

10. SOURCE ATTRIBUTIONS BY AMBIENT DATA ANALYSIS

The BRAVO Study used a variety of methods, as described in Chapter 8 to attribute components of Big Bend area particulate matter to various source regions or source types. The methods used fall into two major categories: (1) methods based principally on the analysis of ambient measurement data, sometimes supported by trajectories derived from meteorological measurements or wind field models, a category of analysis that is often called “receptor modeling,” and (2) methods based principally on air pollution simulation models. At the end, the BRAVO study also merged the two approaches to arrive at a set of hybrid models.

This chapter describes the analyses performed, and results obtained, from application of methods in the receptor modeling category. These data-based attribution methods were described in Sections 8.1 and 8.3. The specific approaches whose attribution applications and findings are described in this chapter include the following:

- The TAGIT tagged-tracer approach, which provided estimates of the contributions of local sources to sulfur concentrations at Big Bend;
- Two factor-analysis based approaches – one using exploratory factor analysis (FA) and the other using empirical orthogonal function (EOF) analysis – which provided qualitative insight into the relative contributions of different types of sources and different source regions to PM_{2.5} and particulate sulfur concentrations at Big Bend;
- Three methods that rely on analysis of transport trajectories – one based on back trajectory residence time analysis and two air mass history-based receptor techniques (Trajectory Mass Balance, TrMB, and Forward Mass Balance Regression, FMBR) – to provide both qualitative and quantitative insight into the contributions of various source areas to sulfur concentrations at Big Bend.

Attributions derived through applications of air quality simulation models and hybrid approaches will be described in Chapter 11. Interpretation and synthesis of the attribution findings presented in this chapter and in Chapter 11 will take place in Chapter 12.

10.1 Sulfur Attributions via TAGIT

The TAGIT (Tracer-Aerosol Gradient Interpretive Technique) data analysis method was used to attribute particulate sulfur and sulfur dioxide at the five BRAVO 6-hour sampling sites in and near Big Bend National Park (see Figure 3-3 for locations) to local and regional sources. As described in Section 8.1.1 and in more detail by Green et al. (2003), TAGIT is a receptor model that can attribute primary or secondary species associated with a source whose emissions are “tagged” by an artificial or intrinsic tracer. For each sample period, the background concentration of the species of interest, such as particulate sulfur, is determined by averaging the concentrations of that species at nearby sites that do not have tracer concentrations that are significantly above background. This background for each sample period is then subtracted from the concentration of the species of interest at impacted receptor sites for corresponding sample periods. The difference is the concentration

attributable to the tagged source. A necessary assumption is, of course, that the source of interest does not contribute to the background

The initial application of TAGIT used the concentrations of the perfluorocarbon tracer oCPDCH, which was released at Eagle Pass, Texas, about 32 km northeast of the *Carbón* I and II power plants in Coahuila, Mexico. The Eagle Pass release location was originally established as a potential surrogate for the *Carbón* plants. However, the oCPDCH concentration pattern did not correlate well with SO₂ from *Carbón* for individual 6-hour sampling periods ($|r| < 0.12$ at all sites, except for $r = 0.34$ at San Vicente). Thus it was concluded that the perfluorocarbon tracer from Eagle Pass did not represent the emissions from the *Carbón* plants well and would not be suitable for an attribution analysis by TAGIT. (Results of this exercise are presented in Green et al., 2003.)

The TAGIT approach was then applied using SO₂ as a tracer for “local” sources. In this approach, the SO₂ concentration at the 6-hour site with lowest SO₂ for each sampling period was assumed to characterize regional SO₂ and particulate sulfur concentrations for the 6-hour period. The differences between SO₂ and particulate sulfur levels at this site and the SO₂ and particulate levels at the other sites were then taken to represent the “local” contribution, which is presumed to be dominated by emissions from the *Carbón* power plants (although other smaller sources may also play a role at times).

The results of this second analysis are summarized in Table 10-1. Average contributions of local sources to particulate sulfur at the five sites¹ were estimated to range from about 4% to 14%. On the other hand, the local contribution to SO₂ attribution was estimated to range from 61% to 75%.

Table 10-1. Average study-period TAGIT attributions of particulate sulfur, SO₂, and total sulfur (\pm the standard errors of the means) to local source emissions.

	Big Bend	Ft. Stockton	Marathon Ranch	Persimmon Gap	San Vicente	All
Particulate sulfur attribution (ng/m ³)	136 \pm 18	38 \pm 21	95 \pm 21	138 \pm 20	42 \pm 21	91 \pm 9
% of measured particulate sulfur	14 \pm 2	4 \pm 2	10 \pm 2	14 \pm 2	5 \pm 2	10 \pm 1
SO ₂ sulfur attribution (ng/m ³)	273 \pm 38	518 \pm 40	434 \pm 39	531 \pm 53	179 \pm 29	397 \pm 19
% of measured SO ₂ sulfur	68 \pm 10	76 \pm 6	76 \pm 7	79 \pm 8	61 \pm 10	75 \pm 4
Total sulfur attribution (ng/m ³)	408 \pm 50	556 \pm 51	529 \pm 52	669 \pm 65	221 \pm 41	488 \pm 24
% of measured total sulfur	31 \pm 4	36 \pm 3	35 \pm 3	40 \pm 4	19 \pm 3	33 \pm 2

¹ The sixth 6-hour site, at Monahans Sandhills, was not used for this analysis because a small nearby SO₂ source apparently impacts it from time to time.

These results imply that, on average over the 4-month study, the *Carbón* power plants were significant contributors to SO₂ concentrations in the Big Bend area, but contributed a small fraction of the particulate sulfur (sulfate). Combining the two species, we find that TAGIT attributed 19 to 40% of the total sulfur (the sulfur in SO₂ plus the sulfur in particulate matter) to local sources.

The portion of the sulfur that was not assigned to local sources was attributed to more remote, “regional” sources. According to the TAGIT analyses, 19% of the local sulfur and 86% of the regional sulfur is in particulate form, the remainder being in gaseous form in SO₂. Thus, most of the regional SO₂, but relatively little of the local SO₂, has been converted to particulate sulfur. The relatively low fraction of conversion of local SO₂ to particulate sulfur is consistent with the relatively short 15-18 hour estimated transport time from the vicinity of the *Carbón* power plants to the 6-hour sites. (This transport time was estimated using the BRAVO timing tracers released at Eagle Pass.)

10.2 Attribution of PM_{2.5} Components via Exploratory Factor Analysis

As described in Section 8.1.3, factor analysis was applied to the four-month BRAVO aerosol data set to investigate the principal types of sources that contributed to the observed concentrations. The report by Mercado et al. (2004), which is enclosed in the Appendix, describes the process and results in detail. The following summarizes the key results of the factor analysis.

Two filtered subsets of the total aerosol data set were used for the factor analyses. The regional data set, included concentrations of PM_{2.5} mass and of 21 elements throughout Texas. The Big Bend data set included concentrations of 10 elements, 6 ions, and the 8 carbon fractions (O1, O2, O3, O4, OP, E1, E2, and E3) that derive from the TOR analysis of filter samples for carbon. This data set only covers sites in Big Bend National Park.

The Principal Component Factor method with Varimax rotation was used to extract orthogonal factors. Four meaningful factors, which represent components that appear to vary together, were produced for the regional data set and five for the Big Bend data set.

