in the western U.S. were unchanged on the haziest compared to the least hazy days of the study period (6% and 3% respectively).

12.6 Big Bend Haze Conceptual Model

The conceptual model printed in **bold type** *is incorporated into the text that helps to explain and justify the conceptual model.*

Figure 12-5 shows the five-year composite (1998 through 2002) of the light extinction (sum of light scattering and absorption) throughout the year, from measurements made every three days at Big Bend National Park. This figure demonstrates seasonal variations of the total haze levels and of the composition of the particles responsible for haze. **Sulfates, organic carbon, and coarse mass particles are responsible for most of the Big Bend haze** (see the pie diagrams in Figure 12-5). **Particles composed of light absorbing carbon (LAC), soil, and nitrates are relatively minor contributors to Big Bend haze. Spring and early summer is the period of greatest haze, late summer and fall have episodes of high haze interspersed with relatively clear periods, and winter is generally the clearest time of year. During spring and early summer a combination of carbonaceous (i.e., organic and light absorbing carbon), sulfate and coarse particulate matter contribute substantially to the haze, while during late summer and fall sulfate particulate compounds are a larger fraction of the haze.**

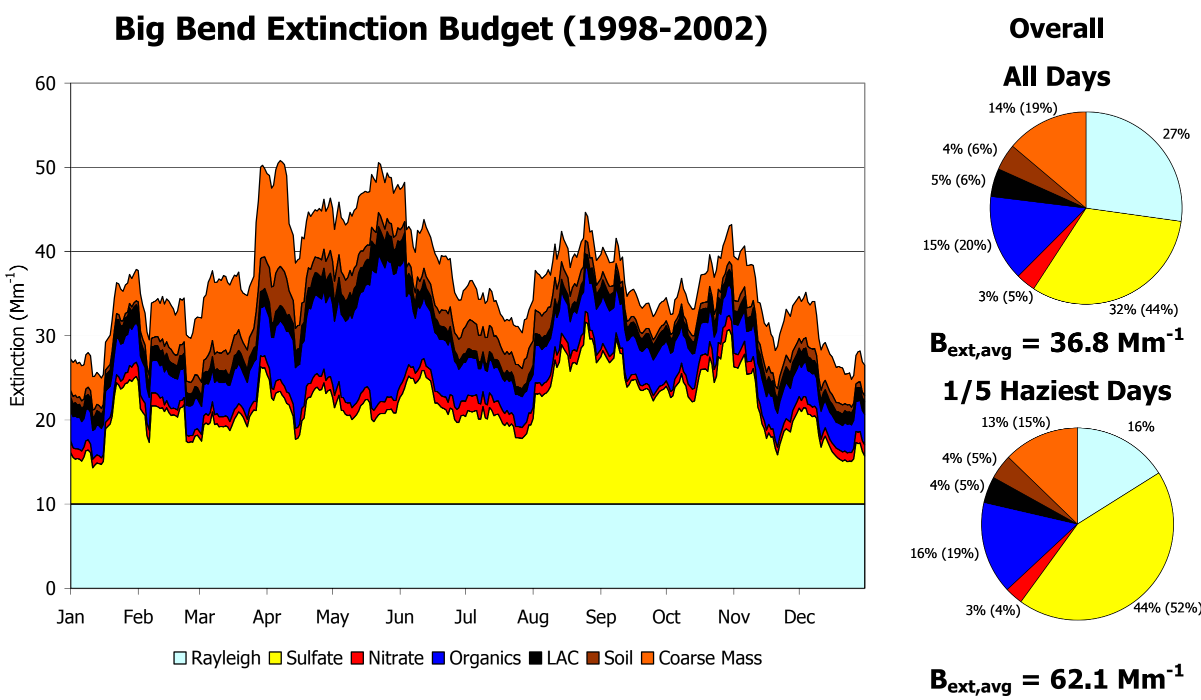
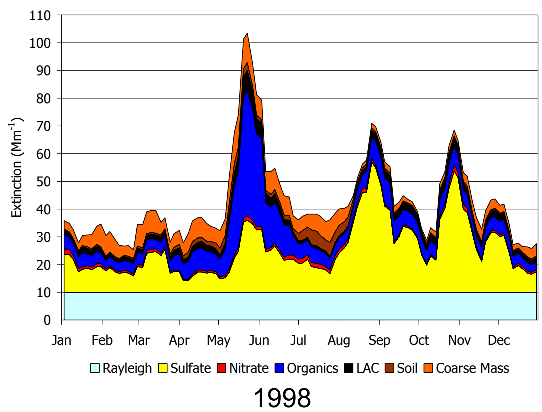
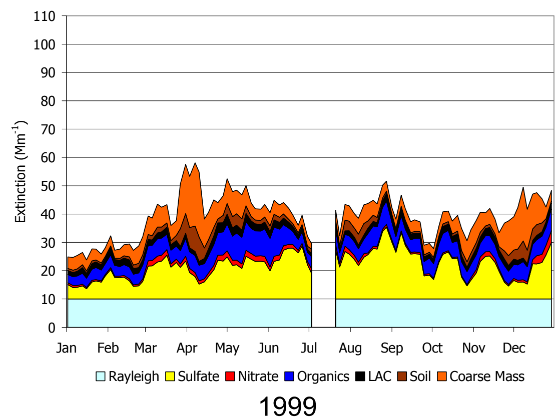
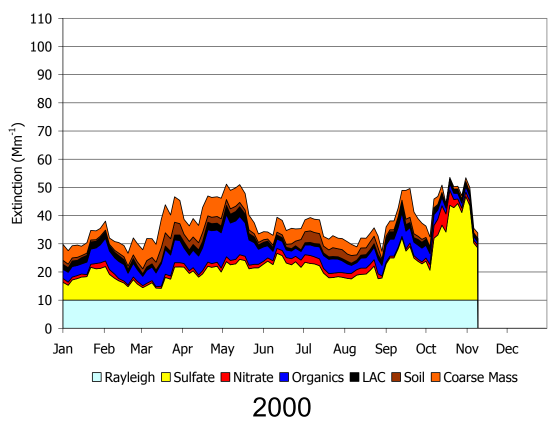


