Final Program Plan for the Big Bend Regional Aerosol and Visibility Observational Study (BRAVO)

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1. Introduction

1.1 Reason for study

As a result of concerns over visual air quality at Big Bend National Park, a preliminary regional visibility study was conducted in Texas and northern Mexico in September and October 1996. A brief overview of the study and consensus results are presented here. A more detailed description of the study and the reasons for conducting the preliminary study are contained in the report "Big Bend National Park Regional Visibility Preliminary Study" prepared by the Big Bend Air Quality Work Group for the USEPA, National Park Service, and the Mexican governmental agencies PROFEPA and SEMARNAP on January 7, 1999.

The primary objective of the 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 Big Bend National Park. The study was not intended or designed as an attribution study to quantify impacts of specific sources on Big Bend air quality. The study was intended to obtain information on pollutant gradients over a broad area of Texas and northeast Mexico to assist in the design of a future study to identify the causes of visibility impairment at Big Bend (Big Bend Air Quality Work Group, 1999). The study was conducted at 19 monitoring stations (10 in Texas, 9 in Mexico- see Figure 1-1) from September 9 through October 13, 1996. The sites sampled $PM_{2.5}$ at all sites and PM_{10} at Big Bend and Guadelupe Mountains national parks. The $PM_{2.5}$ filters were analyzed for chemical composition.

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

It was noted that care should be taken in interpreting the results of the study due to its' limited duration and geographical coverage. Consensus was not reached by the work group on all issues. Key consensus results are paraphrased below:

?? To the northeast of Big Bend are large sources of sulfur associated with selenium, likely from coal-fired power plants at distances that can exceed 700 km. These sources sometimes cause high concentrations of fine particulate and fine particulate sulfur through much of Texas, including Big Bend National Park.

?? On some occasions with southerly flow, Mexican emissions appear to be associated with significant sulfur concentrations at Big Bend.

?? During periods with southeasterly winds, emissions from both Mexico and the United States may contribute to $PM_{2.5}$ mass and fine particulate sulfur at Big Bend. Also, because of the lack of correlation between sulfur and selenium and vanadium, sources in addition to power plants are contributing to these concentrations.

?? Transport from areas to the northwest of Big Bend is associated with relatively low concentrations of fine particulate mass and fine particulate sulfur.

?? Relative humidity plays a large role in visibility impairment at Big Bend.

?? Fine particulate sulfur plays a large role in visibility impairment at Big Bend and most of the particulate sulfur is in the form of sulfate.

The work group made the following recommendations:

1. A more extensive field study will be needed to quantify the impacts from specific sources to visibility impairment at Big Bend National Park.

2. The spatial domain of the study should be expanded, particularly to the northeast, the south, and into the Gulf of Mexico.

3. The design of the extensive study should be based on the findings from the final report of the preliminary regional study. The results of the preliminary study and the extensive study to follow should be analyzed in the context of historical measurements made at Big Bend National Park.

BRAVO is the more detailed study to follow the preliminary study. The United States and Mexico did not reach agreement on study design; as a result, BRAVO includes monitoring in the United States only. The monitoring program conducted for BRAVO is described in section 4.

1.2 Organizational Structure

Overall direction of the BRAVO study is the responsibility of the BRAVO steering committee. The steering committee has representatives of the United States Environmental Protection Agency (USEPA), the National Park Service (NPS), and the Texas Natural Resources Conservation Commission (TNRCC). A sub-committee of the steering committee is comprised of representatives of non-governmental organizations (NGOs), such as industry and environmental groups. While comments on BRAVO are welcome from all members of the public, the steering committee will actively solicit comments from the NGO committee regarding study plans, data analysis methods, and study results.

The technical sub-committee includes investigators that are collecting data or doing data analysis, including quality assurance. This sub-committee will provide a forum for presentation of technical analysis as well as scientific debate regarding the conclusions of various data analysis methods.

1.3 Goals

The primary goals of the Big Bend Regional Aerosol and Visibility Observational Study (BRAVO) are to understand the long-range, trans-boundary transport of visibility-reducing particles from regional sources in the U.S. and Mexico and to quantify the contributions of specific U.S. and Mexican source regions and source types responsible for poor visibility at Big Bend NP.

It is the goal of BRAVO to take advantage of the best and most successful aspects of previous visibility attribution studies. Previous air quality studies in the desert southwest (including SCENES, VIEW, VISTA, WRAQ, RESOLVE, WHITEX, and Project MOHAVE) and the U.S.-Mexico Preliminary Study provide a great deal of background information useful to the planning of this project.