The components that were included in each factor of the regional data set are given in Table 10-2. A particular component was included in one of these factors if the absolute value of the corresponding factor loading was greater than 0.30. (All of the factors listed in Table 10-2 had positive loadings.) The top 50 factor loadings for each of the four factors were contoured and displayed on the regional maps shown in Figures 10-1 through 10-4. In these maps, higher factor loadings may indicate a potential source area for a particular factor.

Table 10-2. Components with the most significant factor loadings for each factor of the regional data set.

Factor 1	Factor 2	Factor 3	Factor 4
Na, Al, Si, K, Ca, Ti, V, Mn, Fe, Rb, Sr, Y, Mass	S, Zn, As, Se, Br, Mass, H	K, Zn, As, Br	Cu, Zn, Pb

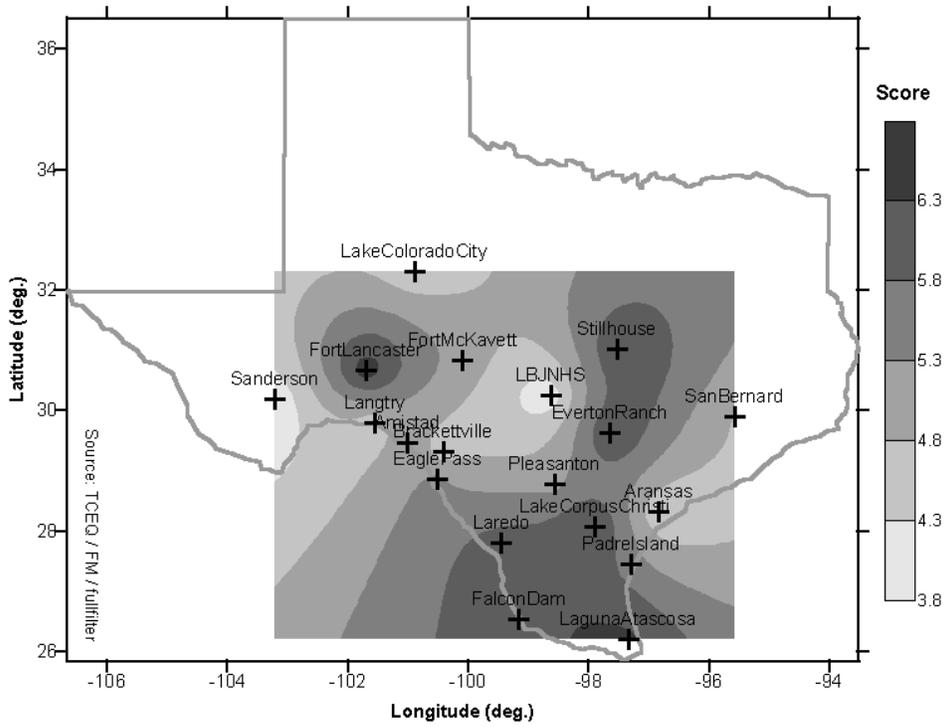


Figure 10-1.
Contour plot of locations of top 50 loadings scores for Factor 1 (Soils).

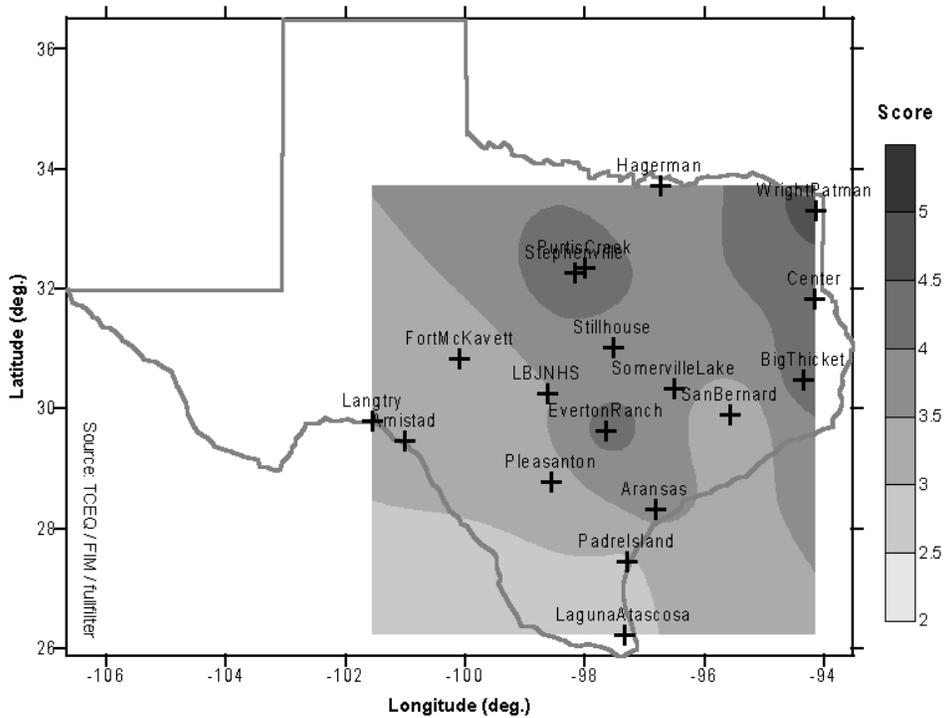


Figure 10-2.
Contour plot of locations of top 50 loadings scores for Factor 2 (Coal Burning).

Table 10-2 suggests that Factor 1 is related to crustal or soil elements. Factor 1 accounted for approximately 57 percent of the variance. The top 50 loadings of this factor occur in the southern part of Texas, as shown in Figure 10-1. Factor 2 accounted for about 30 percent of the total variance. Factor 2 suggests a relationship to coal burning due to the combination of sulfur (S) and hydrogen (H) and the tracer selenium (Se). The top 50 loadings of this factor occur in eastern Texas, with the highest factor scores near the Texas-Louisiana border, as shown in Figure 10-2. Factor 3 was an undetermined factor that accounted for about 7 percent of the total variance. Most of the top 50 loadings of Factor 3 were concentrated in southeastern Texas. Factor 4 suggests smelter influence with the combination of copper (Cu), zinc (Zn) and lead (Pb). It accounted for just under 5 percent of the total variance. The top 50 loadings of this factor were distributed throughout the study area, as shown in Figure 10-4.

Turning now to the Big Bend data set, the most significant components of the five factors (labeled BB1 through BB5) are displayed in Table 10-3. (Compare these factors with very similar ones that were displayed in Table 6-3. There are minor differences because the data set used for the factor analyses of Table 6-3 included both 6-hr and 24-hr samples, while the data set for Table 10-3 included only 24-hr samples.) The selection criterion was again that the absolute value of the factor loading corresponding to a component was greater than 0.3. Note that the loading for vanadium in Factor BB5 was a negative -0.44.

Table 10-3. Components with the most significant factor loadings for each factor of the Big Bend data set.

Factor BB1	Factor BB2	Factor BB3	Factor BB4	Factor BB5
Al, Si, K, Ca, Ti, V, Mn, Fe, Rb, Sr, NO ₃ ⁻ , Na ⁺ , Mg ²⁺ , Ca ²⁺ , O1	H, S, Zn, As, Se, Br, SO ₄ ²⁻ , NH ₄ ⁺ , O3, O4, OP, E1	Zn, Pb, Br, NO ₃ ⁻ , K ⁺ , Ca ²⁺ , O3, O4, E1	O1, O2, O3, OP, E1, E2, E3	Na, V*, NO ₃ ⁻ , Na ⁺ *The factor loading for V is negative.