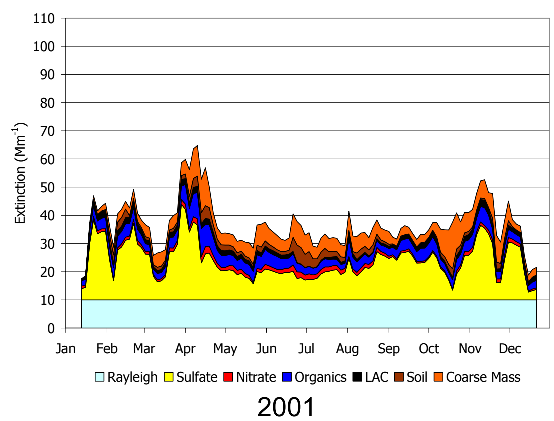
Figure 12-5. *Big Bend National Park five-year composite contributions to haze by components. The time plot was smoothed using a 15-day moving average. The pie graphs show the average percent contributions to light extinction for all days (top) and the annual haziest 1/5 of the days (bottom). Percent contributions to particulate haze (the non-Rayleigh light extinction) are shown in parentheses.*

Figure 12-6 contains the five individual year plots that are summarized in Figure 12-5. Particulate components that contribute to Big Bend haze have large interannual variations in magnitude and timing, as shown in these plots. The broadness of the multi-year averaged springtime peak of carbonaceous/sulfate/coarse particle haze in Figure 12-5 is in fact a composite of different patterns, some with narrow peaks (e.g., 1998, a year of unusually heavy smoke impacts), others with broader periods with some combination of elevated carbonaceous or sulfate or coarse particulate concentrations. Similar interannual variations are also evident in the summer and fall periods when elevated particulate sulfate contributes to haze episodes.









