1) Introduction

The Big Bend Regional Aerosol and Visibility Observational (BRAVO) study was a multi-year assessment of the causes of haze in the Big Bend National Park, Texas (BBNP). Big Bend is located in southwestern Texas along the Mexican-Texas border. During the 1990s, the haze at Big Bend and other sites in West Texas and southern New Mexico had increased, further obscuring Big Bend's scenic beauty [*Malm et al.*, 2000b; *Malm et al.*, 2001a]. The BRAVO study was performed in response to the increased haze and the construction of the Carbón facilities, two coal-fired power plants in Mexico, approximately 125 miles southeast of the park. Past studies at Big Bend indicated that emissions from both the United States and Mexico contributed to the haze, but the impact due to individual source regions was unknown. A description of the planning process for BRAVO can be found in *Green et al.* [2000]. BRAVO study participants include the National Park Service (NPS), the U.S. Environmental Protection Agency (EPA), Colorado State University (CSU), the Texas Commission on Environmental Quality (TCEQ), and the Electric Power Research Institute (EPRI), among others.

The primary objective of the BRAVO study was to identify the source regions and source types responsible for haze at BBNP. This includes qualitative understanding of the long range transboundary transport of haze from regional sources in the U.S. and Mexico to Big Bend, and the quantitative contribution of specific U.S. and Mexican source regions and source types responsible for Big Bend's haze. Sources and source regions of particular interest were the Mexican Carbón I & II power plants, industrial source areas along the Texas gulf coast and in Monterrey and Tula, Mexico, coal-fired power plants and refineries in Texas and large SO_2 source regions in the southeastern and midwestern U.S. The BRAVO study also had a number of research objectives including the characterization of inorganic and organic aerosol components, developing and testing relationships between measured aerosol composition, concentration, and physical properties and light scattering, and measuring the hygroscopic properties of the aerosol components.

The focus of this report is to provide a detailed description of the modeling and analytical methods that were conducted by the NPS and CSU in support of BRAVO. These include "receptor-oriented" and "source-oriented" models, along with an approach labeled "synthesis inversion analysis" which represents an innovative hybrid technique that can be useful in identifying biases in the source-oriented model. These complementary approaches have resulted in a greatly improved understanding of the pollution sources that contribute to haze in BBNP. In addition, the chemical composition and optical properties of the aerosol responsible for the haze are examined. Several findings of the BRAVO study have already been published [*Brown et al.*, 2002; *Hand et al.*, 2002; *Chow et al.*, 2003; *Malm et al.*, 2003].

1.1 Big Bend National Park Setting

In a remote area of southwestern Texas, where the Rio Grande makes a sweeping turn along the U.S.-Mexico border, lies an area known as the "Big Bend Country." Within this expanse sits BBNP, a 324,247 hectare (1,252 square miles) reserve established as a national park in 1944 and designated as a Biosphere Reserve in 1976 (Figure 1-1). Big Bend is a land of contrasts. The Rio Grande has created deep canyons with sheer walls, and portions of the Rio Grande are designated as a Wild and Scenic River. The majority of the park consists of Chihuahuan desert, with the Chisos Mountains providing an alpine ecosystem in the midst of the desert. It is a region of large biological diversity containing more than 1,000 species of plants,

including 65 cactus species, and 434 bird, 78 mammal, 71 reptile and amphibian, and 35 fish species [*Big Bend Natural History Assoc.*, 1990]. Endangered species include the peregrine falcon, black-capped vireo, Mexican long-nose bat, Big Bend gambusia (a fish), and three threatened cacti [*Big Bend Natural History Assoc.*, 1990]. Because of its contrasting landscapes, however, Big Bend is also known and appreciated for the beauty of its scenic vistas located in both countries.

Although early travelers called the land "el despoblado" – the unpopulated land – there is a rich history associated with the land extending back in time to ca. 8500–6500 B.C. The area is remote and sparsely populated, with approximately 13,000 people occupying an area about the size of the State of Maryland (12,407 square miles). In the 1930s many people who loved the Big Bend country saw that this land of contrast, beauty, and solitude was worth preserving for future generations—an effort that resulted in the establishment of Big Bend Ranch State Park and BBNP.