Table 10-3 suggests that Factor BB1 was most likely associated with soil, with the most prominent factor loadings (>0.60) coming from elements such as aluminum (Al), silicon (Si), potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), iron (Fe), rubidium (Rb), strontium (Sr), and the magnesium ion (Mg²⁺). Other variables with significant loadings on this factor were vanadium (V), nitrate (NO₃), the sodium ion (Na⁺), and one of the organic carbon groups, O1. Factor BB1 accounted for 39 percent of the total variance.

Factor BB2, which explained 27 percent of the variance, was sulfate-related, with the heaviest loadings (>0.90) coming from sulfur (S), hydrogen (H), sulfate (SO₄), and ammonia (NH₄). Other important variables loading on this factor were selenium (Se), bromine (Br), organic carbon groups O2 and O4, and elemental carbon group E1. The inclusion of selenium suggests this second factor could be associated with coal combustion, a primary source of emissions that lead to the formation of sulfates, while the presence of organic carbon fractions implies that another source category may also be involved.

Factor BB3 saw the largest factor loadings (>0.60) from zinc (Zn), lead (Pb), and Br. The K^+ and Ca^{2+} ions, as well as O3, O4, and E1, were also significant. Zinc and lead often indicate smelter influence. Another possible contributor to this factor is motor vehicles. Factor BB3 explained 13 percent of the variance.

Organic and elemental carbon groups O2, O3, OP, E1, E2, and E3 had significant loadings on factor BB4, while factor BB5 was associated with Na, Na^+ , and NO_3 . These factors accounted for 12 and 9 percent of the variance, respectively. The last factor is consistent with other BRAVO findings that suggest that nitrates are present as sodium nitrate, rather than ammonium nitrate. Interestingly, V had a strong negative loading on factor BB5 (-0.44), which meant significant vanadium concentrations were not present with the other species that loaded on this factor.

In summary, the factor analyses found three identifiable underlying factors in both the regional and Big Bend data sets: a soil related factor, a coal burning related factor and a smelter related factor. The fact that these factors were observed in both analyses indicates some robustness. These results also indicate that there are factors common to Big Bend and all of Texas.

Additional review of the aerosol data set revealed additional supporting information. The maximum daily fine particulate matter concentrations were found to be more frequent in northeast Texas, which suggests that there are strong sources in northeast Texas or high concentrations are transported into northeast Texas. Big Bend sites did not demonstrate this behavior. Analysis of spatial average concentrations revealed that average concentrations tend to be higher in the northeast part of Texas for most species. Many of the soil-related species concentrations tended to be higher in the first half of the study. Coal burning related species average concentrations were higher in northeast Texas for the entire study. Big Bend average concentrations remained relatively constant throughout the study.

10.3 Attribution of Big Bend Particulate Sulfur and Soil via EOF Analysis

One of the methods used for exploring spatial and temporal relationships in the BRAVO fine particulate data was Empirical Orthogonal Function (EOF) analysis, which simplifies all the daily spatial patterns into a few that, when linearly re-combined, explain most of the variance in the data. The EOF method is described in Section 8.1.2 and its application to BRAVO is described in detail in the CIRA/NPS report on BRAVO (Schichtel et al., 2004), which is provided in the Appendix. This section provides a summary of key results from the application of EOF analysis to determine spatial patterns of fine particulate sulfur and iron (an indicator of soil).

An EOF analysis requires that there be no missing concentration values. Estimated concentrations filled in occasional gaps, but measurements at all sites during most of July and at three sites for the entire study period were sufficiently incomplete that they could not be included in the BRAVO EOF analyses. Consequently, some of the concentration distributions presented here may differ slightly from those in other portions of this report.

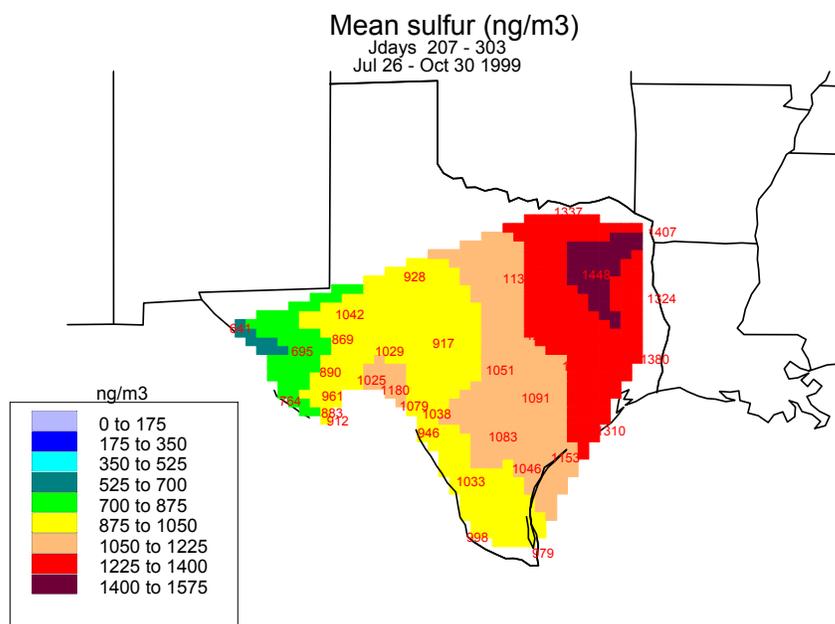


Figure 10-5.
Distribution of mean particulate sulfur concentrations over the portion of the study period when all sites had sufficiently complete data for EOF analysis.

Figure 10-5 shows mean particulate sulfur concentrations for the period of 26 July through 30 October 1999 at the sites that had sufficiently complete data for EOF analyses. Concentrations are highest in the northeast corner of the monitoring domain and lower towards the southwest, except for an area near the *Carbón* power plants. Correlations between sulfur concentrations at Big Bend and those measured at other BRAVO sites are 0.6 or greater out to approximately 400 km from Big Bend and fall to below 0.3 at sites in eastern and northeastern Texas that are 700 km or more from the park. Peak sulfur concentrations occur during different months of the study in different areas of the state, with northeast Texas having maximum values during August, while sites closer to Big Bend had maximums during September. Sites nearest the *Carbón* power plants experienced less monthly variation in sulfur concentrations than did sites in other corners of the monitoring domain.

Figure 10-5 does not provide information on concentrations in Mexico. However, as was described in Section 2.4, a preliminary study consisting of 19 fine particle monitoring sites in both Texas and Mexico was conducted prior to BRAVO, during September and October 1996. Seven monitoring sites were common to both studies; at five of these sites the differences between the mean September and October sulfur concentrations were 10% or less. The largest difference was 22% at Amistad, with 1996 having the higher concentrations. At Big Bend, the difference between 1996 and 1999 was about 1%.

The generally good correspondence of Texas sulfur concentrations between the two studies allows plotting the 1996 and 1999 means for these two months on a single map to visualize the “typical” mean sulfur concentrations for September and October over a larger area that includes both northeast Mexico sites of 1996 and the northeast Texas sites of 1999. This map is shown in Figure 10-6, which also includes a comparison of the mean concentrations at the seven sites that were common to both studies. (Implicit in this

presentation of merged data is the assumption that the good correspondence in Texas for the two years also applies to Mexico.)