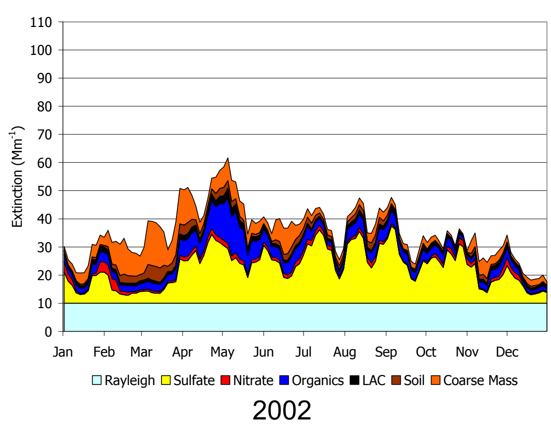


Figure 12-6. *Big Bend extinction budget time plots for individual years. These time plots were smoothed using a 15-day moving averages.*

Big Bend is remotely located relative to the major sources that contribute to the particulate matter responsible for its haze. That is not to say that occasional visibility impairment from nearby disturbed soil, wind-suspended dust, or smoke from local fires does not occur, but these are not the predominant sources of haze at Big Bend. 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 arrives 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. Histograms of the five-year average and each individual year's monthly residence times for different discrete potential source regions in the U.S. and Mexico are shown in Figure 12-7.

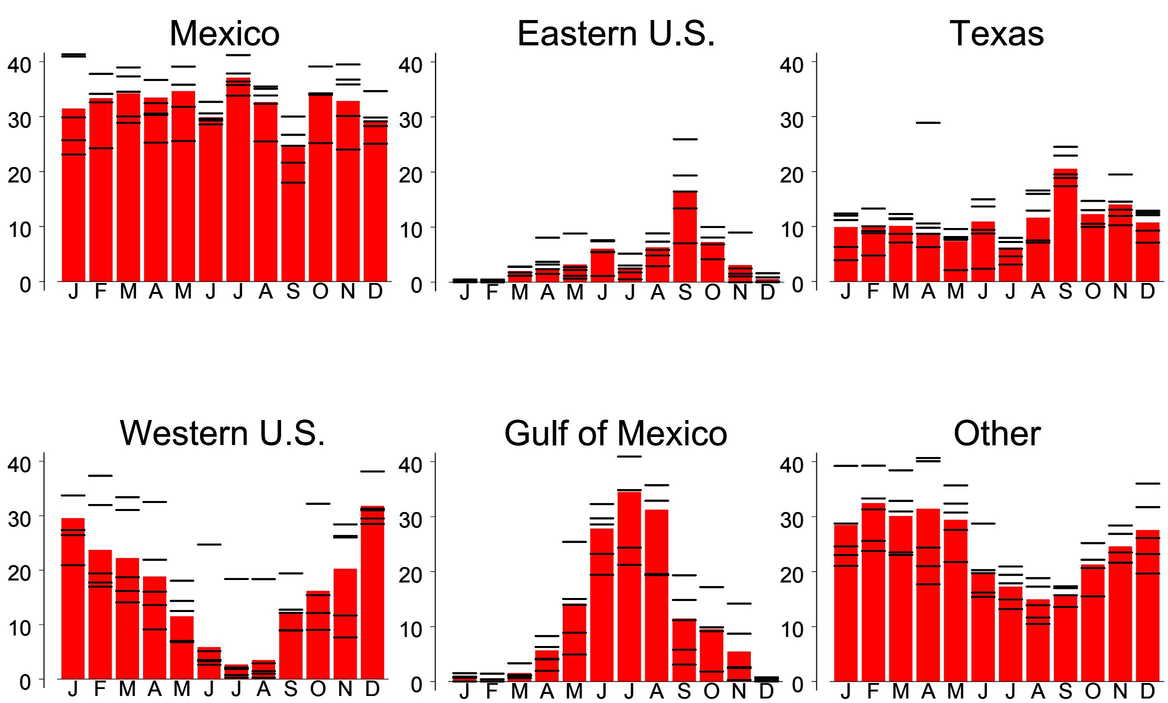


Figure 12-7. *Monthly fractions of time that air parcels spend in a region prior to arrival at Big Bend in 1998 to 2002 are shown as solid bars, based on five-day back trajectory calculations. The short horizontal lines indicate the values for each of the five yeasr that make up the five-year average bars. The plot labeled "Other" represents locations beyond the five regions shown here.*