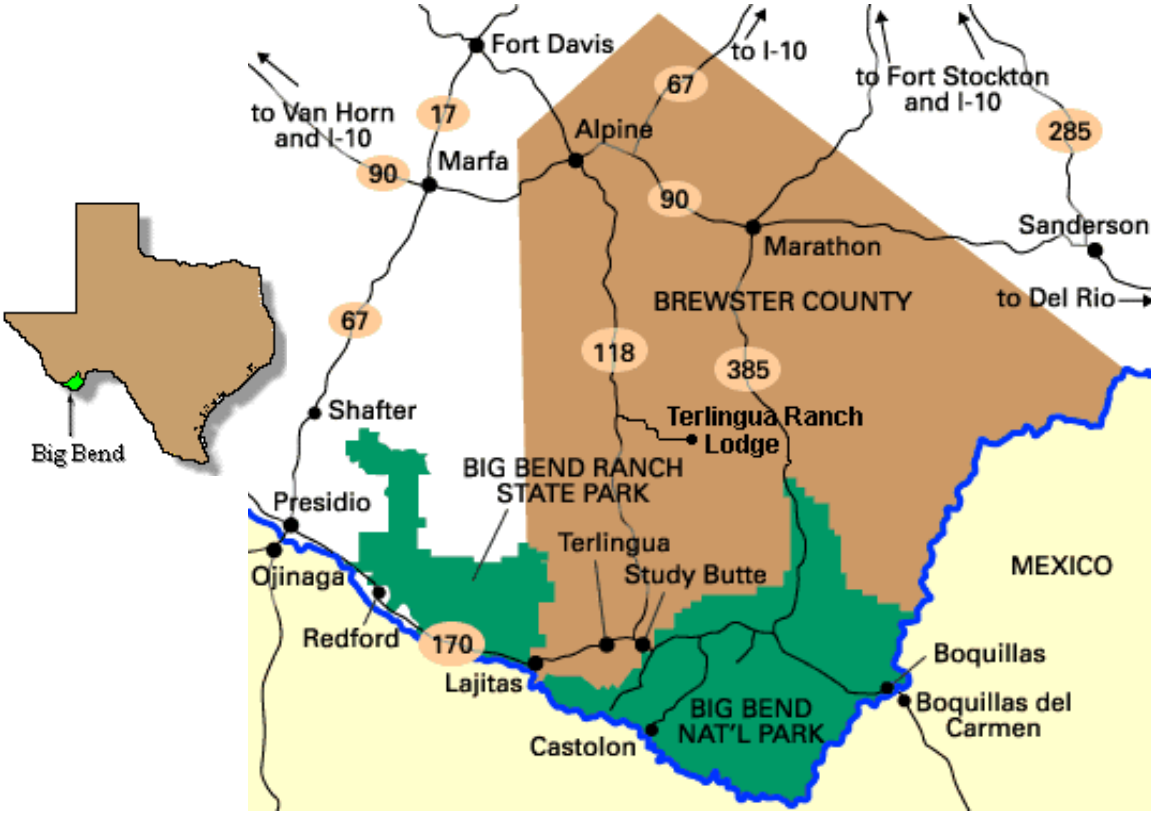

Figure 1-1. Location map of Big Bend National Park in southwestern Texas.