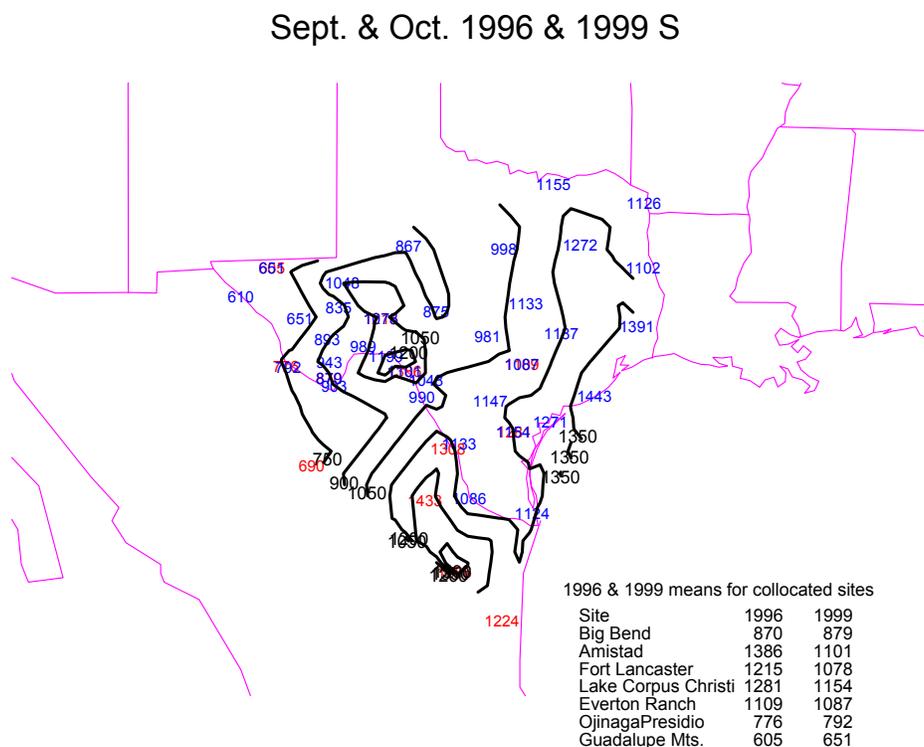


Figure 10-6. Composite of mean sulfur concentrations (ng/m^3) measured during September and October in 1996 (the preliminary study) and 1999 (the BRAVO Study).

Figure 10-6 shows that mean fine sulfur concentrations across Texas and Mexico in September and October were greatest in eastern Texas, near the *Carbón* plants and around the Monterrey area (at the southern end of the contours). In general, particulate sulfur concentrations decreased from east to west.

Returning to the 1999 BRAVO measurements alone, the highest fine particulate sulfur concentrations at Big Bend during the BRAVO study period occurred during four episodes – August 21, September 1-2, September 14-15, and October 12. The Sept. 1-2 episode also had the highest organic carbon and second highest elemental carbon concentrations of the BRAVO study. The spatial concentration patterns for these four episodes are all different, with the patterns for August 21 and October 12 being the most similar. The latter two days had higher sulfur concentrations in northeast Texas and around the Big Bend area while central Texas had lower values. September 15 had the highest sulfur concentrations around Big Bend and on the southern Gulf Coast while concentrations in northeast Texas were the lowest in the state. On September 1, the highest sulfur concentrations were in central Texas with the lowest being in three pockets on the east, far west, and southwest.

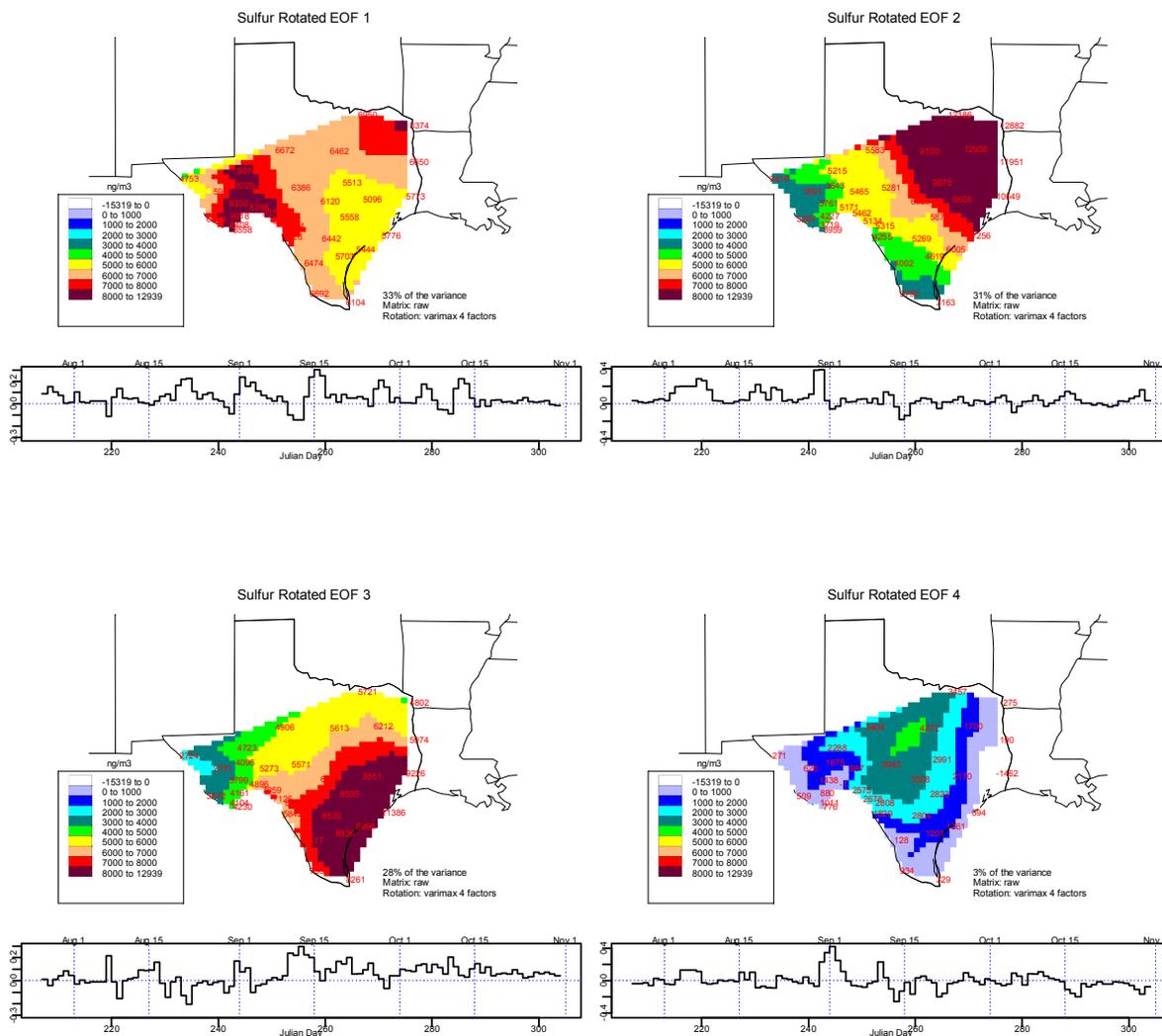


Figure 10-7. The four EOF analysis-derived spatial factors for particulate sulfur and their temporal weights during most of the BRAVO Study period.

