11. SOURCE ATTRIBUTIONS BY AIR QUALITY MODELING

This chapter describes several applications of regional air quality simulation models to attribute the $PM_{2.5}$ sulfate component of the Big Bend area haze to emissions from various geographic regions. These mathematical models, described in Section 8.4, simulated the transport, diffusion, chemical transformation, and deposition of the emitted air pollutants and thus estimated the concentrations of various air pollutants over the study area. Inputs to the models were the emissions inventory described in Chapter 4 and the meteorological field generated by the MM5 meteorological model, described in Section 8.2.3. The use of regional air quality models for evaluating the contributions of various source regions complements the receptor concentration and trajectory based analyses that were described in Chapter 10.

The specific approaches whose sulfate attribution applications and findings are described in this chapter include the following:

- The REMSAD model, a simplified photochemical model that was used to simulate every hour of the BRAVO Study period in 36x36 km grid cells over a domain that includes most of the contiguous United States and Mexico. Contributions to Big Bend area sulfate concentrations were attributed to three geographic regions in the U.S., to Mexico, and to transport from outside the modeling domain. Contributions from subregions, including the *Carbón* power plant, were also estimated.

- The CMAQ-MADRID model, a more complex model, that was used to simulate every hour of the BRAVO Study period in 36x36 km grid cells over a domain that approximately encompassed Texas, one tier of states around Texas, and northeastern Mexico. Contributions to Big Bend area sulfate were again attributed to the same five regions as those described above.

- A creative synthesis of each of the REMSAD and CMAQ-MADRID models with concentration measurement data in the study area, which produced the hybrid "Synthesis Inversion" method of source attribution. This approach compensates for some of the systematic errors present in the simulations of the two air quality models and thus should provide more accurate attributions of Big Bend aerosol.

Interpretation and synthesis of the attribution findings contained in this chapter, as well as of those contained in Chapter 10, are presented in Chapter 12.

11.1 Sulfate Attribution via REMSAD

The REMSAD model, described in Section 8.4.2, was used to estimate the distribution of ground level sulfate concentrations throughout its modeling domain for all hours of the BRAVO Study period. This base emissions simulation on a 36x36 km grid was first evaluated against measurement data, as described in Section 9.9, to assess the performance capability of the model.

The contributions of emissions in four regional source areas to sulfate concentrations at Big Bend National Park were then estimated by rerunning the model several times, each with the SO_2 emissions in a different region set to zero. The results obtained are summarized here. The approach and the results are described in detail in the NPS/CIRA report on the BRAVO Study (Schichtel et al., 2004), which is enclosed as an appendix to this report.

The four regions used for such sensitivity simulations, shown in Figure 11-1, are Texas, Mexico, the eastern United States, and the western United States. A fifth source "region" whose contribution was evaluated represents boundary concentrations, which reflect pollutants transported from outside of the model domain and the recirculation of pollutants that originated within the domain.

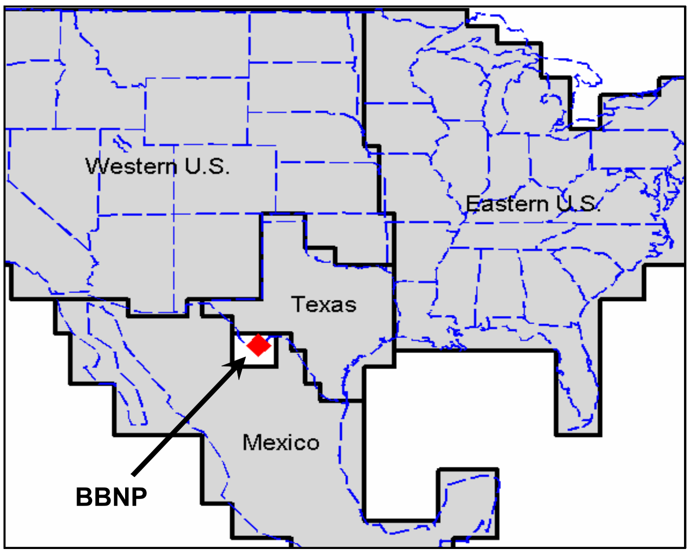

Figure 11-1. *Map of the REMSAD modeling domain and the four principal geographic regions to which sulfate at Big Bend National Park (red diamond) was attributed. SO_2 emissions in the white region immediately surrounding Big Bend National Park are near zero and were not included in the attribution analyses.*

Two emission sensitivity simulations were carried out for each of the five source regions, using two different emission inventories:

1. An "emissions in" inventory, in which sulfur emissions from the source region of interest were left unchanged, but sulfur emissions outside of that region were removed, and
2. An "emissions out" inventory, in which sulfur emissions were removed from the source region of interest, but sulfur emissions outside of this region were left unchanged.

The attribution results were relatively similar between the two approaches, with small differences that are believed to be due to nonlinear atmospheric chemistry.[1] It should be emphasized that in all cases only sulfur emissions (i.e., SO_2 and primary $SO_4^{=}$) were modified; and other emissions within the REMSAD inventory (e.g., NO_x, VOC, CO, etc.) were left at their base case levels.

[1] The nonlinearity is small, though. The response of sulfate concentrations simulated by REMSAD was nearly linear with changes in emitted SO_2.

Additional "emissions out" simulations were conducted for evaluating the impact of the *Carbón* I/II power plant near the Texas-Mexico border and of sub regions of the four main regions indicated in Figure 11-1. Also, the influence of using sulfur boundary concentration estimates from July-October averages generated by the GOCART global model was evaluated. These boundary conditions, in effect, establish the contribution to sulfate from sources outside of the modeling domain.

Example surface-level sulfate concentrations for the base emissions simulation and five of the "emissions in" sensitivity simulations are shown in Figures 11-2 through 11-7 for a sulfate episode that occurred in mid-August during the BRAVO field study. The boundary conditions were those defined by the GOCART model. (Note that these figures are just examples to illustrate how the apportionment process was carried out, and the interpretive discussion here illustrates the kinds of information that can be drawn from this process. Because these examples are just for one hour of one day, it is inappropriate to draw general conclusions about Big Bend sulfate apportionment from them.)

In this particular example, observed and REMSAD-simulated sulfate concentrations at Big Bend National Park were both approximately 4 $\mu g/m^3$. Elsewhere, elevated sulfate is evident in the base emissions simulation shown in Figure 11-2, with concentrations ranging from 10 $\mu g/m^3$ to over 20 $\mu g/m^3$ in a region that extends from eastern Texas toward Ohio and Pennsylvania. (Note, however, that REMSAD has a tendency to overestimate sulfate concentrations in the eastern portion of its domain, as discussed in Section 9.9.) The simulated sulfate concentrations are lower over the western U.S., most of Mexico, and the Gulf of Mexico, with concentrations there generally ranging between 0 $\mu g/m^3$ and 2 $\mu g/m^3$.

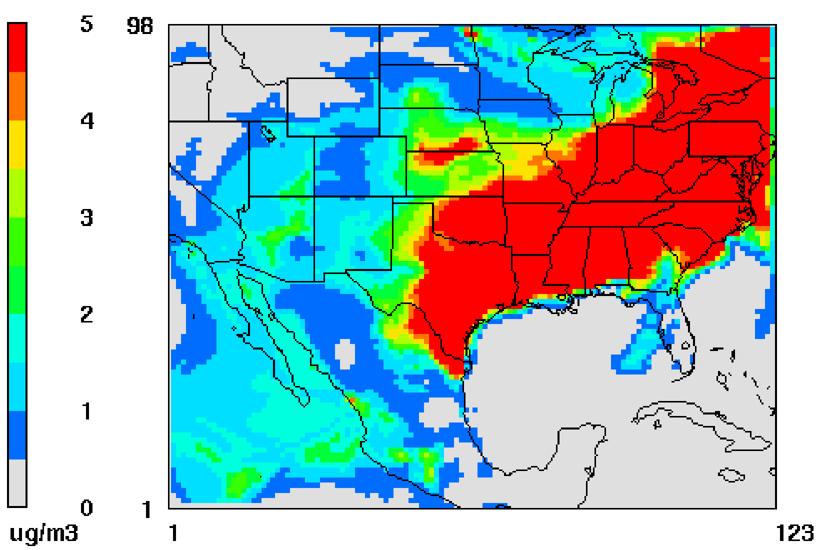

Figure 11-2. *REMSAD simulation of sulfate concentrations on 17 August 1999 at 1500 UTC using the full BRAVO emissions inventory. Numerals along the edges of the map indicate the coordinates of the grid cells.*

The contribution of each source region (and the contribution of the concentrations specified at the model boundary) to total simulated sulfate levels everywhere in the modeling domain for this period can be assessed by examining Figures 11-3 through 11-7. For example, the magnitude of simulated sulfate attributed to eastern U.S. sources is portrayed in Figure 11-3, with simulated sulfate concentrations exceeding 20 $\mu g/m^3$ in the middle and eastern portions of the model domain. (As before, these numerical values should be taken with caution because of REMSAD's tendency to overestimate sulfates in this portion of the domain.) Comparison of Figure 11-3 with Figure 11-2 illustrates the dominance of eastern U.S. sources on the total simulated sulfate pattern on this day. This should be anticipated, since the majority of the SO_2 included in the BRAVO Study emissions inventory within the REMSAD domain is emitted in the eastern U.S. region.