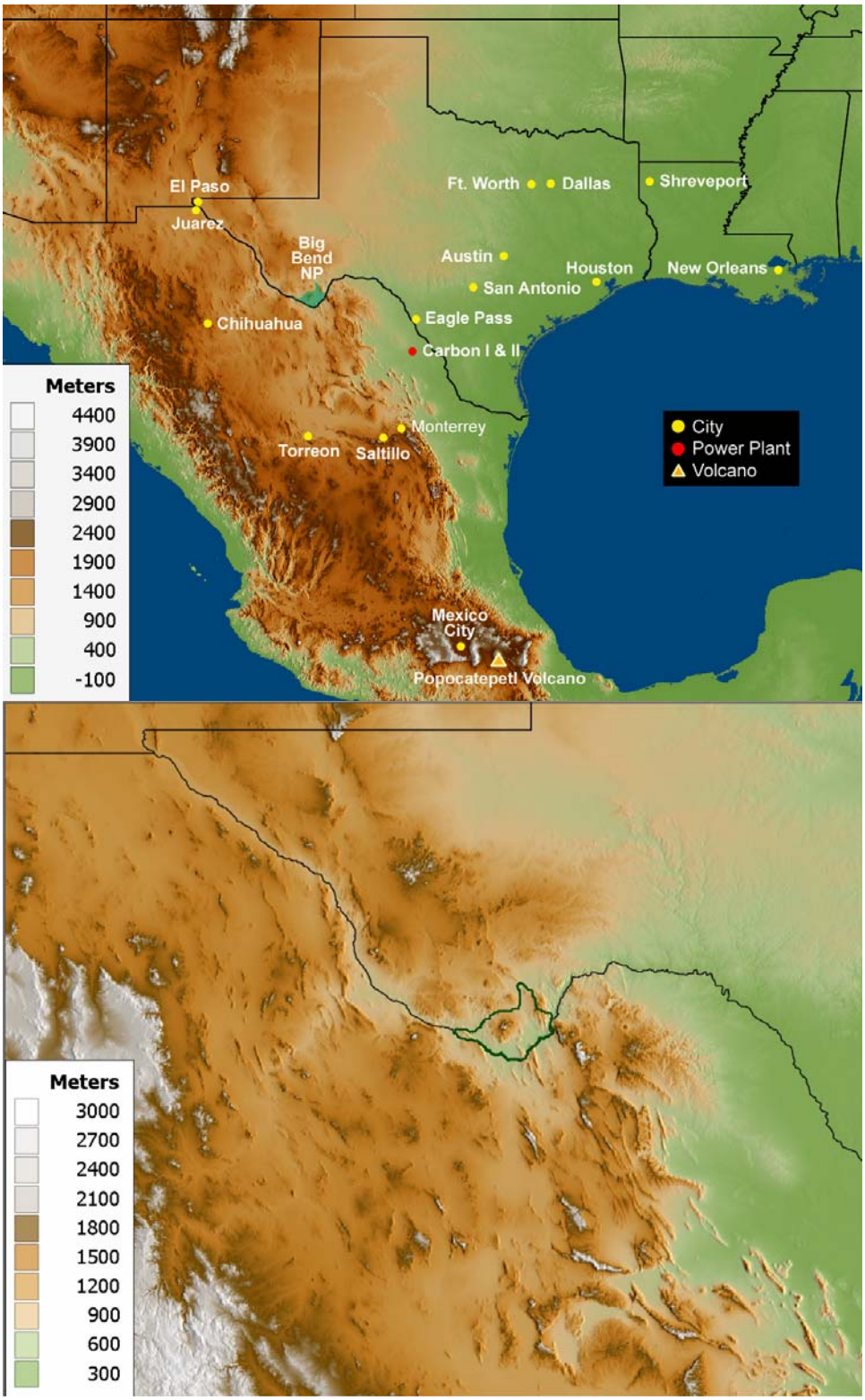

Figure 1-2. Texas and Mexico (above) and the terrain surrounding Big Bend National Park in western Texas and northern Mexico (below).

Big Bend National Park and most of Mexico and west Texas is characterized by complex mountainous terrain (Figure 1-2) which influences both regional and meso-scale transport of

pollutants to the Big Bend region. The Sierra Madre mountain range, located 100–300 km east of Mexico's Gulf Coast, abruptly rises 1 to 2 km above the surface. This is near the top of the boundary layer and hence this mountain range provides an effective barrier to flow from the Gulf of Mexico, channeling airflow from the southeast or northwest toward west Texas. Near Big Bend NP, the Rio Grande cuts a large valley into the mountain ranges. This valley could channel northwesterly flow along the Sierra Madre mountain range to the Big Bend region. Understanding these complex flow patterns is an important component of the BRAVO study.

1.2 Preliminary Study

As a result of concerns over visual air quality at BBNP, a preliminary regional visibility study (1996 Scoping Study) was conducted in Texas and northern Mexico in September and October 1996 [*Gebhart et al.*, 2001]. The primary objective of the preliminary study was to obtain information that would allow for the identification of possible source regions in both countries and source types responsible for visibility degradation at BBNP. The study was conducted at 19 monitoring stations from September 9 through October 13, 1996 (Figure 1-3). The sites sampled $PM_{2.5}$ (particulate matter with a diameter less than 2.5 μm) at all sites and PM_{10} (particulate matter with a diameter less than 10 μm) at Big Bend and Guadalupe Mountains national parks. The $PM_{2.5}$ filters were analyzed for chemical composition.

The preliminary study found that fine particulate sulfate plays a large role in visibility impairment at Big Bend National Park, and that sulfur sources in both the U.S. and Mexico are likely to be contributing to sulfate measured at BBNP. The preliminary study work group made the recommendation that a more extensive field study should be conducted to quantify the impacts from specific sources to visibility impairment at Big Bend National Park; the BRAVO study is the more detailed study recommended in the report of the preliminary study. The United States and Mexico did not reach an agreement on the design of the study, and hence Mexico did not participate in BRAVO.

Figure 1-3. Map showing monitoring sites for preliminary visibility study.

1.3 Big Bend's Seasonal Haze Composition and Long-Term Trends

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

Estimates of the contributions to light extinction by the major aerosol components can be made from the measured concentrations of those species. Light scattered by particle-free air, known as Rayleigh scattering, is assumed to be a constant value. Though Rayleigh scattering places a limit on our abilities to see distant scenic features clearly, many do not considered it a haze component since it is a natural and fixed consequence of the earth's atmosphere. Particulate haze refers to the non-Rayleigh portion of the light extinction that is the result of both man-made and naturally occurring particles in the atmosphere. Knowledge of the contributions to the total light extinction (including Rayleigh scattering) is useful for judging the perceptibility of changed conditions, while knowing the contributions to particulate haze is a better way to assess the varying components of haze levels. Figure 1-4 shows the five-year composite (1998 through 2002) of the light extinction (sum of light scattering and absorption) from measurements made every three days at Big Bend National Park.