Determining the contribution to BBNP haze implies a quantitative evaluation of intensity, spatial extent, frequency, and duration. The intensity of haze contributed by a source includes both an absolute physical measure of haze (e.g., contribution to the extinction coefficient) and its perceptibility (e.g. as displayed by computer image processing algorithms).

In addition to determining impacts from individual sources, simultaneous assessment of all the important regional sources of haze at BBNP is desirable. This would allow for the formulation of more effective emissions control strategies in both countries that would ultimately result in the improvement of air quality in BBNP and throughout the region.

Other goals that are relevant to the BRAVO Study include:

?? Determination of the chemical constituents of fine particles responsible for regional hazes along the U.S.-Mexico border, inclusive of Big Bend;

?? Determination of the effects of meteorology including moisture from the Gulf of Mexico on visibility-reducing particles.
?? Evaluate and improve the accuracy of atmospheric models and source attribution methods through the use of atmospheric tracers and updated source emissions profiles.

2 Background

Visual air quality at a site depends largely upon the size, chemical composition, and concentration of atmospheric particles (aerosols). These aersosol properties are in turn dependent upon many factors, including: the relationship between the receptor site (e.g. Big Bend) and sources of pollutant emissions and the atmospheric transport and dispersion relating the source and receptor location, chemical transformation of emissions between source and receptor, (e.g. gas-to-particle conversion) wet or dry deposition, and relative humidity at the receptor.

Following a brief description of the Big Bend area will be a look at pollutant emissions for sulfur dioxide. The seasonally varying transport patterns affecting Big Bend National Park will then be examined, followed by a summary of light extinction and aerosol chemical component data for Big Bend. Finally, conditional probability plots will be shown indicating the probability that light extinction or chemical species were high at Big Bend when air passed over each geographic area en route to Big Bend.

2.1 Setting

In a remote area of southwestern Texas, where the Rio Grande makes a large U-turn along the US-Mexico border, lies an area known as the "Big Bend Country." Within this expanse lies BBNP, Texas,--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 2-1). Big Bend is a land of contrasts: the Rio Grande--portions of which have been designated as a Wild and Scenic River; desert--BBNP is 97 percent Chihuahuan Desert; and mountains--the Chisos Mountains--which tower 2400 meters (7800 feet) above the desert sea and the Sierra del Carmen across the river in Mexico. Along the Rio Grande are deep cut canyons--Santa Elena, Mariscal, and Boquillas--alternating with narrow valleys walled by towering cliffs (US Dept. of Interior, 1983). It is a region of large biological diversity containing more than 1,000 species of plants, including 65 cacti, 434 birds, 78 mammals, 71 reptiles and amphibians, and 35 fish (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 Indians, the Spanish, the Mexicans and the Anglos have all been part of Big Bend's history (Big Bend Natural History Assoc., 1989). Nonetheless, 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 State Park and BBNP.