Just as the compositions and concentrations of particles responsible for Big Bend haze have considerable interannual variation, the individual year trajectory residence time histograms in Figure 12-7 show that **there is considerable interannual variability in the combinations of source regions that are likely to contribute to Big Bends haze at any time of year.**

Coarse mass and fine soil contributions to haze at Big Bend tend to be greatest between February and July most years. Airflow during the first few months of that period is from the west, including northwestern Mexico and southwestern U.S., regions that contain low ground cover playas and other areas that are subject to wind-blown dust events and are the likely sources of some, perhaps many, of the periods with high coarse mass and fine soil in the early spring. There is at least one Asian dust event over North America (April 26, 2001) that resulted in quite high coarse mass and fine soil at Big Bend. Other episodes with Asian dust at Big Bend are likely, but don't appear to be frequent. During the summer, coarse particles (predominantly soil) and fine soil are frequently transported by winds from the east, from Africa across the Atlantic Ocean and Gulf of Mexico to Big Bend and the southeastern U.S. and northwestern Mexico. This is routinely seen by satellite remote sensing (Herman et al., 1997), by back trajectory analyses (Gebhart et al., 2001; Prospero, 1995), and confirmed by the characteristic elemental composition of African dust compared with dust from the U.S. (Perry et al., 1997)

Carbonaceous (organic and light absorbing carbon) particles contribute most to Big Bend haze during the spring and early summer. Smoke from large seasonal fires in Mexico and Central America has been documented as the source of some of the largest of these episodes and may be responsible for much of the carbonaceous particulate matter contributions to haze during this time of year (e.g., May 1998). Secondary organic carbon particles (i.e., those formed in the atmosphere from gaseous organic compounds) also contribute to Big Bend haze, as was shown by carbon speciation special studies during the BRAVO Study (Section 5.2.3).

Sulfate compounds are often the largest contributor to particulate haze any time of year, but especially so in the late summer and fall. Particulate sulfate at Big Bend originates from numerous SO_2 sources across various geographic regions. No single SO_2 source or source region is a dominant contributor to seasonal or monthly-averaged particulate sulfate at Big Bend. However, some of the multi-day-long episodes of elevated particulate sulfate concentrations are predominantly from a single source region, as shown in Figure 12-2.

During the late summer and fall, the most intense haze episodes are associated with relatively infrequent airflow patterns that can transport a substantial fraction of the particulate sulfate at Big Bend from sources in the United States. SO_2 emissions sources in Texas and in states east of Texas contribute more particulate sulfate during intense haze episodes than do the states west of Texas. Emissions from eastern U.S. source areas can be transported to Big Bend directly across Texas from the east or northeast, or more to the south over the Gulf of Mexico where their paths turn to the northwest and cross either northern Mexico or southern Texas.

Frequent air flow from the southeast during the spring, summer and fall results in contributions of particulate sulfate from SO_2 sources in northeastern Mexico that are much more frequent than those from the United States. As a result of being frequently upwind, SO_2 sources in Mexico are thought to contribute more on average over a year to Big Bend particulate sulfate than do U.S. sources. As the largest SO_2 emission source in a frequently upwind region, the *Carbón* power plants, located in Mexico about 225 km east-southeast of Big Bend contribute more than any other single facility to average particulate sulfate concentrations at Big Bend. SO_2 sources in Mexico, including the *Carbón* power plants, do not seem to be primarily responsible for any of the most intense haze events in the late summer and fall, though they contribute to the haze during some of these episodes. (See Figure 12-2.)

Clearest visibility conditions at Big Bend occur most frequently in the winter, when flow is most often from the north or west over areas of relatively low emissions density, and least frequently in the spring when airflow is from the southeast and can include smoke impacts from seasonal fires in Mexico and Central America. During the summer and fall, airflow from the southeast that brings marine air from the Gulf of Mexico rapidly over northeastern Mexico is associated with the clearest visibility conditions during those seasons, as shown in Figure 12-8.