EOF analysis of the particulate sulfur data that was used to construct Figure 10-5, followed by Varimax rotation, produced the four orthogonal factors that are portrayed in Figure 10-7. These four factors cumulatively explain 82% of the variance in the sulfur concentrations, with the first three factors accounting for most of that explanation in roughly equal proportions.

The first factor (EOF 1), which explains 33% of the variance in the sulfur measurements, has highest values in the southwest and northeast corners of the state with lower values between. This suggests two likely source areas and transport pathways for sulfur for days weighted highly for this pattern. First, particulate sulfur appears to be transported into Texas from the northeast or there are sulfur sources in the northeast corner of

the state that influence the particulate sulfur concentrations there. Second, particulate sulfur is either being transported into Texas from the south or is being generated in southwest Texas. The highest time weights for this pattern include the days of some of the highest particulate sulfur concentrations at Big Bend including especially September 15 and, to a lesser extent, September 1, October 12, and the mid-August episode.

The spatial pattern for EOF 2, which explains almost as much of the sulfur variance (31%) as EOF 1, is indicative of transport from northeast to southwest. This pattern has the strongest positive time weights on August 29-30, just before the high sulfur concentration at Big Bend on September 1.

EOF 3, explaining 28% of the variance, has highest values along the Texas Gulf Coast, suggestive of transport from the Gulf of Mexico or from the Houston area inland to central Texas. Highest time weights for this pattern are just prior to the September 15 episode at Big Bend.

EOF 4 explains only 3% of the sulfur variance and has highest concentrations in central Texas with lower values around the edges.

Thus, in summary, the EOF analysis suggests that most of the observed sulfur behavior in the area of most BRAVO Study measurements (i.e., Texas) is consistent with the existence of particulate sulfur emissions sources, sulfur particle formation, and/or particle sulfur inflow into the study area at northeastern Texas, southwestern Texas, and southeastern Texas (not all at the same time, though).

Spatial and temporal patterns of iron concentrations, which are representative of the concentration distribution of fine soil, were quite different from those of sulfur. By far the highest iron concentrations occurred during the summer and, in contrast to sulfur, mean iron concentrations were highest at the southernmost monitoring sites rather than in northeast Texas. While fine soil is, on average, less than 15% of the measured fine mass at Big Bend, it accounted for more than 50% during a few days early in the study. In the EOF analysis for iron, factors significantly different from zero occurred only during July and early August. Previous analyses of historical particulate data at Big Bend (Perry et al., 1997; Gebhart et al., 2001) have indicated frequent episodes of Saharan dust impact at the park during the summer. The spatial and temporal patterns in the BRAVO iron data suggest a similar phenomenon early in the BRAVO study period, with the decreasing concentrations from south to north indicating the predominant transport pathway.

Results of EOF analyses for selenium, vanadium (and other tracers of Mexican emissions), sodium, bromine, and lead are presented in the CIRA/NPS report on BRAVO (Schichtel et al., 2004), which is contained in the Appendix.

10.4 Transport Patterns to Big Bend during Periods of High and Low Sulfur Concentrations

Back trajectory analyses using the CAPITA Monte Carlo model (described in Section 8.3.3) were conducted to identify the air mass transport routes associated with the highest and lowest particulate sulfur concentrations at Big Bend. Wind fields from both the BRAVO 36 km MM5 simulations and the National Centers for Environmental Prediction (NCEP) Eta

Data Assimilation System (EDAS) were used to define the five-day trajectories. Since EDAS wind fields were not available during October 1999, NCEP's FNL meteorological data were used instead for that month. (See Section 8.2 for a description of the various wind fields.)

The predominant air mass transport routes were assessed by creating residence time probability distributions. This was done by aggregating the amount of time all air masses resided over a given region and normalizing the result by the total air mass residence time over the time period of interest. The most likely transport directions to a receptor are then along the ridges of the probability fields. For the analyses under discussion here, the air mass histories were sorted according to whether the particulate sulfur concentration at Big Bend was low (in the lowest 20%) or high (in the highest 20%). The resulting residence time analyses yield representations of transport pathways during high and low particulate sulfur days

Incremental probability fields were also calculated to delineate regions preferentially associated with transport during the high or low sulfur days. The incremental probability field is the difference between the sorted and everyday probability fields and thus represents the areas that are more or less likely to be traversed during periods of high or low particulate sulfur compared to an average day.

Examination of such transport pathways during particulate sulfur episodes showed that there were three common pathways associated with elevated particulate sulfur at Big Bend -- from eastern Texas, from the southeastern U.S. and from northeastern Mexico. Examples of these patterns for three representative episodes are shown in Figure 10-8. The largest concentrations occurred when the transport route traversed several of these regions. For example, the September 1 episode had transport over all three regions and produced the

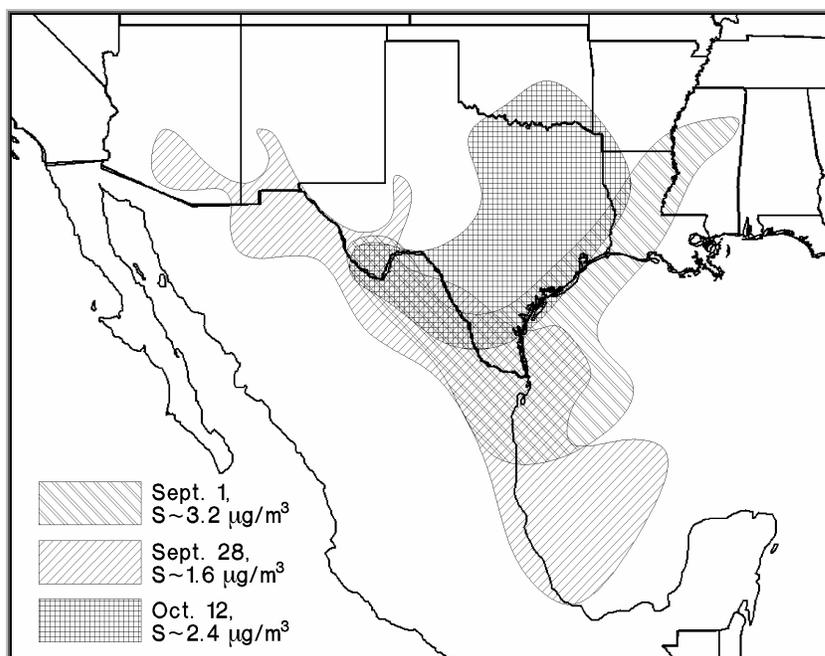


Figure 10-8. Air mass transport patterns to Big Bend during three particulate sulfur episodes. Each shaded region shows the most likely pathway followed by the air mass prior to reaching Big Bend. The transport pathways were created using residence time analysis and the contour lines bounding the shaded regions encompass 75% of the residence time hours.

highest particulate sulfur concentrations ($3.2 \mu\text{g}/\text{m}^3$) during the BRAVO study. In addition to these three pathways, elevated particulate sulfur concentrations were also associated with prior transport over the Midwest (Missouri, Kentucky and Tennessee), though this was infrequent and the air masses tended to be elevated and traveled at higher speeds than those along the main three pathways.