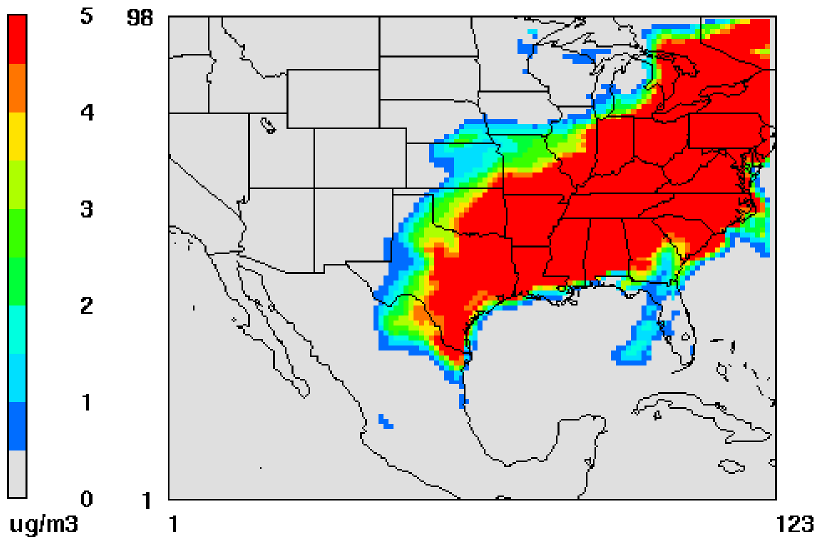

Figure 11-3. *REMSAD simulation of sulfate concentrations from emissions in the Eastern U.S. source region on 17 August 1999 at 1500 UTC.*

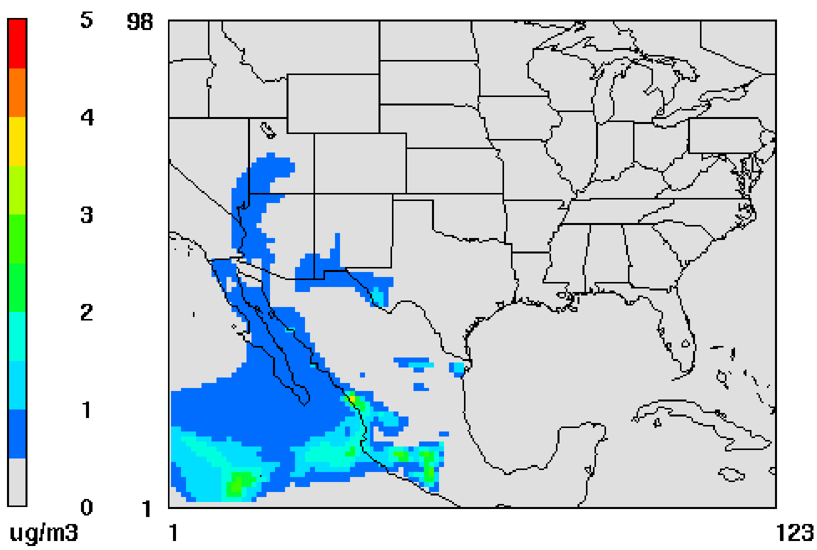

Figure 11-4. *REMSAD simulation of sulfate concentrations from emissions in the Mexican source region on 17 August 1999 at 1500 UTC.*

Mexican sulfur sources, particularly the Popocatepetl volcano, resulted in elevated simulated sulfate concentrations off the western coast of Mexico, and the sulfate plume of the *Carbón* I/II power plant, with concentrations in excess of 1.5 ug/m^3 near Big Bend National Park, is evident along the western Texas–Mexico border (Figure 11-4). (However, actual Mexican influences may have been greater than shown here because the BRAVO emission inventory only included emissions from the northern half of Mexico.)

Texas sulfur sources, located primarily in eastern Texas, contributed to simulated sulfate levels ranging from 0.5 µg/m^3 to 3 µg/m^3, which extend into western Texas and north into Oklahoma and Kansas (Figure 11-5). Finally, for this particular period, the influences of western U.S. sulfur sources (Figure 11-6) and domain-boundary sulfur concentrations (Figure 11-7) are negligible on sulfate concentrations simulated at Big Bend.

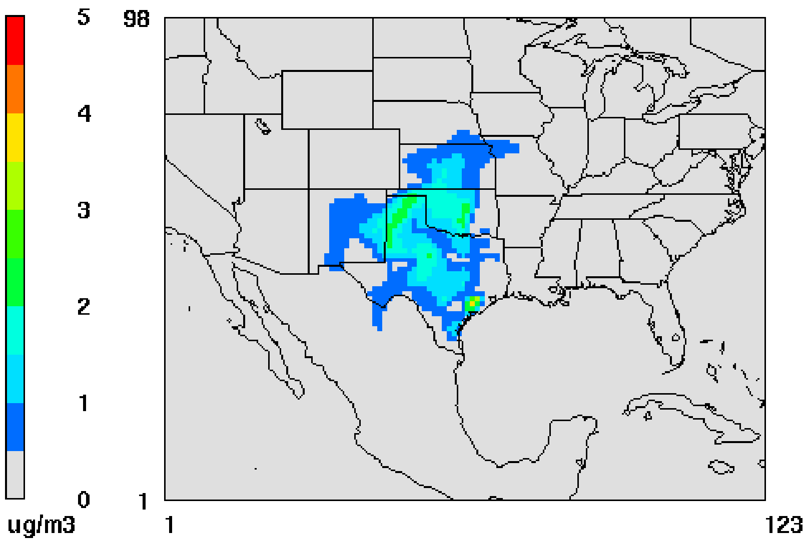

Figure 11-5. *REMSAD simulation of sulfate concentrations from emissions in Texas on 17 August 1999 at 1500 UTC.*

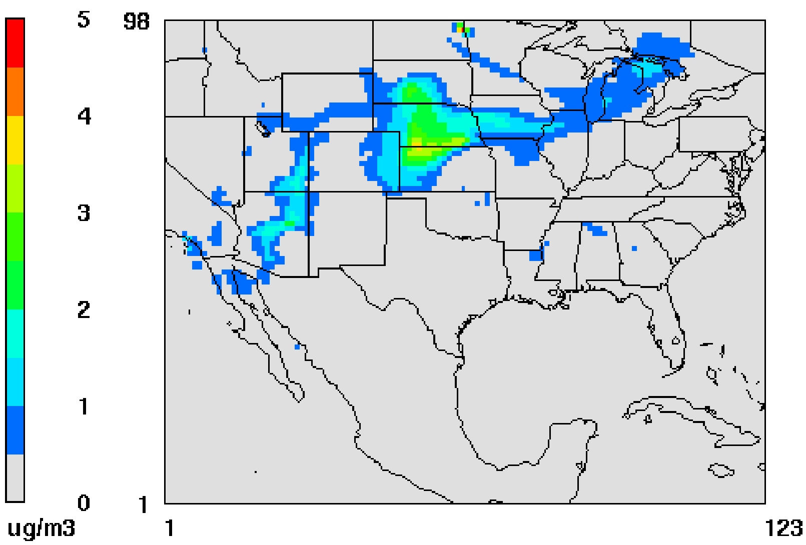

Figure 11-6. *REMSAD simulation of sulfate concentrations from emissions in the Western U.S. source region on 17 August 1999 at 1500 UTC.*

A notable feature apparent in the concentrations fields shown in these figures is the extent to which a source region can influence simulated $SO_4^=$ concentrations downwind. For example, during this particular mid-August episode, sulfur emissions from eastern U.S. sources appear to contribute more than 5 µg/m^3 to simulated sulfate concentrations in eastern Texas and the border region of eastern Mexico, as shown in Figure 11-3. Mexican sources contribute about 1 µg/m^3 to simulated sulfate concentrations in southwestern Utah and western Arizona (Figure 11-4), and similar levels in the vicinity of the Great Lakes are attributed to sulfate from western U.S. sources (Figure 11-6). The impact of the sulfur boundary concentrations specified by GOCART is primarily confined to the domain periphery, with a large contribution evident in the Northeast (Figure 11-7).

From simulations such as the example just described, regional emissions attributions to sulfate at Big Bend NP were calculated for each day, for each month, and for the four-month BRAVO Study period, using both the "emissions in" and "emissions out" methods. Some results for the "emissions out" method are shown in Figure 11-8. (Results for the "emissions in" method were similar.) Panel (a) in Figure 11-8 shows the contribution of each source region to study-period-average simulated sulfate concentrations at Big Bend National Park. The left two bars, which represent the total observed and simulated sulfate concentrations at Big Bend, show that there is a tendency for REMSAD to underestimate average sulfate concentrations there by about 20% (2.5 μg/m^3 observed vs. 2.0 μg/m^3 simulated). Possible explanations for this underestimation include: 1) SO_2 emissions may be underestimated for some regions, 2) wind field errors result in not correctly transporting SO_2 and sulfate, 3) SO_2 conversion rates are too slow, or 4) wet or dry SO_2 and $SO_4^{=}$ deposition is too great. The impact of these potential errors will influence the predicted source attributions.