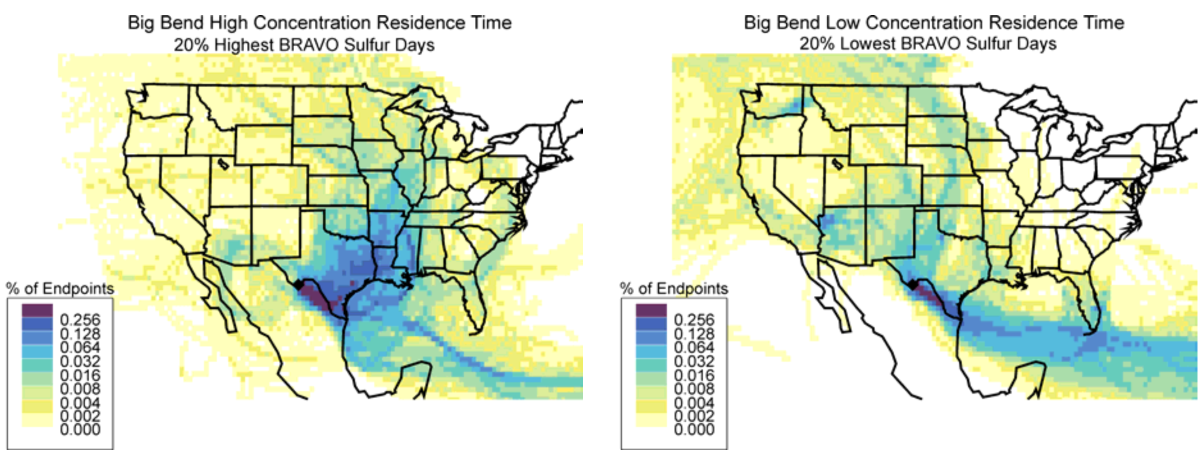


Figure 12-8. *Percent of time that air parcels en route to Big Bend spent over various locations during five-day trajectories for periods with the 20% highest concentrations of particulate sulfate compounds at Big Bend (left) and for the periods with the 20% lowest concentrations of particulate sulfate compounds at Big Bend (right) during the BRAVO Study period of July through October 1999.*

12.7 Lessons Learned and Recommendations

The BRAVO Study is the most recent and in many ways the most extensive of a series of remote-area visibility impairment source attribution studies (Beck, 1986; Malm et al., 1989; Richards et al., 1991; Watson et al., 1996; Pitchford et al., 1999). Some aspects of the study effort proved to be more important than others, some results were anticipated while others were surprising, and some questions were adequately addressed though others were not. The purpose of this section is to provide a perspective from the BRAVO Study technical team to those who are contemplating future visibility or aerosol attribution studies, and to suggest topics for future investigation concerning Big Bend haze conditions. The section is presented as a series of bullets organized by topic area.

12.7.1 Overall Design and Management

- Study management attempted to involve non-government stakeholders from the beginning of the study with varying success. The electric utility industry, including the Electric Power Research Institute (EPRI), became actively involved and funded contributions to the technical program from the onset. Environmental organizations tracked the program by participating in meetings and conference calls.

- The greatest disappointment with regard to stakeholder involvement was our failure to convince officials from Mexico to allow conduct of measurements, tracer release and emissions sampling south of the border. Efforts were undertaken to minimize the impact of this limitation on Big Bend attribution findings, however opportunities were lost to better specify Mexico's source impacts at Big Bend and to improve our understanding of impacts in Mexico by emission sources of both countries.

- The benefits of stakeholder involvement include improved study credibility that comes from a transparent planning and management process, the ability to effectively respond to stakeholder technical issues while resources and opportunities are still available, and the chance that perhaps some of the stakeholders who might otherwise have been critical of some aspects of the study and its results would instead be well informed spokesmen for the study.

- The downside of active stakeholder involvement is the considerable time and cost associate with the coordination, communications, and responding to issues of the larger group of participants. Overall the benefits outweigh the cost.

- The study was designed with an emphasis on the source attribution of haze caused by particulate sulfate during the late summer and fall. The reasons for this have been specified elsewhere in this report. Future SO_2 emissions reductions will ultimately increase the relative importance of the non-sulfate particulate matter on Big Bend haze, with the result that additional haze investigations emphasizing carbonaceous and crustal particulate matter impacts may be necessary.