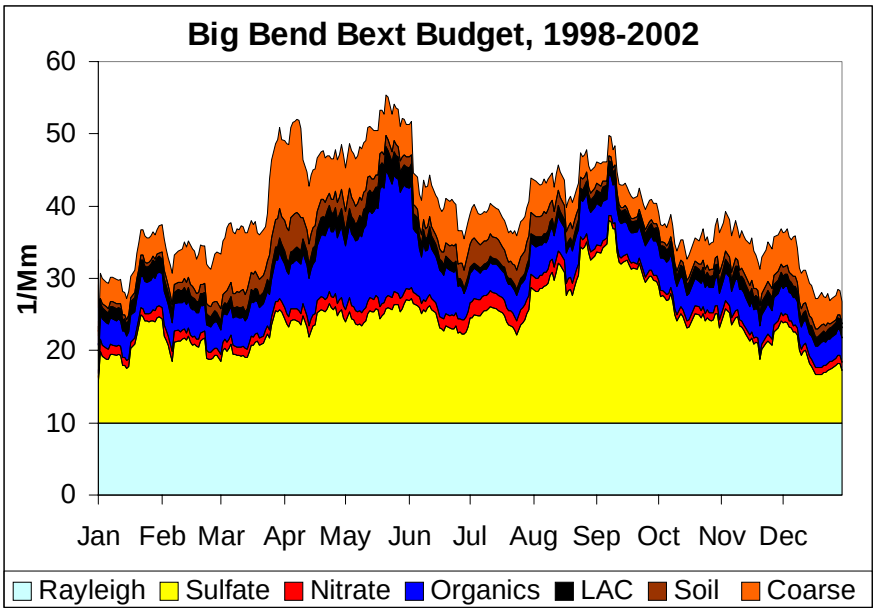

Figure 1-4. Big Bend five-year composite contributions to haze by components. This figure was generated from IMPROVE aerosol data collected at Big Bend NP from 1998–2002.

In general, there are two periods of high haze at Big Bend National Park: one in the spring, when particulate sulfate and carbonaceous compounds contribute similar amounts to haze, and another in the late-summer/fall when particulate sulfate compounds are the largest contributors to haze. Particulate sulfate compounds generally contribute more to haze than any other individual aerosol component. Carbonaceous particulate matter – organic compounds and light absorbing carbon (LAC) – generally constitute the second largest individual aerosol component contributing to haze at Big Bend NP. Information from other studies shows that during late spring episodes, concentrations of carbonaceous compounds are increased due to biomass burning in Mexico and Central America. Dust – a combination of fine soil and coarse mass – can also contribute significantly to haze during March and April.

Figure 1-5 presents Big Bend's trends in the reconstructed particulate light extinction values from 1990–2002. These trends were generated from the IMPROVE fine aerosol data measured at Big Bend NP. As shown, the haze during the worst 20% of the haze days has increased from about 40 Mm^{-1} in 1992 to ~55 Mm^{-1} in 2000, or at a rate of ~17 Mm^{-1} per 10 years during the 1990s as determined by the Theil regression analysis. The haze during the best 20% haze days has not significantly changed during this time period.

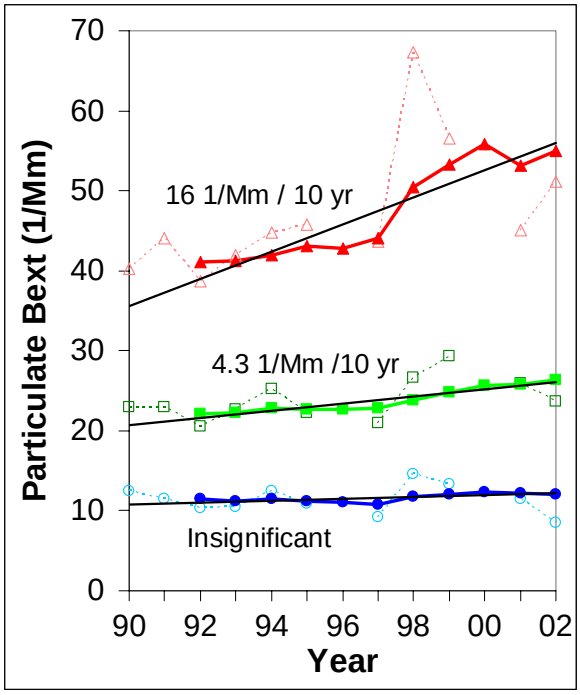

Figure 1-5. Trends in Big Bends reconstructed particulate light extinction for the worst 20% of the haze days (top trend), the middle 20% of the haze days (middle trend) and best 20% of the haze days (bottom trend). The open symbols are annual values and the closed symbols are a 5-year moving average. The Theil regression line and slope are plotted for the 5-year moving average values. The worst and middle 20% trend lines are significant at a p-value below 0.01.