As the monthly averages in panels (b) through (e) of Figure 11-8 show, however, this bias does not manifest itself consistently on a monthly basis. For example, simulated sulfate concentrations at Big Bend during July and August are approximately half the observed values, while the underestimate in September is smaller and there is an overestimate of about 25% in October. This variation in bias corresponds to different flow regimes that were evident during the BRAVO study. For example, trajectory analysis indicates that transport to Big Bend was predominantly from Mexico during July and some of August. Transport patterns during September and October resulted in more influence from eastern U.S. and Texas sources, which is reflected in the larger relative eastern U.S. contribution in panels (d) and (e) in Figure 11-8.

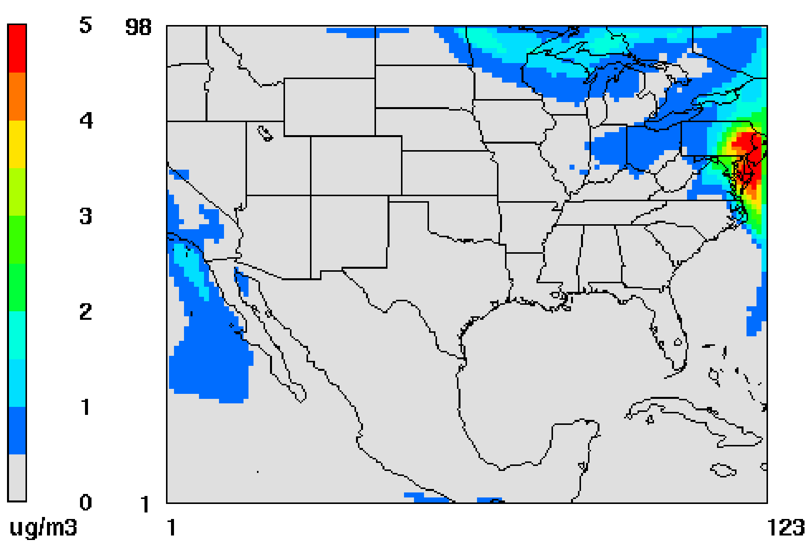

Figure 11-7. *REMSAD simulation of sulfate concentrations attributable to sulfur concentrations defined along the modeling domain boundaries by the GOCART global model on 17 August 1999 at 1500 UTC.*

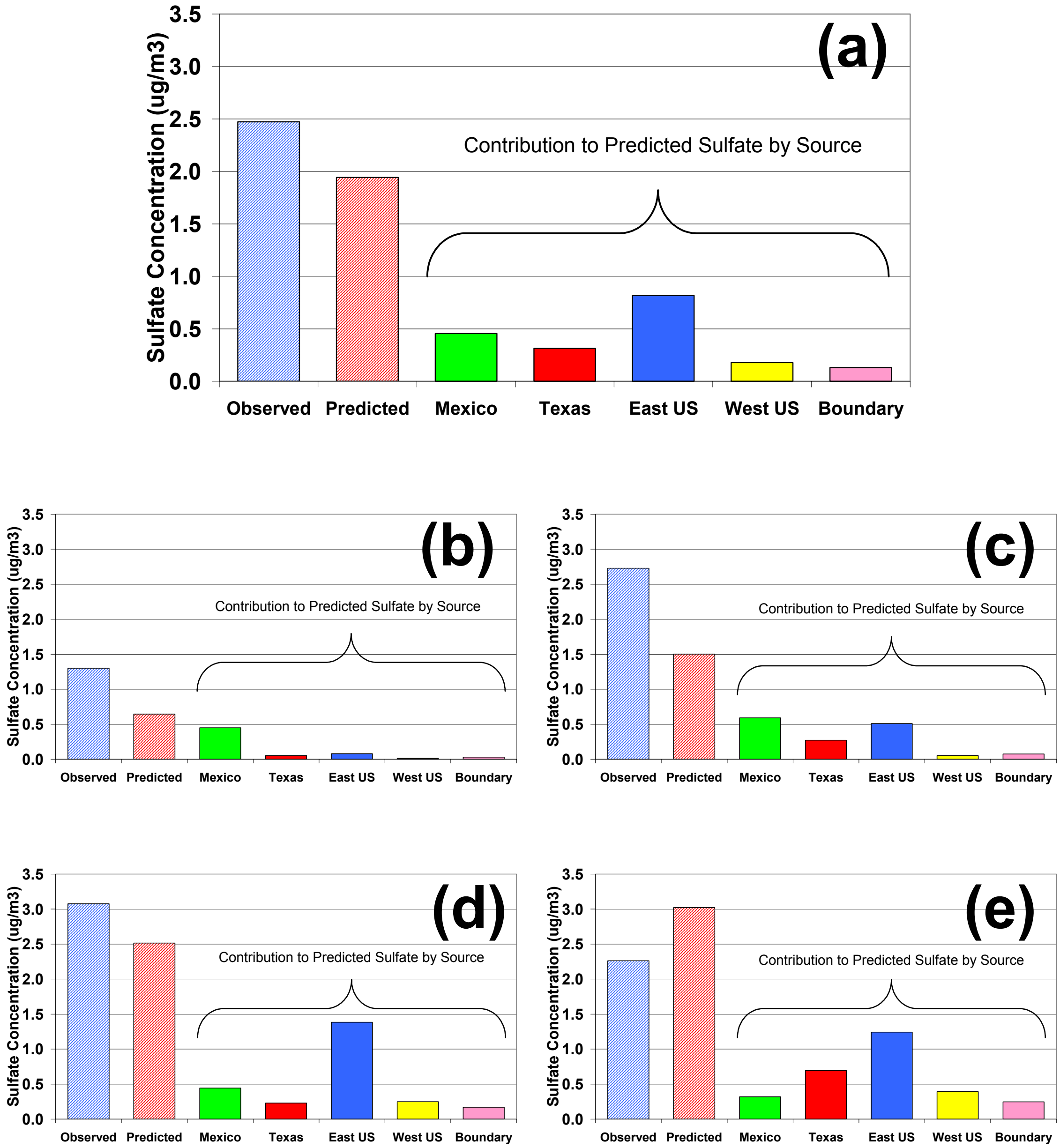

***Figure 11-8.** Observed and REMSAD-estimated sulfate concentrations at Big Bend and REMSAD-estimated contributions by source region (using the "emissions out" approach) for (a) the 4-month BRAVO Study period and (b-e) July through October, respectively.*

The corresponding relative study-period and monthly sulfate attributions at Big Bend are presented in Figure 11-9. The quantities indicated there are the ratios, in percent, of the average REMSAD-estimated sulfate concentration over the given period to the total estimated sulfate concentration at Big Bend over that same period. The monthly pie charts show clearly how the relative attributions differ in most months from the average study period attributions, with a transition from a Mexican-dominated influence in the early part of the study (panels (b) and (c)) to a regime where eastern U.S. sources and, to a lesser extent, Texas sources, dominate. For example, Mexican contributions to simulated Big Bend sulfate drop from 70% in July to 11% in October, while the contribution from eastern U.S. sources rises from 12% in July to 55% in September and 41% in October.