- The four-month study period was chosen to allow us to investigate conditions during periods of both southeasterly flow and northeasterly flow to Big Bend. A less expensive approach, considered during the planning process, would have been to have two disjoint month-long study periods (e.g., July and October). The longer continuous study period proved to be important because it showed that there is a high degree of variability in the superposition of the contributions of various source regions (see Figure 12-3) that might not have been apparent with shorter study periods. An even longer study period (e.g., April – October) would have been better.

12.7.2 Field Measurements

- The air quality monitoring plan included an array of sophisticated monitoring techniques at Big Bend that improved our understanding of the aerosol and resulting haze at the receptor sites (the six sites relatively near Big Bend with 6-hr sampling periods for tracer, particles and SO_2) plus an extensive network of 24-hour particle, SO_2 and tracer monitoring sites in the region to support spatial analyses methods and air quality model performance evaluation, with an emphasis on sulfur species. This design generally worked well and supported the data analysis and modeling as planned.

- The tracer release/monitoring study was the most costly component of the study. Although the tracer release portion of the tracer study performed very well, a number of the samplers performed poorly and the analysis throughput was insufficient, resulting in extremely poor data recovery. During the first month of the study period, the decision was made to concentrate on maintaining good data recovery at the six 6-hour sites at the expense of 1-hour and some 24-hour sampling. In spite of the high cost and disappointing performance, the tracer data measured at the 6-hour monitoring sites proved valuable for the evaluation of the attribution approaches, which in this application was critical to the attribution results.

- Several major components of the study were substantially under-utilized including the airborne monitoring and the chemical source profile sampling/analysis. Both were successful in gathering meaningful data, but neither data set was utilized in the subsequent assessment of the causes of Big Bend haze. The chemical source profiling was conducted to support the use of trace component types of receptor modeling, which proved nonproductive. The difficulty of integrating airborne data with ground-based measurements severely limited their potential uses.

- Trace component types of receptor modeling (e.g., CMB) were not productive because the trace particulate compositional data were not sufficiently sensitive to support the receptor modeling at Big Bend where concentrations of trace constituents were near or below detection limits, and $PM_{2.5}$ mass is often dominated by secondary aerosol from a mixture of distant precursor sources. Similarly, the organic carbon speciation sampling was not sufficiently sensitive to quantitatively measure the important marker species. To support this type of receptor attribution analyses for locations that are at great distances from significantly contributing source regions, higher sensitivity compositional analyses are needed.

12.7.3 Source Attribution Approaches

- By design, the BRAVO Study employed a number of different approaches for source attribution assessments including air quality simulation models, transport-regression approaches, and a spatial distribution analysis. The advantages of using multiple techniques include utilization of more of the available data, and the creative synergy resulting from collaboration among different analyst organizations. These advantages promoted more thorough assessments, and provided the ability to apply a weight of evidence methodology.

- The air-quality modeling and transport-regression approaches are featured in the report since they are the basis for its attribution results. However, a number of qualitative and descriptive techniques (e.g., particulate sulfur animation maps, trajectory and wind field animation) were of significant help in formulating the conceptual models that investigators could then compare to results of the more quantitative attribution approaches. Examples of these are shown in Section 8.6 and in the CIRA/NPS report (Barna et al., 2004), which is included in the Appendix.

- The BRAVO Study emission inventory included the continuous emissions monitoring (CEM) data for large point sources in Texas and surrounding states (not available in Mexico) with daily time resolution, where normally only annual averages are used with surrogates to provide temporal variations. The BRAVO Study EI also included the development of a northern Mexico emissions inventory because at the time there were very limited alternatives. In spite of these innovations, additional efforts are needed to assess and improve existing inventories so that more accurate and credible emissions data can be generated.

- The original CMAQ modeling plan called for the simulation of two 10-day episodes at high spatial resolution. This was changed to a lower spatial resolution simulation (36km grid dimensions compared to 12km nested to 4km) of the entire study period because of tracer-simulation performance issues. This tradeoff of less spatial resolution for a longer simulation period (computational resource limitations did not permit both) was fortuitous in that it permitted CMAQ simulations of many more of the highly variable mixtures of influence of the various source regions.