As shown in Figure 10-9, the 20% of the days with the highest particulate sulfur concentrations at Big Bend were associated with low level and slower than average transport from Arkansas and Louisiana, down through eastern Texas and up along the Texas-Mexican border to Big Bend. Compared to the average transport pattern during BRAVO, air masses on the high particulate sulfur days were most likely to reside in eastern Texas and in the vicinity of the *Carbón* plants (as shown in the right hand panel of Figure 10-9).

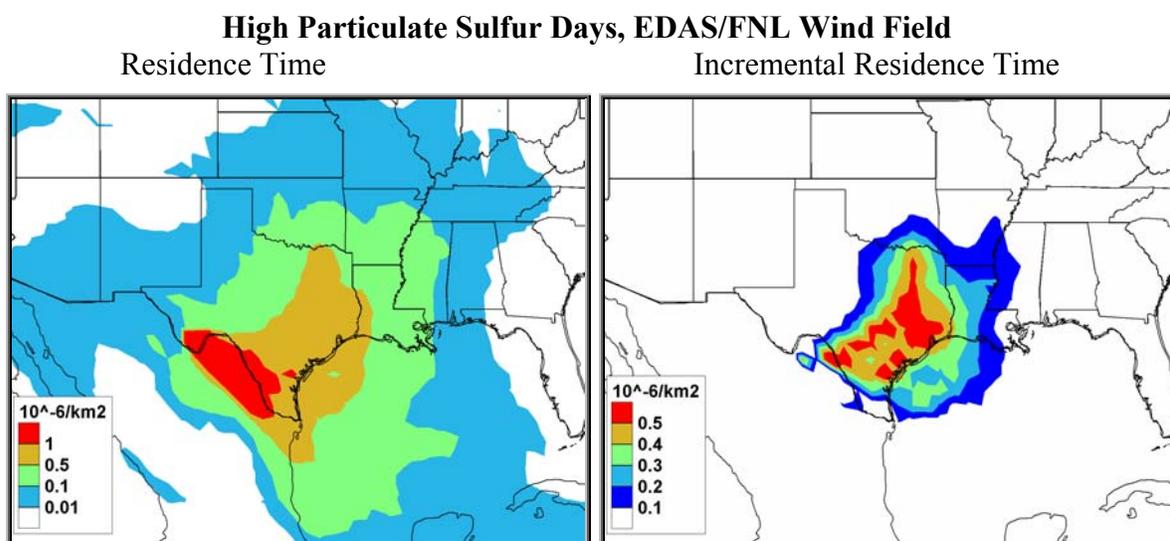


Figure 10-9. Residence time probability distributions showing transport pathways during high particulate sulfur days, based on the EDAS/FNL wind fields. (Left) Residence time plot showing the most likely areas where the air mass resided prior to reaching Big Bend. (Right) Incremental probability plot showing the regions where air masses are more likely than average to have resided prior to reaching Big Bend.

The residence time analyses produced with different wind field showed small but important differences in transport patterns, as can be seen by comparing Figure 10-9 (produced with EDAS/FNL wind fields) with Figure 10-10 (produced with MM5 wind fields). The air mass histories generated using the EDAS winds showed greater transport from northeastern Texas than those of MM5, while the MM5 air mass histories had a higher probability of transport from greater distances to the east and northeast of Big Bend. As was noted in Section 9.2, the MM5 wind speeds tend to be greater than those of EDAS/FNL. However, as also noted in Section 9.2, both wind fields produced similarly reasonable representations when simulating the perfluorocarbon tracer releases, and therefore neither pattern can be considered more correct than the other.

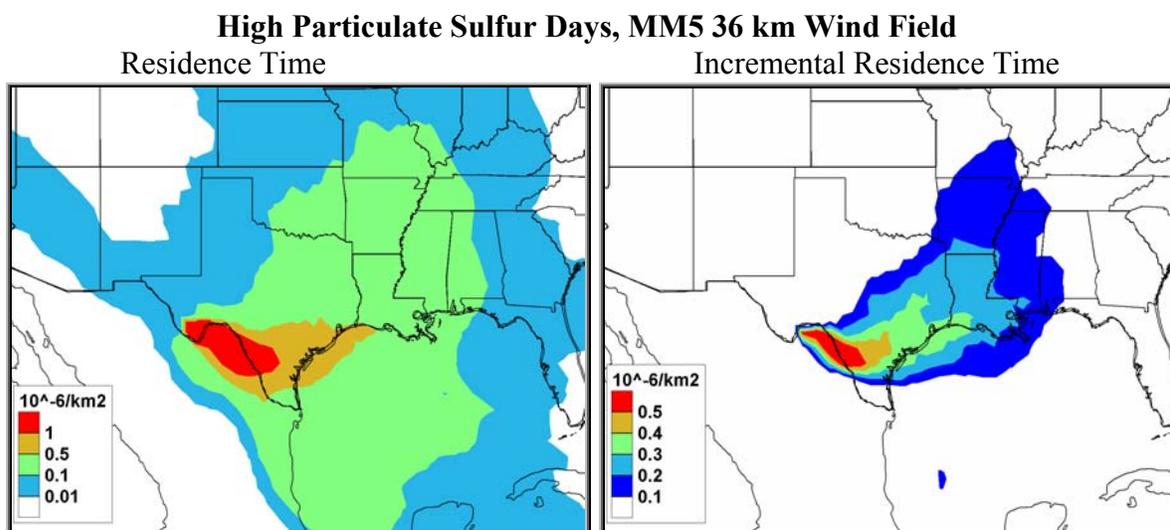


Figure 10-10. Residence time probability distributions showing transport pathways during high particulate sulfur days, based on the BRAVO 36km MM5 wind fields. (Left) Residence time plot showing the most likely areas where the air mass resided prior to reaching Big Bend. (Right) Incremental probability plot showing the regions where air masses are more likely than average to have resided prior to reaching Big Bend.

In contrast to the behavior on the high particulate sulfur days, Figure 10-11 shows that transport to Big Bend during the low particulate sulfur days is persistently from the Gulf of Mexico along northeastern Mexico and, to a lesser degree, from the north from the plains states. Along these two transport pathways, the transporting air masses are closer to the ground, generally below 1 km, and the transport wind speeds are higher than average.

These probability distributions show that transport from eastern Texas and southeastern U.S. is associated with elevated particulate sulfur concentrations at Big Bend and that this transport route is not associated with low sulfur concentrations. These results, combined with the fact that eastern Texas and the Southeast have high sulfur dioxide emissions, support the notion that these areas contribute to the sulfate concentrations at Big Bend.

Northeastern Mexico also has large sulfur point and area sources, including the *Carbón* power plants and the Monterrey urban and industrial center. The air masses with elevated particulate sulfur concentrations at Big Bend were more likely than average to have previously resided over the *Carbón* plants, but it was found that this region is a transport corridor for air masses coming from eastern Texas to Big Bend. In addition, prior transport over the *Carbón* plant and Monterrey regions was sometimes associated with low Big Bend sulfur levels. These low sulfur air masses came directly off of the Gulf of Mexico with higher speeds and/or precipitation occurring prior to reaching Big Bend. The higher speeds decrease the accumulation of pollutants in the air mass and the precipitation can remove SO_2 and sulfate particles. Therefore, while elevated Big Bend particulate sulfur concentrations are associated with prior transport over northeastern Mexico, it is not known from this analysis if these sources significantly contribute to Big Bend's particulate sulfur concentrations.