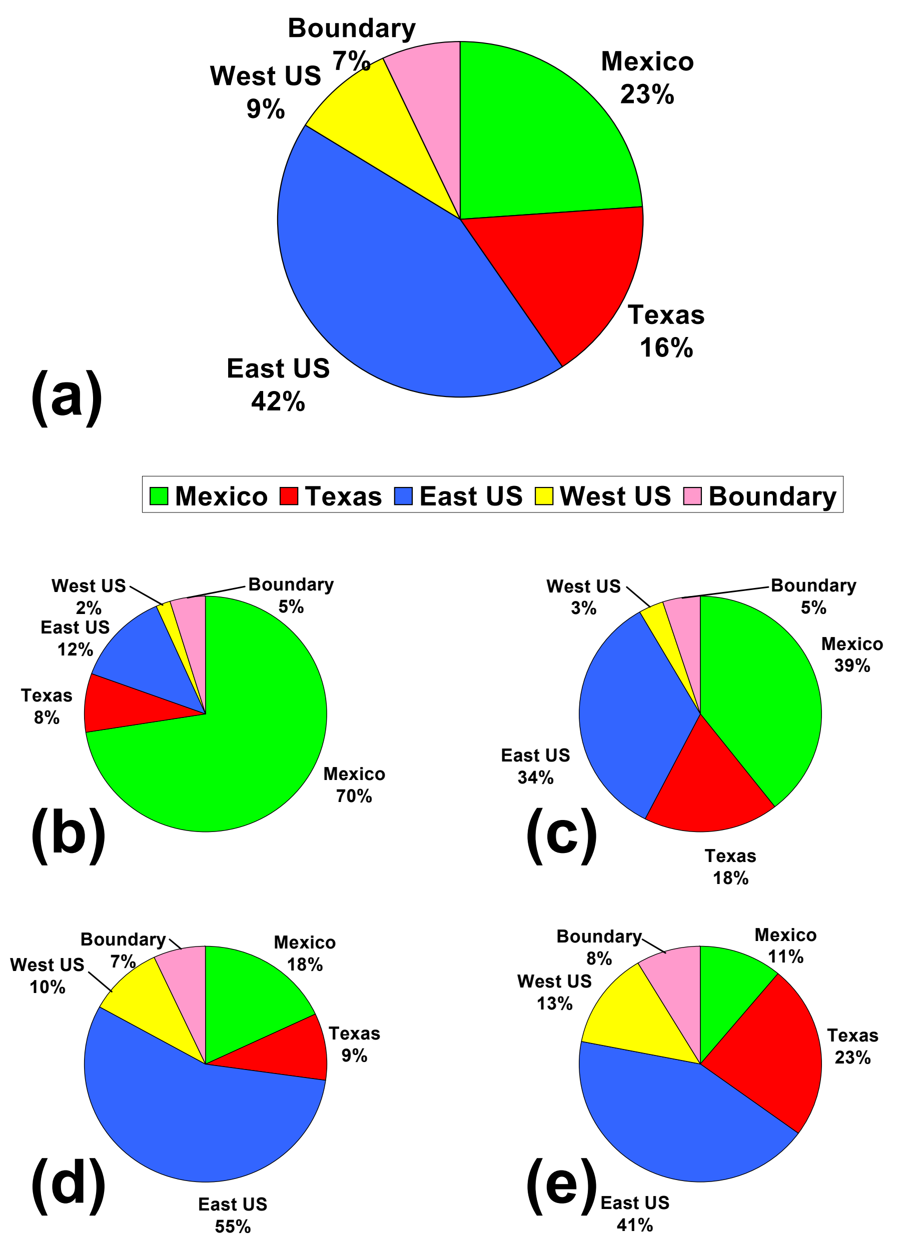

Figure 11-9. *REMSAD-estimated relative attributions, of average sulfate concentrations at Big Bend for each source region (using the "emissions out" approach) for (a) the 4-month BRAVO Study period and (b-e) the months of July through October, respectively.*

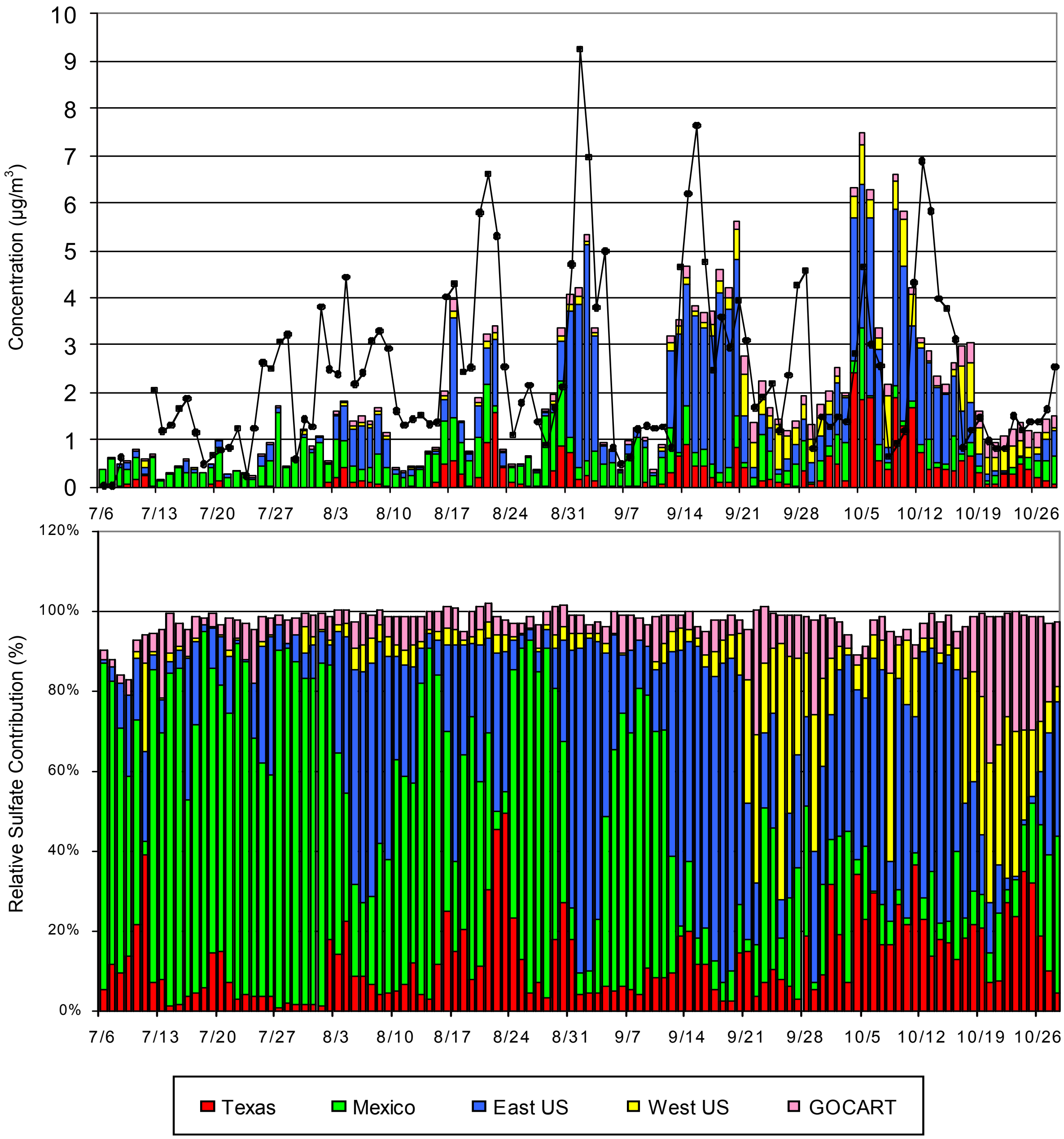

Figure 11-10. *Daily REMSAD attributions of sulfate concentrations at Big Bend to the four source regions and the GOCART boundary concentrations, based on the "emissions out" approach. Top: Absolute concentrations and comparison with measured fine particulate sulfur concentrations (black line). Bottom: Concentrations relative to base case simulated values (100%).*

Sulfate source attributions at the K-Bar site in Big Bend National Park were also examined on a daily basis. Figure 11-10 displays the simulated daily sulfate contribution by each source region. In the top panel, the heights of the bars represent the total simulated sulfate concentration, which can be compared with dots that indicate the daily measured concentrations at K-Bar. In the bottom panel, the daily attributions are shown as percentages of the base case simulated sulfate concentrations. (Note that the sum of the regional attributions is not always exactly 100% of the simulated base case total, due to nonlinearities in the processes.)

During July and the first half of August, the daily REMSAD simulated sulfate concentrations were consistently smaller than the observed concentrations, as shown in the upper panel of Figure 11-10. During this period, transport was predominantly from Mexico, as reflected by the large relative attribution to Mexican sources in the lower panel. The absolute contribution from Mexican sources is generally small (less than 1 $\mu g/m^3$) during this period, though. During this period, and continuing through mid-September, there are occasional periods when the contribution of sulfate from eastern U.S. sources becomes dominant.

From mid-August onward, the high sulfate episodes show a major component of eastern U.S. sulfate. This is especially evident for the sulfate episodes in early and mid-September, when the relative proportion of simulated eastern U.S. sulfate exceeded 80% for part of each episode. Note that during these two episodes the REMSAD-simulated concentrations at Big Bend fell well below the observed values. Mexican emissions dominate the relatively clean period between these two September episodes.

The two October sulfate episodes also show a major contribution from eastern U.S. sources, but Texas sources, and to a lesser extent Mexican and western U.S. sources, also have a considerable impact. In contrast to the September episodes, there is a substantial over-estimation of the October 5th sulfate peak, and the model then estimates high concentrations three days earlier than they were observed on October 12th. The intervening periods between the late September and October sulfate episodes show a more evenly mixed distribution between all four source regions.

Table 11-1 shows the absolute and relative sulfate attributions predicted at Big Bend NP for seven sulfate episodes that occurred during the four-month BRAVO Study period. As discussed above, there is a tendency for REMSAD to underestimate sulfate contributions during the first half of the study. During the entire study, Episode 6 (3–7 October) was the only episode during which REMSAD overestimated sulfate concentrations at Big Bend NP. Note that the attribution results for the second October sulfate episode (Episode 7, 11–16 October) should be interpreted with care, since the time of the predicted peak does not match the observations (see Figure 11-10).

In addition to the four large source regions discussed above, sulfate apportionment at Big Bend NP was also carried out for smaller subregions. Those "emissions out" analyses attributed 14% of the total sulfate at Big Bend to emissions from the *Carbón* I/II power plant. Details of the subregional analyses can be found in the NPS report on the BRAVO Study (Schichtel et al., 2004), which is included in the Appendix to this report.

Table 11-1. REMSAD source attributions of fine sulfate at the K-Bar site during seven selected episodes. For each episode, the values in the upper row represent the episode-average simulated concentrations (in µg/m^3) attributable to each source region and to the GOCART boundary concentrations. The values in the lower row represent the percentage of the average simulated concentration of sulfate during the episode that is attributed to each source region. (The sum may not be exactly 100% because of rounding.)