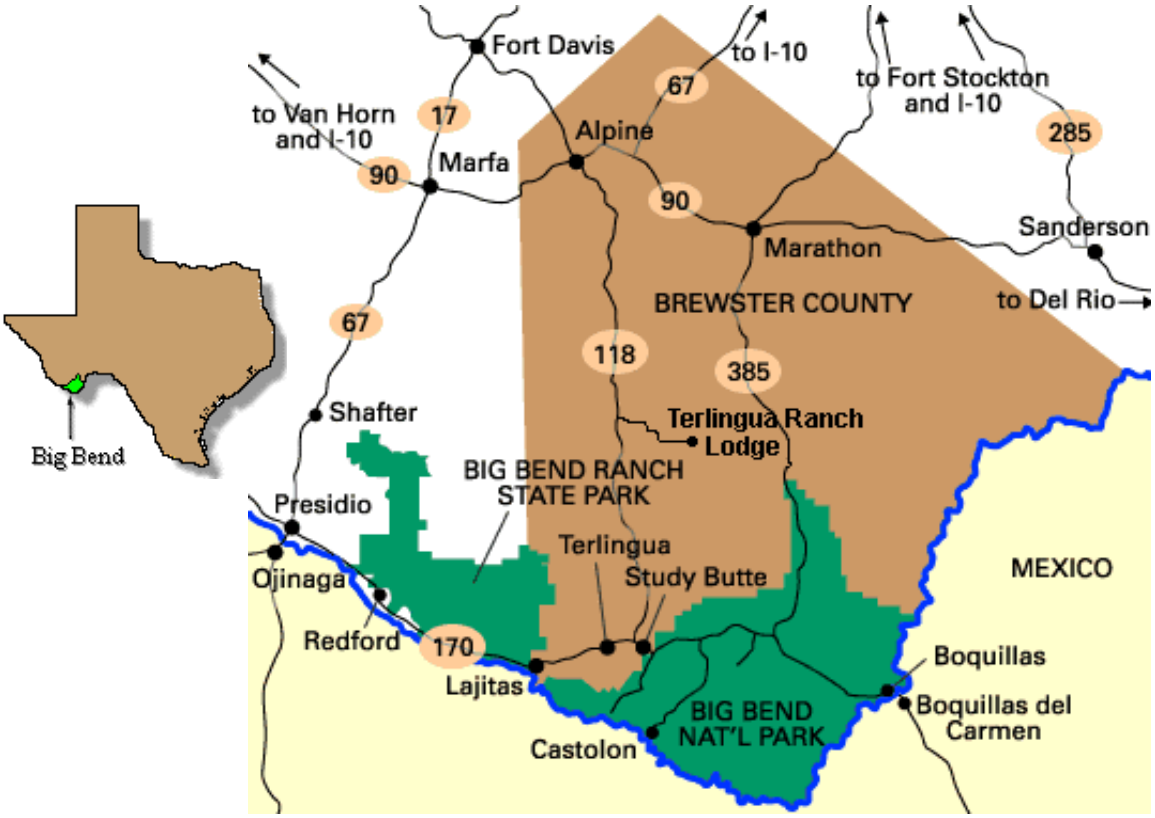


Figure 2-1. Location map of Big Bend National Park in southwestern Texas.

2.2 SO_2 Emissions Sources

According to the preliminary study and long-term monitoring at Big Bend, sulfate is an important component of haze at Big Bend National Park and results from atmospheric conversion of SO_2. Thus, emissions of SO_2 are of particular concern to the BRAVO study. Figure 1 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 Carbon 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.