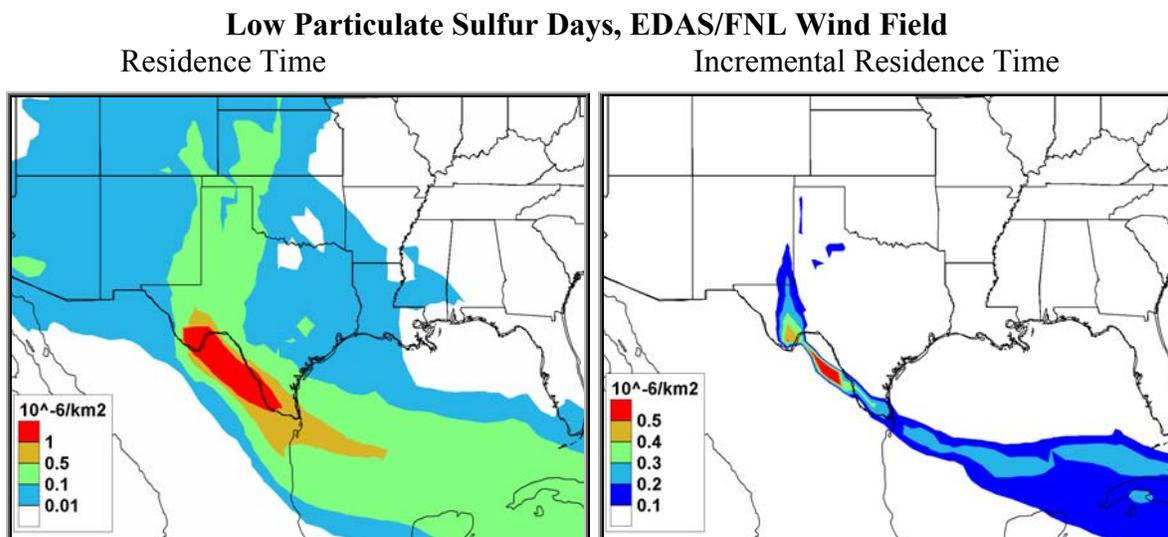


Figure 10-11. Residence time probability distributions showing transport pathways during low particulate sulfur days, based on the EDAS/FNL wind fields. (Left) Residence time plot showing the most likely areas where the air mass resided prior to reaching Big Bend. (Right) Incremental probability plot showing the regions where air masses are more likely than average to have resided prior to reaching Big Bend.

10.5 Attribution of Big Bend Particulate Sulfur via Trajectory Mass Balance (TrMB)

Trajectory Mass Balance (TrMB) is a method in which measured concentrations at a receptor are assumed to be linearly related to the frequencies of air mass transport from various source regions to that receptor. (See Section 8.3.5 for a more detailed description of the method.) TrMB was used to estimate the 4-month average contributions to fine particulate sulfur measured at Big Bend National Park from several source regions (shown in the map in Figure 8-2) during July-October 1999. The approach and results are summarized here; see the CIRA/NPS report (Schichtel et al., 2004) in the Appendix for more detail.

The sulfur concentrations used for the TrMB analysis were the daily medians of all available 24-hr average particulate sulfur concentrations measured at K-Bar from July 5 through October 29, 1999. Although there are measured concentrations both before and after these dates, these are the time limits of what can be modeled using the BRAVO MM5 wind fields.

Back trajectories were started from Big Bend National Park and traced backwards in time for 5, 7, and 10 days. Original TrMB analyses for BRAVO utilized only 5-day back trajectories, but the TrMB technique generally attributed less sulfate to distant source areas and more to closer areas than did the REMSAD air quality model. A possible reason for this result is that there was transport of sulfur from sources more than five days distant, either on average or on a significant number of days during BRAVO. Trajectory lengths were therefore increased to determine if this alone would cause the TrMB results to more closely resemble the REMSAD attributions.

As has been described earlier, a variety of trajectory model and wind field combinations were tested with known attributions of the tracer data (Section 9.3) and simulated sulfate from the REMSAD model (Section 9.6). Based on the results of these tests, the trajectory model and wind field combinations used for sulfur attributions at Big Bend consisted of HYSPLIT with EDAS/FNL and CAPITA Monte Carlo with MM5, both with 5-, 7-, and 10-day trajectories, and ATAD with MM5 for 5-day trajectories only. (The ATAD computer code cannot generate longer trajectories.) Results given here for HYSPLIT are aggregates of the attributions for all trajectory start heights, in order to dampen the sensitivity of HYSPLIT results to start height.²

The results of the analyses with these various combinations are summarized in Table 10-4 for the four major TrMB source regions – Eastern U.S., Western U.S., Texas, and Mexico – described in Table 8-2. (Table 8-2 also links the source regions used for TrMB with the ones used for the REMSAD modeling of Section 11.1. See Section 8.5 for a full discussion of the various characterizations of source regions)

The results in Table 10-4 vary somewhat depending on the trajectory model and wind field combination used, though for most of the 27 smaller subregions the differences between combinations are within the uncertainties due to the standard errors of the regression coefficients. The model performance statistics at the bottom of the table show that the CAPITA Monte Carlo model with MM5 winds could explain more than 60% of the variance in the measured particulate sulfur concentrations at Big Bend, with the longest trajectories showing the best performance. ATAD with MM5 was almost as good, even though it was

Table 10-4. Relative attributions of median 24-hour particulate sulfur at Big Bend to each major source region by TrMB using various trajectory model/wind field combinations. The uncertainties given are based on the standard errors of the regression coefficients. Model performance statistics are provided in the bottom three rows.

Trajectory Length (days)	CAPITA MC with MM5			HYSPLIT with EDAS/FNL			ATAD with MM5
	5	7	10	5	7	10	5
Eastern U.S. Attribution	23%	26%	24%	7%	14%	16%	17%
Western U.S. Attribution	14%	21%	25%	8%	8%	6%	3%
Texas Attribution	19%	12%	12%	45%	36%	30%	20%
Mexico Attribution	45%	41%	40%	39%	42%	48%	50%
Mean observed S (ng/m ³)	836	836	836	836	836	836	836
Mean TrMB S (ng/m ³)	833	833	835	808	796	787	823
R ²	0.62	0.67	0.69	0.48	0.50	0.46	0.59

² HYSPLIT, which uses the gridded wind fields without the vertical averaging of ATAD and without the random vertical motion of the CAPITA Monte-Carlo model, is more sensitive to start location, start height, and placement of individual endpoints than the other two models.

limited to five-day trajectories. HYSPLIT with EDAS/FNL had somewhat poorer performance, with $R^2 \leq 0.5$ and slightly poorer agreement between the mean TrMB and measured particulate sulfur concentrations.

In general, all combinations assign approximately the same total attribution to Mexico, in a range from 39-50% with a median of 42%. With MM5 input in the CMC model, longer trajectories result in somewhat less attribution to Mexico, while the reverse is true for HYSPLIT with EDAS/FNL input for which longer trajectories result in slightly more sulfur being attributed to Mexico.