	Mexico	Texas	Eastern U.S.	Western U.S.	GOCART Boundary	Total Simulated	Observed
Episode 1	0.61	0.02	0.09	0.01	0.04	0.77	1.73
7/22 - 7/31	79%	2%	12%	1%	5%		
Episode 2	0.66	0.58	0.77	0.08	0.11	2.20	4.18
8/16 - 8/23	30%	26%	35%	4%	5%		
Episode 3	0.38	0.28	2.71	0.10	0.13	3.67	5.93
8/31 - 9/4	10%	8%	74%	3%	4%		
Episode 4	0.46	0.51	2.48	0.15	0.18	3.86	4.41
9/12 - 9/17	12%	13%	64%	4%	5%		
Episode 5	0.38	0.15	0.31	0.52	0.14	1.52	3.09
9/25 - 9/28	25%	10%	20%	34%	9%		
Episode 6	0.59	1.39	2.55	0.39	0.19	5.46	2.87
10/3 - 10/7	11%	25%	47%	7%	3%		
Episode 7	0.32	0.67	1.58	0.19	0.15	3.03	4.64
10/11 - 10/16	11%	22%	52%	6%	5%		

11.2 Sulfate Attribution via CMAQ-MADRID

The CMAQ model with the MADRID aerosol module (CMAQ-MADRID), which was described in Section 8.4.3, was also used for attributing Big Bend sulfate to source regions. The results of the CMAQ-MADRID attribution analyses are summarized here. The modeling approach and its results are described in detail in the EPRI report (Pun et al., 2004), which is enclosed in the Appendix to this report. For all of these analyses, the CMAQ-MADRID was applied in its base case configuration, which included boundary conditions scaled to IMPROVE and CASTNet observations, as described in Section 9.11.1.

For the attribution analyses, the CMAQ domain (shown in Figure 11-11), which was smaller than the REMSAD domain (shown in Figure 11-1), was also divided into four geographical source regions for attribution analysis: Mexico, Texas, eastern U.S., and western U.S. (excluding Texas). Although the CMAQ source regions, other than Texas, were smaller than those of REMSAD, the CMAQ attribution analyses included consideration of inflow from surrounding areas, as estimated by the REMSAD model (with its use of GOCART model boundary conditions), and therefore the attributions assigned by both models to various source regions should be equivalent.

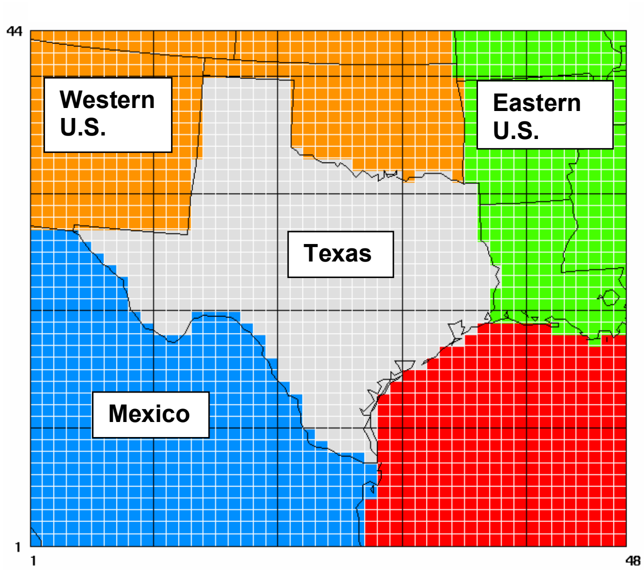

***Figure 11-11**. Source regions used for CMAQ-MADRID sulfate attributions. No source attribution simulations were conducted for the open water Gulf of Mexico (red) region.*

Five sensitivity simulations were conducted. Since REMSAD serves as an outer nest to the CMAQ-MADRID simulations, the first sensitivity simulation evaluated the contribution from the boundary conditions of the larger REMSAD domain (as estimated from the GOCART model) to the fine particulate sulfate load in the CMAQ domain. Each of the ensuing sensitivity simulations evaluated the contribution of a particular source region to the fine particulate sulfate load by removing all primary sulfur emissions (SO_2 and primary sulfate) of that region within the CMAQ domain and also their contribution to the conditions at the boundary of the CMAQ domain (by removing the same emissions from the portion of the REMSAD modeling domain that is within the region of interest). (This is the "emissions out" approach that was described in Section 11.1.) The contribution from a source region to fine particulate sulfate at Big Bend National Park was defined as the difference between the base case fine sulfate concentration and the fine sulfate concentration estimated by the attribution sensitivity simulation.

Source attributions at K-Bar were estimated for the duration of the BRAVO study period, for each of the four months, and for seven selected episodes. In spite of the potential that a large perturbation in emissions will produce non-linear responses to SO_2 oxidation and aerosol sulfate dynamics, the contributions from the source regions and the domain boundary typically summed to within 2% of the total final particulate sulfate estimated by the base case simulation.

Table 11-2 indicates the concentrations of sulfate at K-Bar Ranch at Big Bend National Park that the CMAQ-MADRID modeling attributed to each source region for each month and for the entire study period. The last two columns show that the average concentrations estimated by CMAQ-MADRID for these periods closely approximated the measured averages, except for a nearly-50% overestimate in October. This CMAQ-

MADRID analysis shows that the largest overall contributors to sulfate at Big Bend over the 4-month study period are Mexico and the Eastern U.S. region. One of these two regions is dominant during every one of the four months, although the Texas contribution is the second highest in October.

Table 11-2. CMAQ-MADRID estimates of average source region contributions to sulfate concentrations (in µg/m^3) at K-Bar during each of the BRAVO Study period months and during the entire study.

	Mexico	Texas	Eastern U.S.	Western U.S.	GOCART Boundary	Total Estimated	Observed
July	0.75	0.15	0.20	0.01	0.08	1.19	1.24
August	0.94	0.50	0.92	0.06	0.09	2.50	2.79
September	0.78	0.33	1.57	0.19	0.17	3.03	3.10
October	0.77	1.00	1.12	0.34	0.15	3.38	2.31
4-month study period	0.81	0.49	0.96	0.15	0.12	2.53	2.46

Figure 11-12 portrays the relative attribution of sulfate at K-Bar over the entire BRAVO Study period. The quantities there are the ratios, in percent, of the average CMAQ-MADRID-estimated sulfate concentrations over the study period to the total estimated sulfate concentration at K-Bar over that same period. Averaged over the study period, the Eastern U.S. region and Mexico each contribute roughly a third of the sulfate and Texas contributes about a fifth.

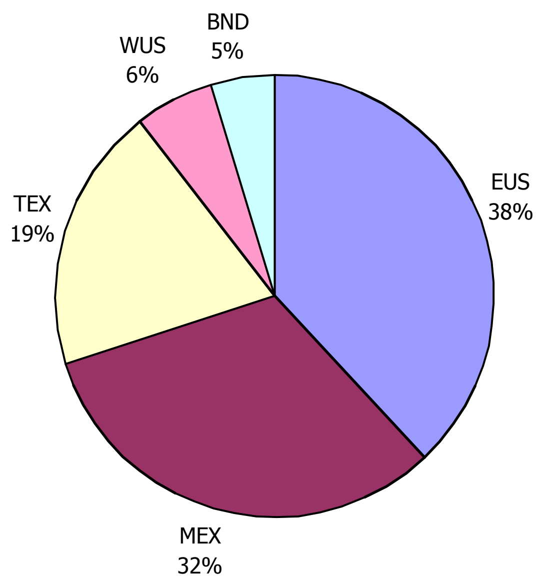

Figure 11-12. *CMAQ-MADRID average attribution of fine sulfate at K-Bar over the 4-month BRAVO Study period, expressed as ratios of estimated average regionally-attributed concentrations of sulfate to average total estimated sulfate.*

The average monthly relative attributions that correspond with the study period values are listed in Table 11-3. This table shows clearly the relative dominance of the Mexican contribution early in the study, the increasing role of the eastern U.S. region by September, and the more even division between Mexico, Texas, and the eastern U.S. region in October.

Table 11-3. Source region attributions of fine sulfate at K-Bar as estimated by CMAQ-MADRID for each month of the study period. Each percentage represents the ratio of the monthly or 4-month study period average concentration attributed to a region divided by the average of the total simulated sulfate concentration.

	Mexico	Texas	Eastern U.S.	Western U.S.	GOCART Boundary
July	63%	13%	17%	1%	6%
August	38%	20%	37%	2%	4%
September	26%	11%	52%	6%	6%
October	23%	30%	33%	10%	4%
4-month study period	32%	19%	38%	6%	5%

Estimates of the daily source region attribution for fine particulate sulfate at K-Bar in Big Bend National Park are presented in Figure 11-13 for the entire BRAVO Study period. The solid black line shows the measured concentrations at K-Bar. The estimated concentrations and relative contributions from each source region vary considerably from one day to the next. The differences between total simulated and measured sulfate concentrations will be discussed later in this section.

It is informative to look at the CMAQ-MADRID attributions for seven episodes that encompass periods of elevated sulfate concentrations at Big Bend. Table 11-4 provides two representations of source region attribution results for fine sulfate at K-Bar during the seven selected episodes. The source region contributions are shown both as average sulfate concentration contributions over the episode and as average percentages of the total CMAQ-simulated sulfate concentrations during each episode

As the final two columns in Table 11-4 show, the episodic Big Bend sulfate concentrations simulated by CMAQ-MADRID did not always agree well with the measurements during these periods of higher sulfate concentrations. There was no consistent bias; in Episode V the average simulated concentration was about 39% of the measured concentration, while in Episode VI the average simulated concentration was about twice the measured value.