1.4 SO_2 Emissions Sources and Trends

As shown in Figure 1-4, particulate sulfate is typically the largest contributor to haze within the park, and is formed in the atmosphere through the oxidation of sulfur dioxide. Sulfur dioxide is a gas that is generally emitted from combustion sources such as coal-fired power plants. Figure 1-6 is a map of the region that shows BBNP and the locations of SO_2 source areas of importance in Mexico and in Texas (other states in the region have much lower SO_2 emissions).

Major SO_2 sources in Texas include oil refineries, coal-fired power plants, and carbon black producers. The majority of the Texas refineries are located along the eastern shore of Texas on the Gulf of Mexico. Historically, coal-fired power plants were built along the lignite belt which runs from the northeast corner of Texas southwest toward the Carbón I & II facilities in Mexico. Carbon black manufacturers are distributed along the east coast of Texas and near the oil fields in the Texas panhandle. In Mexico, major SO_2 emissions are largely due to fuel oil refining and combustion and coal combustion. The Carbón I & II power plants are the largest coal combustion facilities in Mexico. Major refineries and industrial centers are located in Tampico on the east coast, Manzanillo on the west coast, Tula-Vito-Apasco north of Mexico City, and Toluca-Lerma south of Mexico City.

The 1999 SO_2 U.S. emission rates per state are presented in Figure 1-7. The largest SO_2 emissions in the U.S. are in the eastern U.S. states from the industrial Midwest. Most of these emissions are due to coal fired power plants along the Ohio River Valley. In Texas the SO_2

emissions are about 1.1 million tons SO_2/year, most of which occurs in eastern Texas. The surrounding states of Texas emit another million tons of SO_2 per year.

Figure 1-6. Site map of Mexican cities and Texas counties with SO_2 emissions greater than 5000 tons SO_2/yr. The location of Big Bend National Park is also shown.

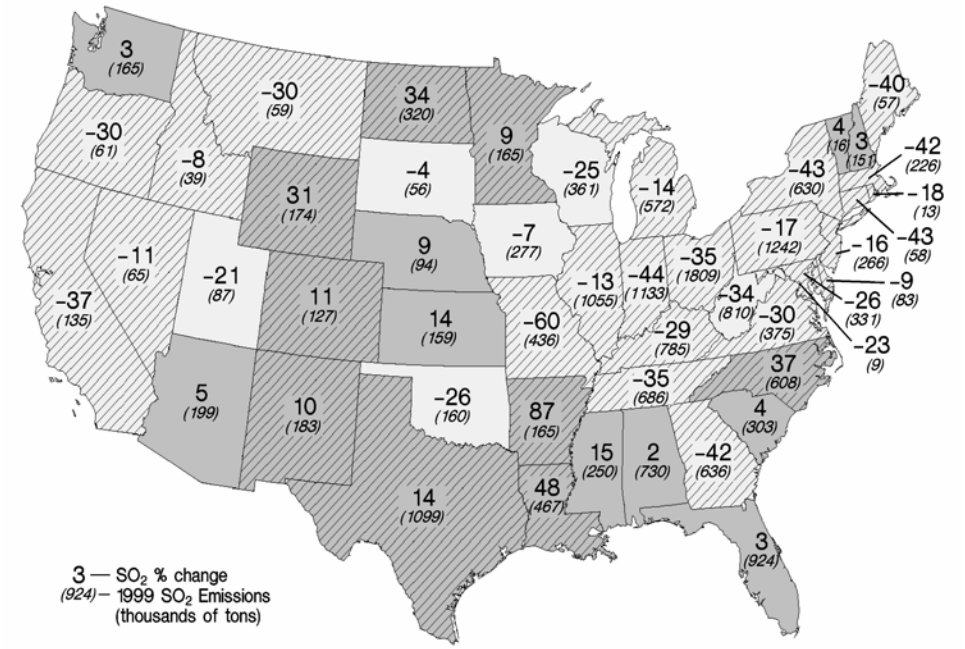

Figure 1-7. The percent change in the SO_2 emissions for each state in the conterminous United States from 1990–1999. The light gray states have decreasing trends while the dark gray states have increasing trends. States with hatch marks have trends that are significant with a two sided P value below 0.1. The percent changes were calculated by dividing the change in emissions over the twelve year period by the 1990 emissions estimated from the trend line. The 1999 SO_2 emission rates for each state are in parentheses. The emission rates are from the National Emission Trend database [U.S. Environmental Protection Agency, 2001].

Figure 1-7 also presents the trends in the SO_2 emissions during the 1990s [*Malm et al.*, 2002]. Most eastern U.S. states from Tennessee and to the north had significantly decreasing trends in emissions, typically on the order of 30% and up to 60% in Missouri (Figure 1-7). In the southeastern U.S. the SO_2 emission trends are flat. The SO_2 emission rates in Texas and its bordering states to the east and west all had significantly increasing trends.