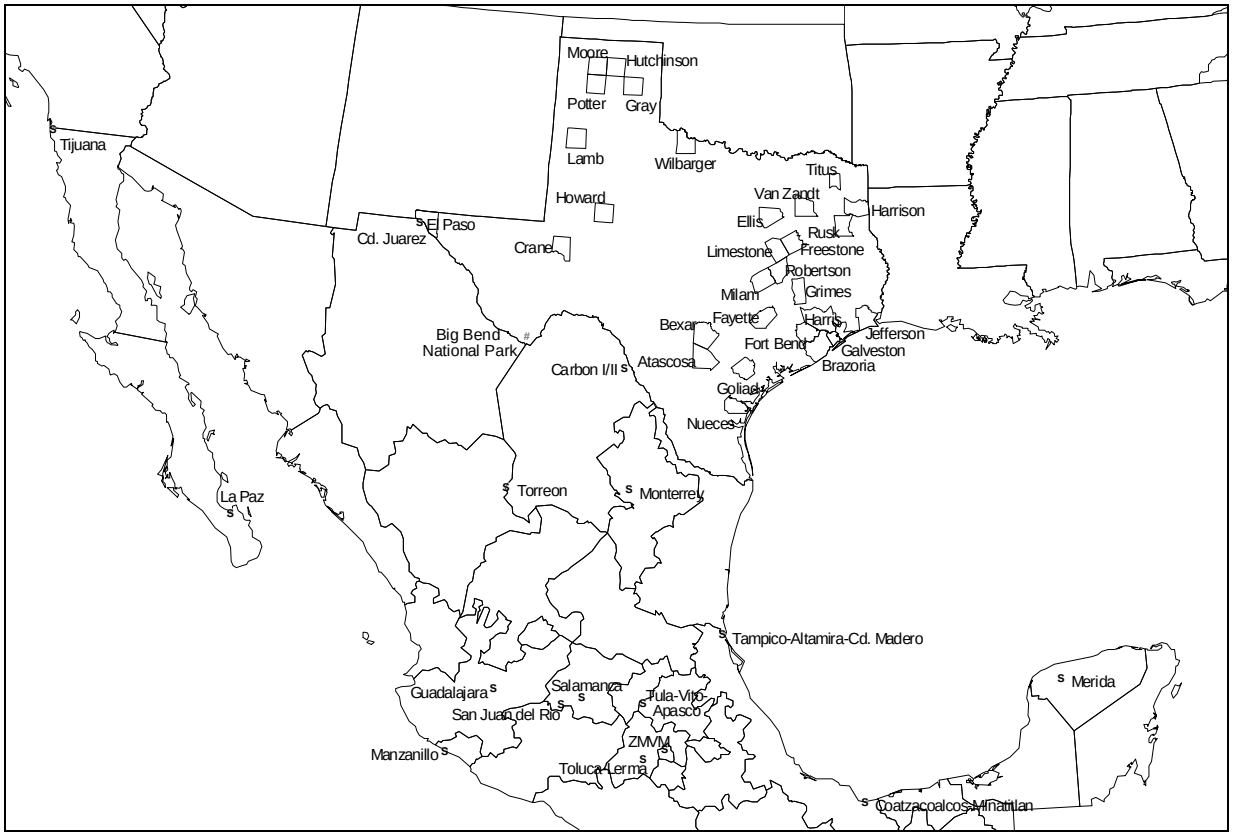


Figure 2-2: Site map of Mexican cities and Texas counties with SO_2 emissions greater than 5000 tons SO_2/yr. The location of Big Bend National Park is also shown.

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 Carbon 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.

Major SO_2 emissions in Mexico are due largely to fuel oil refining and combustion and coal combustion. The Carbon 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.

Figure 2-3 shows point source SO_2 emissions by 1 degree longitude by 1 degree latitude grid cells. The data is based upon information from Instituto Nacional de Ecologia (base year 1994) for Mexican cities with emissions greater than 5000 tons/year and the USEPA AIRS database. Figure 2 shows the greatest concentration of SO_2

emissions in the Ohio River Valley, although the numbers may not fully reflect recent reductions in SO_2 emissions in that area. Closer to Big Bend are significant sources in northern and central Mexico and eastern Texas.