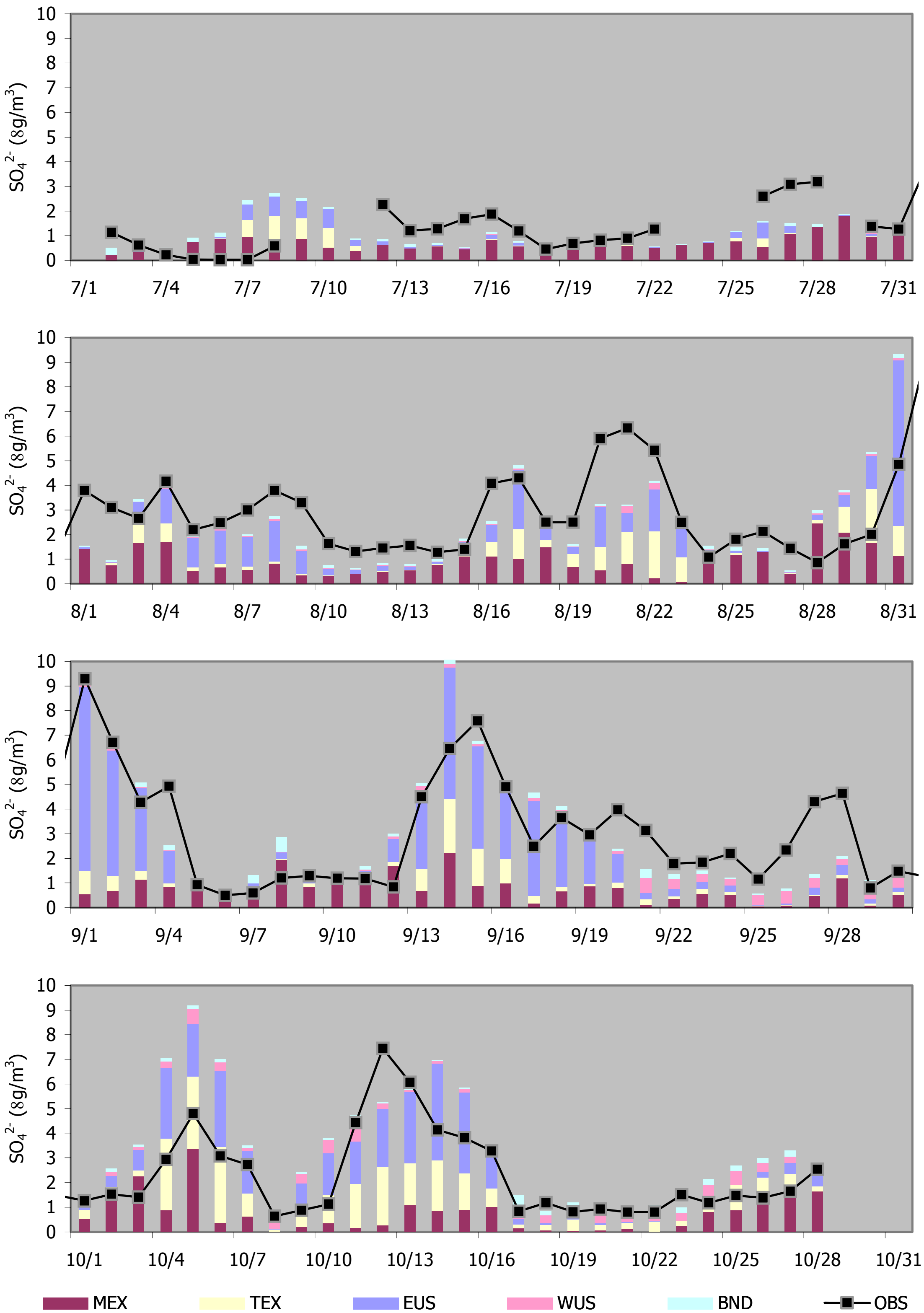

Figure 11-13. *Daily CMAQ-MADRID attributions of sulfate concentrations (in μg/m³) at Big Bend to the four source regions and the boundary concentrations. The observed fine particle sulfur concentration (expressed as sulfate) is indicated by the black line.*

Table 11-4. CMAQ source attributions of fine sulfate at the K-Bar site during seven selected episodes. For each episode, the values in the upper row represent the episode-average simulated concentrations (in μg/m^3) attributable to each source region and to the GOCART boundary concentrations. The values in the lower row represent the percentage of the average simulated concentration of sulfate during the episode that is attributed to each source region. (The sum may not be exactly 100% because of rounding.)

	Mexico	**Texas**	**Eastern U.S.**	**Western U.S.**	**GOCART Boundary**	**Total Simulated**	**Observed**
Episode 1	0.96	0.06	0.15	0.01	0.05	1.24	2.13
7/22-7/31	78%	5%	12%	1%	4%		
Episode 2	0.74	0.97	1.19	0.11	0.11	3.13	4.19
8/16-8/23	24%	31%	38%	3%	3%		
Episode 3	1.00	0.91	4.23	0.07	0.17	6.35	5.35
8/31-9/4	16%	14%	67%	1%	3%		
Episode 4	1.11	1.01	3.38	0.13	0.15	5.75	4.46
9/12-9-17	19%	18%	59%	2%	3%		
Episode 5	0.45	0.05	0.2	0.39	0.11	1.21	3.11
9/25-9/28	37%	4%	16%	32%	9%		
Episode 6	1.50	2.01	2.14	0.30	0.11	5.98	2.99
10/3-10/7	25%	34%	36%	5%	2%		
Episode 7	0.72	1.67	2.63	0.28	0.04	5.34	4.86
10/11-10/16	13%	31%	49%	5%	1%		

In order to assess the implications of these negative and positive biases on the source attributions, the twenty days exhibiting the greatest relative underestimates and the twenty days displaying the greatest relative overestimates were analyzed separately. Details of this analysis are given in Pun et al. (2004) and are summarized here. The two groups show biases of comparable magnitude, but in opposite directions. Considering these sets of 20 days, the CMAQ-MADRID modeling system produced 6 to 8 days of acute underestimates of fine sulfate at K-Bar during every month except October, but it also produced large overestimates of fine sulfate at K-Bar during every month, with the overestimates most frequent in October.

The regional source attributions on these two groups of days were different, as portrayed in Table 11-5, with the days with underestimates showing relatively more sulfate attributed to Mexico and those with overestimates showing relatively more sulfate attributed to Texas and the eastern U.S. region.

The information in Table 11-5, combined with the CMAQ-MADRID model performance information in Section 9.11, suggests that many overestimates at Big Bend occur when air masses arrive at Big Bend from Texas and the eastern U.S. region, which are areas where the CMAQ-MADRID system overestimates sulfur. These overestimated sulfur concentrations appear to be carried over to Big Bend. Conversely, underestimates tend to occur often when air masses arrive at Big Bend from Mexico, which suggests that some aspect of the modeling system (emissions, meteorology, or chemistry) may underestimate the amount of sulfate arriving from Mexico.

Table 11-5. Source region attributions of fine sulfate at K-Bar as estimated by CMAQ-MADRID for the 20 days with the greatest relative underestimates and the 20 days with the greatest relative overestimates. Each percentage represents the ratio of the 20-day average concentration attributed to a region divided by the 20-day average of the total simulated sulfate concentration.

	Mexico	Texas	Eastern U.S.	Western U.S.	GOCART Boundary
20 Days with Greatest Relative Underestimates	50%	9%	22%	11%	8%
20 Days with Greatest Relative Overestimates	32%	25%	34%	6%	5%

Adjustments to the modeling system to compensate for these systematic biases were not made in the course of the CMAQ-MADRID simulations and to the resulting attributions described in this section. They are treated, however, in the merging of CMAQ-MADRID simulation results and measurements in the Synthesized CMAQ-MADRID approach that is described in the next section.

11.3 Refined Sulfate Attribution using Synthesized Modeling Approaches

As described above and in Section 8.4, both the REMSAD and CMAQ-MADRID models were employed to simulate the sulfate concentrations over the BRAVO Study area. The performance of these two models was described in Sections 9.9 and 9.11. Although the performance of both models was consistent with the state of the art of regional modeling, spatial and temporal trends in the errors resulted in large errors at some times and places. For example, as discussed in Section 9.9, REMSAD nearly uniformly underestimated the sulfate concentrations throughout Texas during July and overestimated them in October. The positive bias in eastern Texas was at least partly due to overestimation of contributions from eastern U.S. sources. Similarly, the discussion in Section 11.2 described how there were large biases in CMAQ-MADRID estimates during many elevated sulfate episodes and how those biases appeared to be related to transport from different regions.

In order to account for these biases, the modeled sulfate source attribution results from both models were regressed against observed sulfate concentrations throughout Texas. The same simulated attribution results were then scaled by the regression coefficients to derive alternative source attribution estimates that better fit the measured data. The regression method used is summarized in Section 8.4.4 and is described in detail in the CIRA/NPS report on the BRAVO Study (Schichtel et al., 2004).