The trends in the 80th percentile of measured sulfate concentrations are compared to these emission trends in Figure 1-8 as time series for northeastern, southeastern, south-middle, and western United States regions. See *Malm et al.* [2002] for details on how this comparison was performed. In each plot, the SO_4^{2-} and SO_2 emission scales have a factor of three change between the low and high values. Therefore, equal slopes in the SO_4^{2-} and SO_2 trends lines represent equal percent changes. As shown, each region has a unique time series pattern and the SO_4^{2-} and SO_2 emission trends closely track each. In the western United States from Arizona to Washington, both SO_2 emissions and SO_4^{2-} steadily declined about 15% throughout the 1990s. In the south-middle United States, encompassing Texas, New Mexico, and Colorado, three of the seven monitoring sites had increasing 80th percentile SO_4^{2-} trends with a statistically significant trend of 32% at Big Bend, Texas. These increasing SO_4^{2-} concentrations are reflected in average SO_4^{2-} time series (Figure 1-8), with a steady increase in SO_4^{2-} of ~15% from 1991 to 1999. The SO_2 emission over this region also had a similar 15% increase. In selecting the south-middle aggregation region, Kansas and Oklahoma were excluded, because these states do not have any monitoring sites in them.

The northeastern United States, from Illinois to Maine, had the largest SO_2 emission rates and declines in emissions during the 1990s (Figure 1-7). As shown in Figure 1-8, the northeastern SO_2 emissions decline is primarily due to a nearly 20% drop between 1994 and 1995. The ambient sulfate concentrations closely follow the SO_2 trend with a similar ~7% decline from 1990 to 1995, the same ~20% drop between 1994 and 1995, and the leveling off afterwards. The sharp 1994 to 1995 decline in SO_4^{2-} and SO_2 was the largest absolute and relative year to year change in all four regions. In the southeastern United States, the SO_4^{2-} and SO_2 emissions did not change appreciatively over the time period, but both regions had a decreasing trend in the early 1990s followed by an increasing trend since 1995–1996.