The biggest disagreement between the different trajectory model/wind field combinations is in the mean relative percent of particulate sulfur attributed to Texas. HYSPLIT with EDAS/FNL input attributes about twice as much sulfur (30-45%) to Texas as do ATAD (20%) or CMC (12-19%) with MM5 input. Both the HYSPLIT and CMC trajectory models attribute lower fractions of sulfur to Texas as the trajectory lengths increase.

The ATAD and CMC models with MM5 input both attribute more sulfur (17-26%) to the eastern U.S. region than does HYSPLIT with EDAS/FNL (7-16%). The longer the HYSPLIT trajectories, the larger the fraction of sulfur attributed to the eastern U.S. The greatest percentage attributed to the eastern U.S. by the CMC model was with the 7-day trajectories.

For all trajectory model/wind field combinations the smallest relative attribution was to the western U.S. region, though the percentages attributed by HYSPLIT/EDAS/FNL (6-8%) were only about half what was attributed by CMC/MM5 (14-25%). ATAD/MM5 had the lowest relative attribution to the western U.S. at just 3%. Lengthening the HYSPLIT/EDAS/FNL trajectories caused slightly less relative attribution to the western U.S. region, while longer CMC/MM5 trajectories resulted in higher relative attributions to the western U.S. region.

Comparison of these results with the attributions from the REMSAD regional air quality model (see Section 11.1) shows that TrMB attributes larger fractions of particulate sulfur to Mexico and the western U.S. region and a smaller fraction to the Eastern U.S. region than does REMSAD. This is true for all input model/wind field combinations. Both CMC/MM5 and ATAD/MM5 give approximately the same average attribution to Texas as REMSAD, while HYSPLIT/EDAS/FNL attributes much more to Texas than does REMSAD. Reasons for the differences could include collinearity between TrMB source areas, inaccuracies in the back trajectories, failure of the linearity assumptions, or limitations in the deterministic model, including input data or parameterization of the physics and chemistry within the model.

Variance inflation factors (VIFs) were calculated to indicate the collinearity of a source area with all other source areas in the TrMB analysis.³ (See Schichtel et al., 2004,

³ In a multiple linear regression, the fraction of the total variance in one variable that is predicted by all the other variables is R^2 . The Variance Inflation Factor is the inverse of the fraction of the total variance in one variable that is *not predicted* by the other variables, i.e., $VIF = 1/(1-R^2)$.

included in the Appendix, for details.) Source areas with VIFs of 10 and higher are considered to have significant collinearity with some linear combination of other regions. With one exception (CMC MM5 10-day trajectories from the Central States subregion of the Eastern U.S. source region), VIFs greater than 10 occurred only for source areas to the west and north of Big Bend. Air masses from these areas usually arrived infrequently at Big Bend and the attributed sulfur during BRAVO from these source areas is expected to be low, so collinearity did not generally appear to be a significant contributor to TrMB attribution uncertainty, especially when full regions were considered.

In the CMC MM5 10-day case, the high VIF (10.8) for the Central States indicates that it is difficult to separate the true contributions of this subregion from those of other regions along the same transport pathway, and thus the contribution from that subregion is uncertain.

10.6 Attribution of Big Bend Sulfate via Forward Mass Balance Regression (FMBR)

Forward Mass Balance Regression (FMBR) is an analysis approach in which receptor concentrations are assumed to be linearly related to air mass transport from a number of source regions to the receptor. The transport is estimated using a forward particle dispersion model simulating transport from the source regions to the receptor. The FMBR methodology is described briefly in Section 8.3.6 and in more detail in the CIRA/NPS report (Schichtel et al., 2004). Its evaluation using the measured tracer concentrations was described in Section 9.5, and evaluation using the REMSAD-modeled sulfate concentrations is described in Section 9.7.

For attributing Big Bend sulfate to source regions, FMBR was applied using the 24-hour observed fine particulate sulfur concentrations at the K-Bar Ranch in Big Bend National Park. Multiple sulfur measurements were made at K-Bar so the median daily concentration for each day was used. These are the same data as those used in the TrMB analysis in the previous section. The air mass transport was estimated using the CAPITA Monte Carlo model driven by both the BRAVO MM5 and EDAS/FNL wind fields. Each plume was tracked for 10 days, the duration that was found to produce the best results when tested against the synthetic REMSAD-generated data (see Section 9.6). These plumes were aggregated together to represent transport from the 17 source regions shown in Figure 8-3, and then the results were combined into the same four regions that were used in the presentation of TrMB apportionments in the preceding section.

The results of this process are summarized in Table 10-5 for analyses using both the MM5 and EDAS/FNL wind fields. (Detailed results can be found in Schichtel et al., 2004, which is provided in the Appendix of this report.) SO₂ emissions for each region are also given in this table, for reference.

Using either wind field, the performance of the regression at estimating sulfate concentrations at Big Bend was about the same, with an r^2 of about 0.36 and an RMS error of about 60%, although the bias using the MM5 winds was only -6% compared to -18% using the EDAS/FNL winds. Note that this performance with actual particulate sulfate measurements is not as good as the r^2 of 0.8 obtained when FMBR was applied to the REMSAD-simulated sulfate concentration field (as described in Section 9.7).

Table 10-5. FMBR attribution results and performance statistics using MM5 and EDAS/FNL 10-day transport trajectories.

Source Region	SO ₂ Emissions (tons/yr)	FMBR Attribution ± Error	
		MM5	EDAS/FNL
Texas	1,127,000	24.4 ± 8.0	24.1 ± 12.1
Mexico	2,680,000	55.0 ± 14.1	51.6 ± 14.0
Eastern U.S.	7,060,000	20.5 ± 10.4	24.3 ± 10.4
Western U.S./Central Plains	1,200,000	0.1 ± 4.5	0.0 ± 8.5

Performance Statistics	MM5	EDAS/FNL
Observed Sulfate Avg. (µg/m ³)	2.49	2.49
Predicted Sulfate Avg. (µg/m ³)	2.34	2.04
Bias (%)	-6.2	-18.1
RMS error (%)	59	64
r ²	0.36	0.37

The FMBR analysis found that Mexico was the largest average contributor to Big Bend's sulfur over the BRAVO period at 52-55%, with the *Carbón* plants accounting for about 26% and the Monterrey region for about 18%. Texas accounted for about 24% of Big Bend's sulfur, with all of this contribution coming from eastern Texas. The Eastern U.S. region accounted for the remaining 21%. The Western U.S. region had a mean estimated contribution of 0% with standard errors of 4.5 and 8.5%.

The primary differences between the EDAS/FNL and MM5 results is that the EDAS winds produced a smaller *Carbón* impact, about 20% compared to about 26% using the MM5 winds. In addition, the northeast Texas contribution was larger when using the EDAS/FNL winds, which reflects the tendency of the EDAS/FNL wind fields to produce greater transport from northeast Texas compared to that generated using the MM5 wind field.

As described in Section 9.7, the FMBR technique tends to overestimate the source contributions from nearby source regions and underestimate the contributions from more distant source regions. This result occurs because the impact from a more distant source has greater relative error than that from a nearer source, both because the magnitude of the impact tends to be smaller and because the description of air mass transport tends to have greater error for longer distances. Since regression analyses are biased toward the variables with less error, the result is that the contribution of the closer source may be overestimated.