The resulting scaled modeling approaches are called "Synthesized REMSAD" and "Synthesized CMAQ-MADRID". As described in Section 9.12, the Synthesized REMSAD and CMAQ-MADRID estimated Big Bend sulfate concentrations better than the original models.

The average source contributions to Big Bend's sulfate during the BRAVO Study period, as determined by the synthesized models, are presented in Table 11-6, with values from the original attributions (as described in Section 11.1 and 11.2) provided for comparison. Standard errors of the estimates are given for the synthesized model attributions. Note that the REMSAD results also provide separate figures for the *Carbón* power plant and for the rest of the Mexico source region. Additional information concerning estimates of attributed concentrations and relative contributions is portrayed graphically in Figure 11-14.

Table 11-6. Relative study-period source attributions (in %) of fine sulfate at K-Bar by the synthesized and original models. The values represent the percentage of the average simulated sulfate concentration that is attributed to each source region. Standard errors of the estimates are given for the synthesized model attributions.

	Synthesized Models		Original Models	
	REMSAD	**CMAQ**	**REMSAD**	**CMAQ**
Mexico	39 ± 2.3	38 ± 1.7	23	32
Carbón	23 ± 1.8		14	
Rest of Mexico	16 ± 1.4		10	
Texas	16 ± 1.2	17 ± 1.3	16	19
Eastern U.S.	32 ± 1.2	30 ± 1.2	42	38
Western U.S.	6 ± 0.7	8.5 ± 0.8	9	6
Boundary Conditions	7 ± 0.5	6.4 ± 0.6	7	5

The Synthesized REMSAD and Synthesized CMAQ-MADRID results are nearly identical, with most differences being 2 or less percentage points. This good agreement differs from the original model results shown in the last two columns of Table 11-6, where, for example, the Mexican contribution estimate from CMAQ was 36% larger than that from REMSAD. Therefore, the synthesized inversion approach accounts for the different biases in the two models.

The synthesized REMSAD results show that the Mexico source region was the largest average contributor at 39%, the eastern U.S. region was second at 32%, followed by Texas at 16%. The notable sub regions reflected in the REMSAD attributions include the *Carbón* facility, which contributed 23%, and east Texas (not shown in Table 11-6), which contributed 14%. East Texas includes the Lignite Belt region and about 90% of Texas' SO_2 emissions.

Compared to the original REMSAD and CMAQ source attribution estimates, the Mexican contribution increased, the eastern U.S. contribution decreased, and Texas' contribution remained about the same when the synthesized models were used instead. The REMSAD model, which originally had the poorer performance, showed the largest differences between the synthesized and original source attribution estimates.

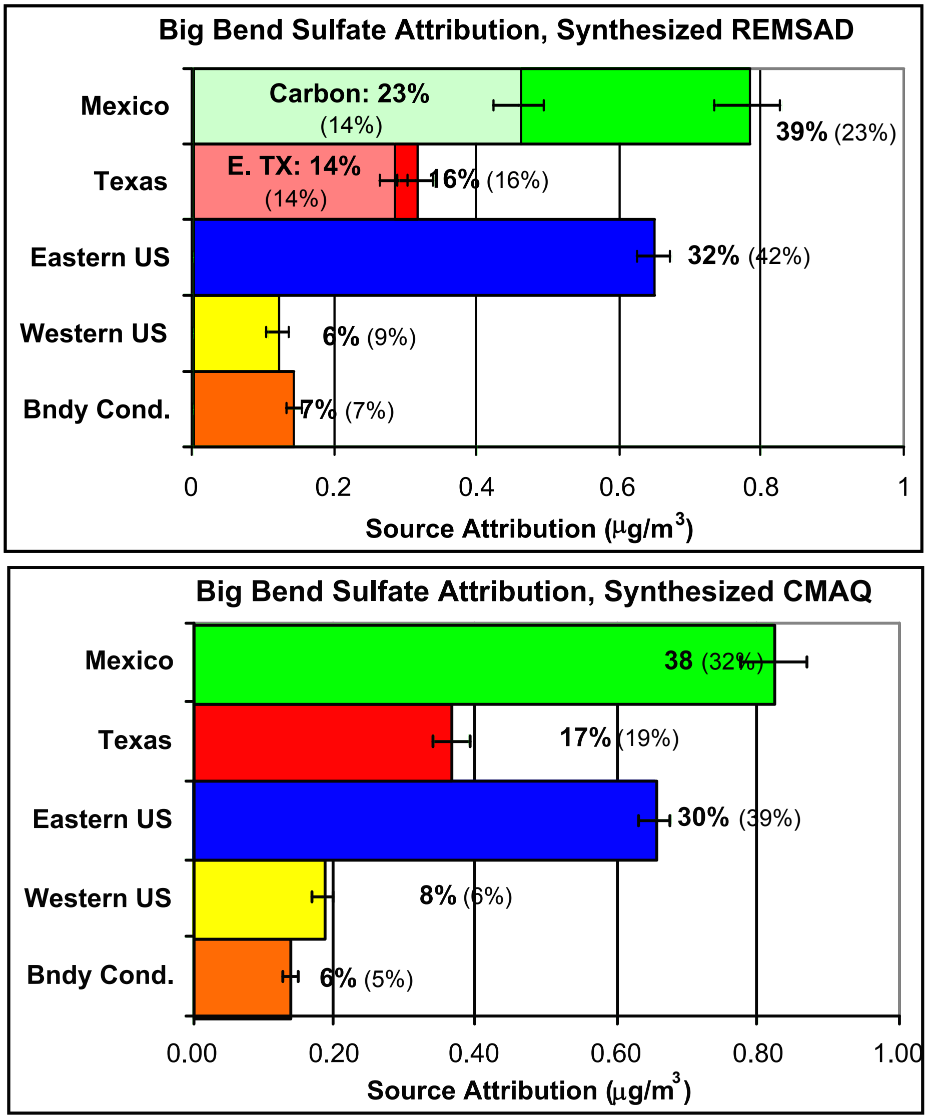

Figure 11-14. *Study-period source attributions of fine sulfate (in µg/m³) at K-Bar by the synthesized and original models. The numerals at the end of each bar represent the percentage of the average simulated sulfate concentration that is attributed to each source region and (in parentheses) the corresponding values derived using the original models. Error bars indicate the standard errors of the attribution estimates.*

It is interesting that the contribution from the *Carbón* facility increased by about 65% when the synthesized approach was used. The REMSAD model was run with the lower *Carbón* SO_2 emission rate of 152,000 tons/yr, which is 63% of the upper estimate of 241,000 tons/yr, so this adjustment effectively produces the concentration estimates that would have resulted from using the higher rate. (See Section 4.3 for a discussion of estimates of *Carbón* plant emissions estimates.)

Figures 11-15 and 11-16 portray, respectively, the Synthesized REMSAD and CMAQ attributions, both in terms of concentration and in terms of relative attribution, for seven multi- day sulfate episodes at Big Bend. (These same episodes were analyzed in the CMAQ-MADRID attributions described in Section 11.2.) The source regions of Mexico, the eastern U.S., and Texas each contributed 30% or more of the simulated sulfate concentration during two or more of these episodes. Usually, more than one of the major source regions simultaneously contributed significantly to the sulfate. Exceptions are the episode around July 22, in which Mexico was estimated to contribute about 80% of the sulfate, and the episode around September 1, in which the eastern U.S. accounted for more than 70% of the sulfate. Of the seven episodes, the July 22 episode had the lowest average sulfate concentrations while the September 1 episode had the largest average concentration.

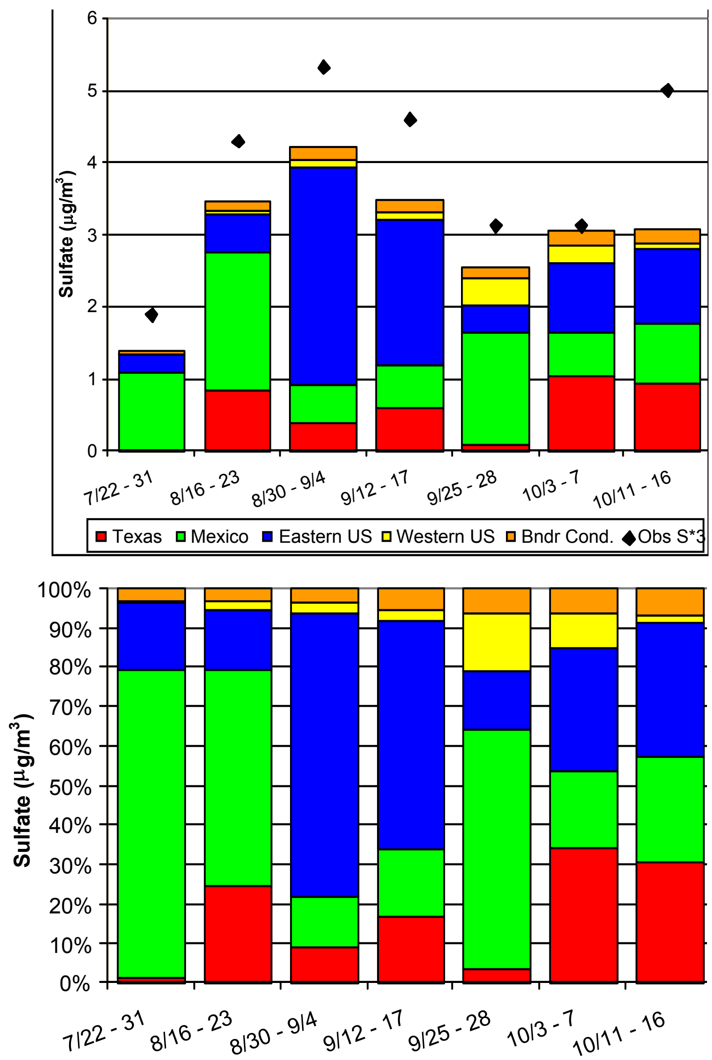

Figure 11-15. *Synthesized REMSAD estimates of K-Bar sulfate source attributions for seven selected episodes. Top: Concentrations averaged over each episode period (diamonds indicate measurements). Bottom: Average relative attribution over each episode period, as percentages of the episodic average of the total simulated sulfate.*