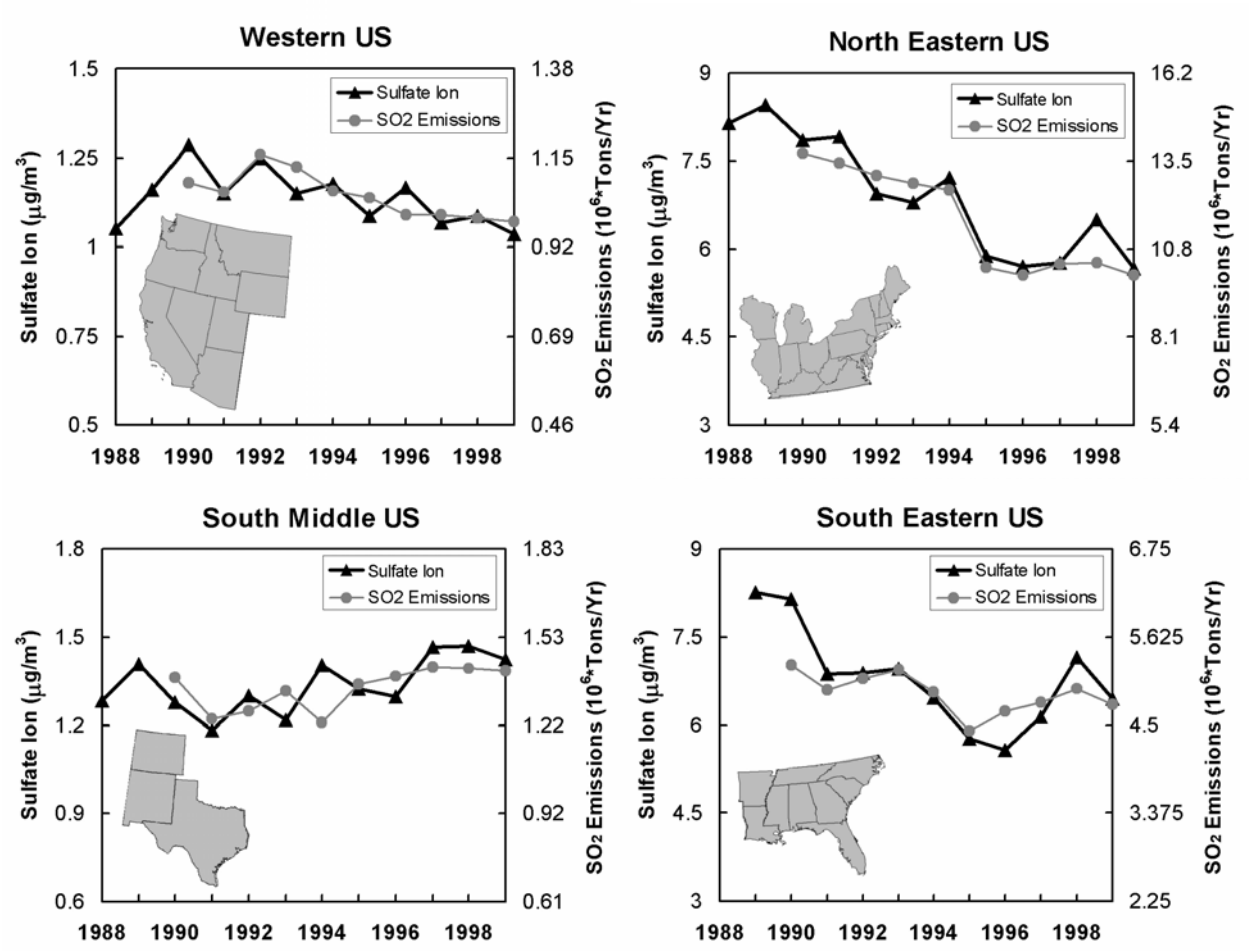

Figure 1-8. Comparison of the ambient sulfate 80th percentile and NET SO_2 emissions aggregated over northeastern, southeastern, south middle and western United States regions. In each plot the SO_4^{2-} and SO_2 emission scales have a factor of 3 change between the low and high values [Malm et al., 2002].

1.5 SO_2 Airmass Transport to Big Bend NP

For a source of sulfur dioxide emissions to contribute to Big Bend's haze, the sulfur dioxide must be transported from the source to Big Bend and the sulfur dioxide converted to particulate sulfate. The rate of conversion of sulfur dioxide to particulate sulfate depends on several factors, and conversion rates can be a few days to as little as a few minutes. For example, the presence of clouds can dramatically accelerate sulfate conversion rates through aqueous-phase chemical reactions. Gas-phase reactions also convert sulfur dioxide to particulate sulfate, although oxidation rates are considerably slower as compared to the aqueous-phase reactions.

All other things being the same, a source region's potential to contribute to haze at Big Bend increases for periods when air parcels frequently pass over and spend more time over the source region prior to transport to Big Bend. Trajectory analysis during a five-year period (1998–2002) shows that transport patterns vary considerably throughout the year, as shown in Figure 1-9. Upwind regions during the months of November through March are primarily to the west of Big Bend; this period generally corresponds to lowest haze levels measured in the park.

In April and May the air flow is frequently from regions to the southeast and west, while June and July are characterized by airflow from regions to the southeast. August through October is the only time of the year with appreciable air flow from regions to the east and northeast, as well as the more common flow from regions to the southeast. This is the period when the highest concentrations of sulfate are measured, and hence is of particular interest. In addition to the general transport patterns described above, it should be noted that throughout the year airmasses en route to Big Bend frequently reside over northern Mexico.