- Another consequence of the original plan of applying the CMAQ model at the high spatial resolution was the need to select a modestly sized domain centered on Texas. Unfortunately this resulted in having much of the eastern U.S. source region, which proved to be a significant contributor to Big Bend haze during the BRAVO Study, outside of the model domain.

- To mitigate modeling biases, air quality measurements were used to adjust REMSAD concentrations used to prescribe CMAQ boundary conditions. This in essence resulted in a one-way nesting of CMAQ into REMSAD with air quality data assimilation at the boundary of the nested domain. Future model applications should consider using this type of approach for air quality data assimilation during nesting.

- Horizontally and vertically varying monthly-averaged global model estimates of SO_2 and sulfate for a different year (2000) were used as boundary conditions for the REMSAD model in place of default, spatially constant global background values. This improved overall performance by reducing haze estimates attributed by the model to sources beyond its domain boundary by about a factor of three on average and proved more consistent with estimates calculated by other techniques. Future modeling on this scale should be conducted using higher-time-resolution-coincident global model predictions for boundary conditions

- Evaluation of the transport-dispersion components of air quality simulation models, trajectory-wind field combinations, and transport regression methods using tracer data proved to be of great value. Similar use of tracers should be a part of any substantial future attribution program until all methods used can routinely pass such challenges.

- Results of the evaluation of the air quality model performance in simulating SO_2 and particulate sulfate at monitoring sites throughout the domain identified some inconsistencies that were not resolved. Future studies should expand on these comparisons to include other particulate components, precursor gases and oxidants at numerous sites throughout the modeling domain in the hopes of a better understanding and an ability to correct inconsistencies.

- Evaluations of both the meteorological and air quality models against meteorological observations uncovered a number of inconsistencies that were not resolved, including wind-field (MM5, EDAS, and FNL) biases compared to the radar wind profiler data, and substantial REMSAD cloud and precipitation simulation biases compared to satellite imagery and surface precipitation measurements. Given the fundamental importance of meteorology to atmospheric processes, additional assessments and improved performance by meteorological models are needed.

- Evaluation of the transport regression approaches using REMSAD output as a sort of virtual ambient data set provided valuable insights concerning the nature and magnitude of uncertainties associated with this type of attribution approach. Evaluations using model output as receptor model input data are worth repeating in subsequent studies.

- The synthesis inversion approach developed for the BRAVO Study provided a way to check for and adjust for biases in source region attribution results from the air quality simulation models by statistically fitting the ambient measurement data. This approach produced what appear to be very reasonable results for this study and so its use is recommended. BRAVO Study time and resource limitations did not permit more than speculation concerning the causes of the air quality model attribution biases. Additional work should be done to better understand the reasons for these biases.

12.7.4 Results

- The most surprising BRAVO Study attribution finding was that an infrequently occurring set of conditions that promotes air flow over SO_2 source regions in the eastern U.S. including eastern Texas was associated with and appears to be responsible for most of the worst haze conditions during the fall at Big Bend. This result could easily be missed by aggregated attribution results (e.g., on a monthly or seasonal basis).

- The high temporal variability of the mix of attributions among the source regions during the study period (Figure 12-2) was also a surprising result with important implications for any attempt to understand how haze levels might change in response to emission changes in any of the source regions (a topic beyond the scope of this report).

- Both the Big Bend haze levels and the frequencies of flow from the different source regions vary considerably from year to year, which undoubtedly complicates efforts to relate long-term haze to regional emission trends.

- Northeast Mexico is frequently upwind of Big Bend from spring through fall, so the greater consistency of impacts by SO_2 sources in Mexico during the study was not surprising.

- Big Bend haze associated with airflow from the southeast over northern Mexico can also include significant contributions from the U.S. during the late summer and fall when U.S. emissions are carried south over the Gulf of Mexico or through Texas to northeastern Mexico en route to Big Bend. An observer located at Big Bend during these episodes, or a data analyst who is not considering long-range transport, could mistakenly conclude from the direction of air flow at Big Bend that the haze is exclusively from sources in Mexico.