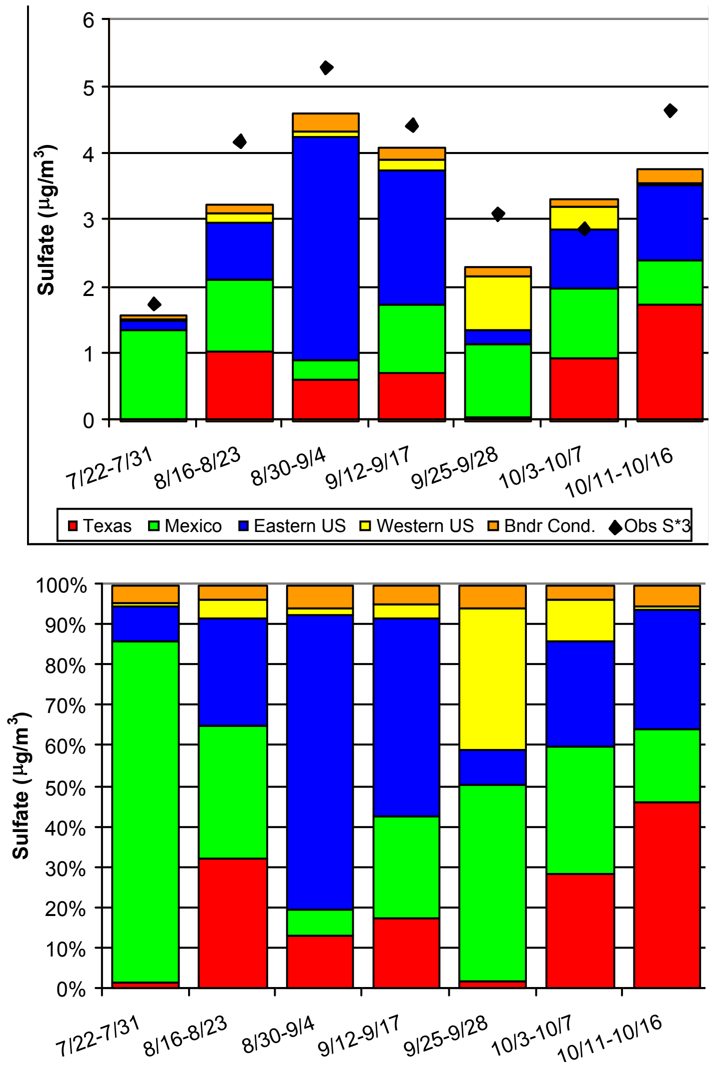

Figure 11-16. *Synthesized CMAQ-MADRID estimates of K-Bar sulfate source attributions for seven selected episodes. Top: Concentrations averaged over each episode period (diamonds indicate measurements). Bottom: Average relative attribution over each episode period, as percentages of the episodic average of the total simulated sulfate.*

Unlike the case for the study period average attributions, there are differences between the attributions for some of the sulfate episodes. For example, during the episode around August 20, Synthesized REMSAD estimated that Mexican sources contributed more than 50% to Big Bend's sulfate (Figure 11-15), while Synthesized CMAQ found Mexico, Texas and eastern U.S. each contributing about 30% of the sulfate (Figure 11-16). Also, during the episode around October 13, Synthesized CMAQ estimated the Texas contribution to be almost 50% compared to a 30% average contribution via Synthesized REMSAD. In situations such as this, the Synthesized CMAQ results are likely to be more trustworthy because the original CMAQ-MADRID results compared better to the observed sulfate data and the Synthesized CMAQ-MADRID results are closer to the original model estimates than those of Synthesized REMSAD. Therefore, the CMAQ-MADRID source attributions required smaller bias corrections, and relied less on the regression analysis to fit the observed data.

Daily Synthesized CMAQ attribution estimates, smoothed by a three-day moving average, are shown in Figure 11-17. The three-day smoothing was necessary since the synthesis inversion used three consecutive days in the analysis. (It has the visual benefit of making the key trends and episodic behavior stand out more.) Each source region's contribution had unique trends over the four-month period.

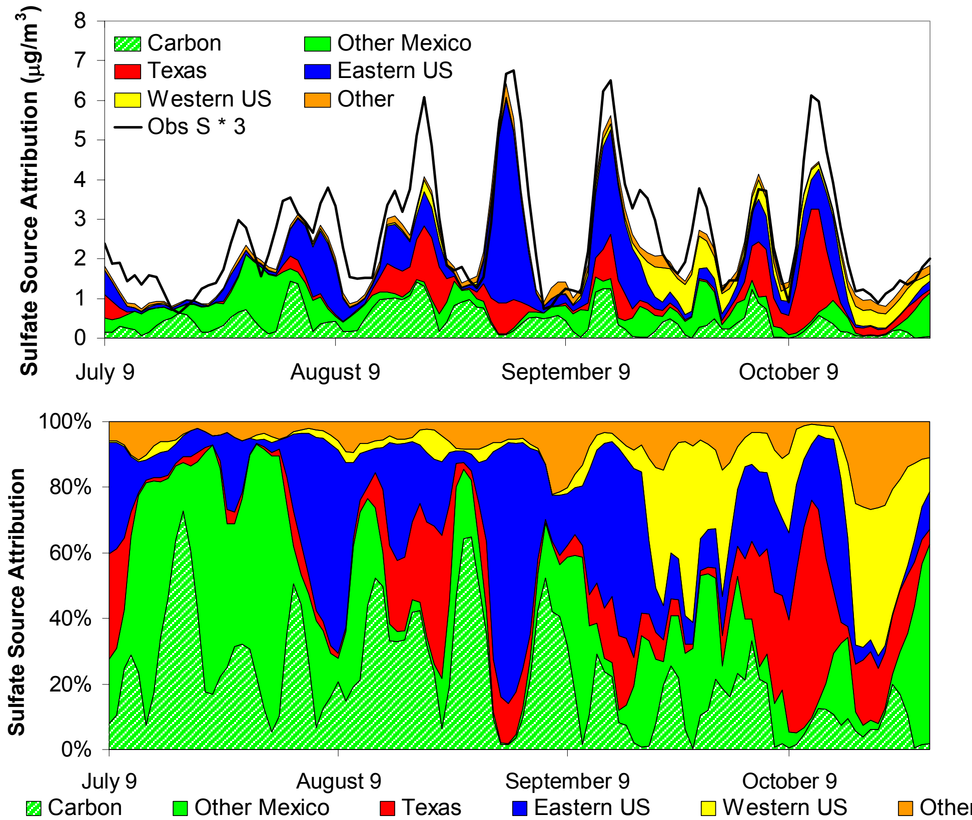

Figure 11-17. *Smoothed daily Synthesized CMAQ-MADRID attributions of sulfate at K-Bar. Top: Simulated and observed concentrations. Bottom: Fraction of simulated total sulfate.*

Mexico's contributions dominated the simulated sulfate concentrations in July and August contributing from 0.5 to 1.5 µg/m^3 of sulfate every day, and occasionally exceeding 2 µg/m^3. The total sulfate concentrations at Big Bend were relatively small then. In September and October, both the absolute and relative contributions from Mexico decreased, to typically less than 1 µg/m^3 per day, and even less by the end of October.

In contrast, the Texas source region had little contribution in July and the largest contribution in October. The Texas source contributions were episodic, with their largest absolute contributions (>1 μg/m^3) during the days when sulfate concentrations were the greatest at Big Bend.

The eastern U.S. contributions also tended to occur during high sulfate episodes. The highest eastern U.S. contribution exceeded 4 μg/m^3 during the episode around September 1. The apparent coincidence of the Texas and Mexican contributions to Big Bend is corroborated by the air mass history analyses described in Section 10.4, which showed that the transport route from the eastern U.S. to Big Bend often passed through Texas.

During the days with the lowest sulfate concentrations, Mexico was the largest contributor to Big Bend's sulfate. From July to September, Mexican sulfate often accounted for more than 80% of Big Bend's sulfate concentrations when the overall concentrations were below 2 μg/m^3. In October, the western U.S. and boundary condition source regions also were major contributors to the lowest sulfur days, together accounting for 60 to 80% of the estimated sulfate from October 19 to 24.