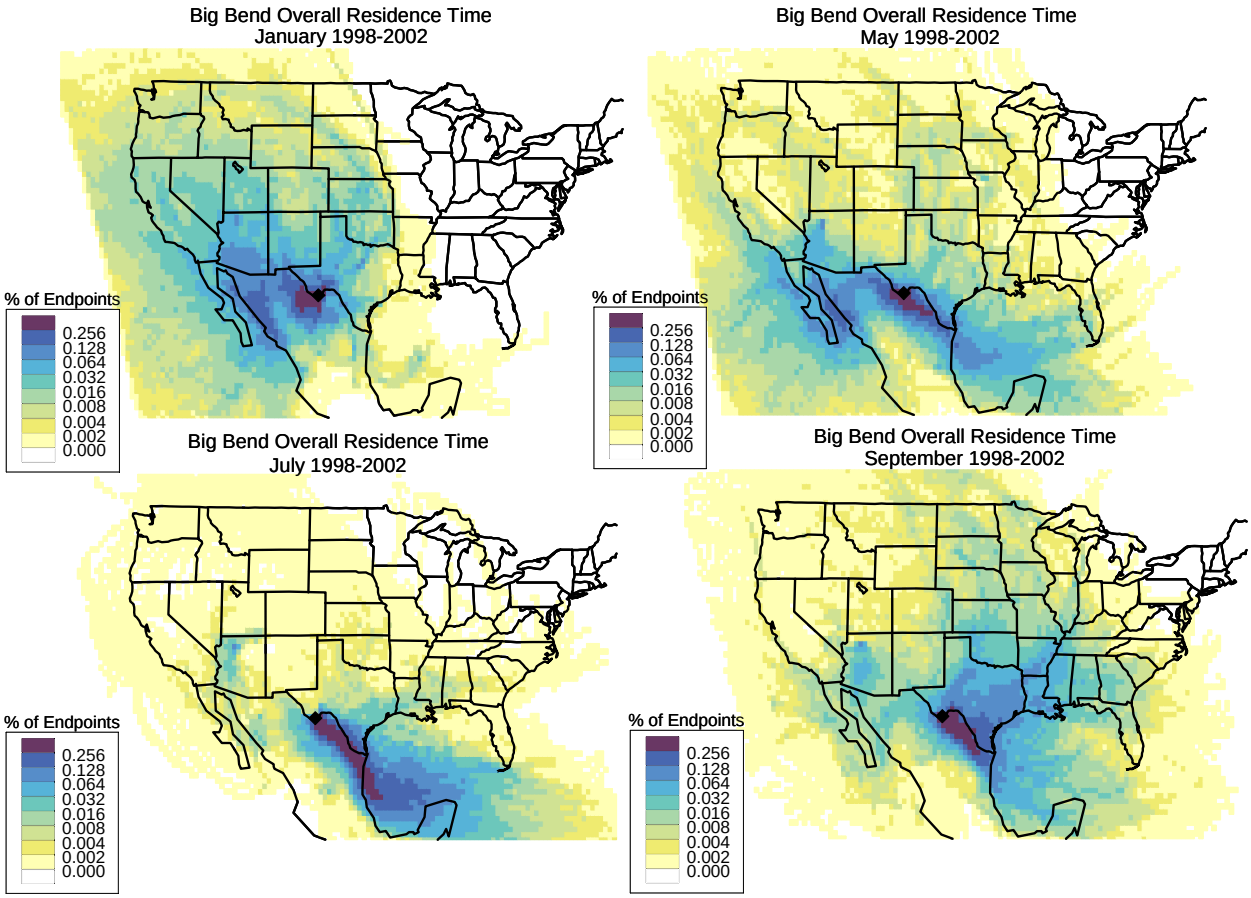

Figure 1-9. Examples of geographic distribution of the fraction of time that air parcels spend during the five days prior to arriving at Big Bend National Park for the months of January, May, July, and September based upon a five-year analysis period (1998 to 2002).

1.6 Techniques for Determining Sulfate Attributions

Sulfates are the single largest contributor to Big Bend's haze, and account for about half of the particulate haze on average (Figure 1-4). As discussed above, sulfate particles are formed through the oxidation of sulfur dioxide, and the largest emitters of this pollutant are anthropogenic sources such as coal-fired power plants.

This report provides a detailed description of the composition and optical properties of haze in the Big Bend region, and also describes the numerous analytical and modeling techniques that were conducted by the NPS and CSU to determine which sources (e.g., Texas, Mexico, the eastern U.S.) were contributing particulate sulfate to BBNP during the BRAVO study period. These techniques include: 1) air quality data analysis 2) airmass history based

receptor models, 3) a regional air quality model, and 4) a synthesis inversion analysis of the regional air quality model.

Several airmass history based receptor analysis methods were used for source attribution. These methods developed statistical relationships between the Big Bend particulate sulfate concentrations and airflow prior to reaching Big Bend to estimate the average source attribution over the study period. Variations of the trajectory methods included the use of two methods of estimating wind over North America (EDAS from the National Weather Service and MM5 applied specifically for the BRAVO study) and the use of back trajectories from Big Bend employed in Tracer Mass Balance (TrMB) [*Gebhart et al.*, 1988; *Iyer et al.*, 1987] and forward transport and dispersion from all potential source regions used in Forward Mass Balance Regression (FMBR) [*Schichtel*, 1996]. Testing of the TrMB and FMBR methods involved reproducing measured tracer concentrations and simulated sulfate concentrations from a deterministic model using both sets of wind information. Trajectories that passed these evaluations were used for attribution of measured sulfate.

The REMSAD regional air quality model [*SAI*, 2001; *Seigneur et al.*, 1999] was also used to predict sulfate attributions from individual source regions and represents a "source-oriented" approach which differs from the "receptor-oriented" techniques described above. REMSAD simulates the physical and chemical processes which control pollutant concentrations in the atmosphere, including transport, dispersion, chemical transformation, wet and dry deposition, and emissions of pollutants and pollutant-precursors from anthropogenic and biogenic sources. Air quality models such as REMSAD depend on the quality of the emissions and meteorological data that are used in the simulation, as well as the accuracy of the advection, transformation, deposition, dispersion, and other numerical algorithms that constitute the model. Biases and uncertainties identified in any of these processes can adversely affect their source attribution estimates.

Finally, a "synthesis inversion analysis" was conducted, which develops a statistical relationship between the daily source attribution results from the REMSAD air quality model and the measured particulate sulfate concentrations in and around Big Bend [*Enting*, 2000; *Enting*, 2002]. This technique is very useful for identifying biases in the original REMSAD model predictions, and can serve as a bridge to help reconcile results from the receptor-oriented techniques and the source-oriented model.