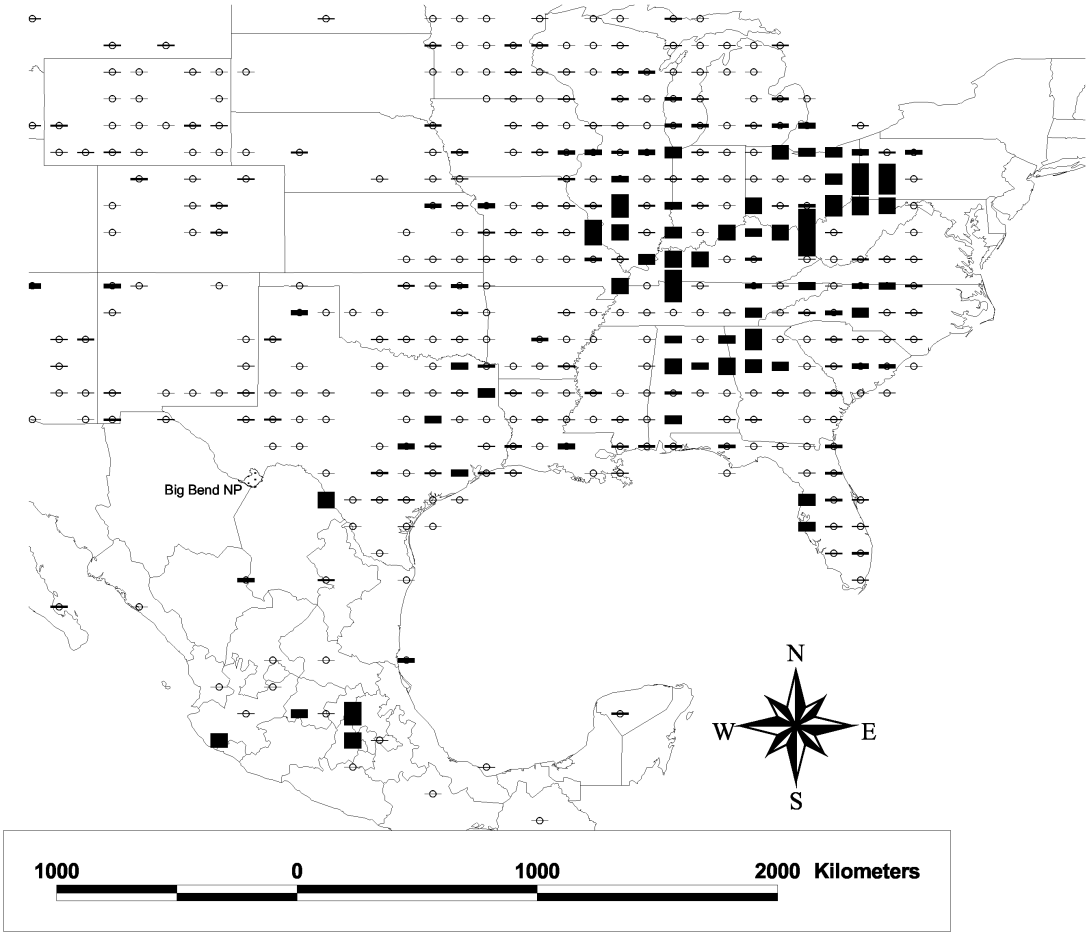


Figure 2-3. Point sources of SO_2 by 1 degree longitude by 1 degree latitude grid cells. The bar at Carbon I/II (see Figure 1) corresponds to 240,000 tons per year.

2.3 Transport Patterns

Transport patterns described here are based upon results of the Atmospheric Transport and Dispersion model (ATAD)(Heffter, 1980). The ATAD model has been used by many researchers for computing forward and backward air trajectories (e.g. Pitchford *et. al.*, 1981, White *et. al.*, 1994, Kahl *et. al.*, 1997, Green and Gebhart, 1997). Advantages of the model are that a long-period of record of upper air observations is available, and because the model requires little computational time, a large number of trajectories can be run for statistical analyses. Disadvantages include the observed winds are available for a somewhat sparse network, are typically collected only twice per day, a single layer-averaged wind is used, vertical motions are not considered, and the model is no longer supported so recent years cannot easily be run.

The ATAD model computes trajectories by averaging observed winds in space and time. It first computes a transport layer depth from temperature soundings using specified criteria to determine whether a significant inversion exists. It averages the winds within the transport layer at each site, then computes a distance weighted average of nearby sites to obtain a wind vector at the specified starting location. After computing the new trajectory position from the wind vector, the model repeats the entire process. For time steps between the observations (typically 12 hours apart), the model performs a temporal interpolation of observed winds as well as spatial interpolation. While individual trajectories may have substantial error, particularly after a few days of simulated transport, in the absence of systematic biases statistical properties based upon large numbers of trajectories should be valid.

Analysis involved using ATAD backtrajectories for Big Bend National Park for the period 1982-1994. A series of analyses were run that provided the frequency with which ATAD backtrajectories passed over 1 degree latitude by 1 degree longitude (1 x 1) grid cells. Frequencies were calculated for annual and one-half month periods to determine the seasonal variations in transport paths. Using light extinction and aerosol data at Big Bend, the probability of high light extinction and high chemical components of haze was determined for periods when backtrajectories went through each 1 x 1 grid cell. This type of analysis, in conjunction with emission density maps can give an *idea* of the regions and sources that are contributing to haze at Big Bend.

Figure 2-4 shows the percent of all ATAD backtrajectories from Big Bend for 1982-1994 that passed through each 1 x 1 grid cell. The total number of backtrajectories was 18,264. Because a 1 x 1 grid cell subtends a smaller angle as distance increases from Big Bend and the backtrajectories have no dispersion, cells at greater distances from Big Bend tend to have lower percentages of backtrajectories passing through them than cells nearer to Big Bend. However, the relative frequency of flows from different directions can be noted by considering the shape of the contoured frequency plot. In addition the tabulation of frequencies by 1 x 1 cells has the feature of weighting cells inversely by their distance from Big Bend, which may be appropriate when considering the effects of the dispersion of distant sources (neglecting conversion processes). In this and following figures, a small black circle (dot) is placed at the center of each grid cell with 10 or more backtrajectories passing through the cell. Contours (color shaded) should be ignored in areas with no dots.

From Figure 2-4, we see that the most frequent annual flow direction for Big Bend is from the southeast. However, substantial variations in average frequency of flow directions occur during the year. In late January, backtrajectories from the west and northwest are at their annual peak, while few backtrajectories come from cells far to the south of Big Bend (Figure 2-5). From late February through late April bimodal distribution is seen with flows mainly from the west and the southeast (e.g. see Figure 2-6), with the westerly mode shifting from west-northwest to west-southwest from February to April. From May through July, the flow becomes progressively more southeast and nearly all backtrajectories are from the southeast in July (Figure 2-7).

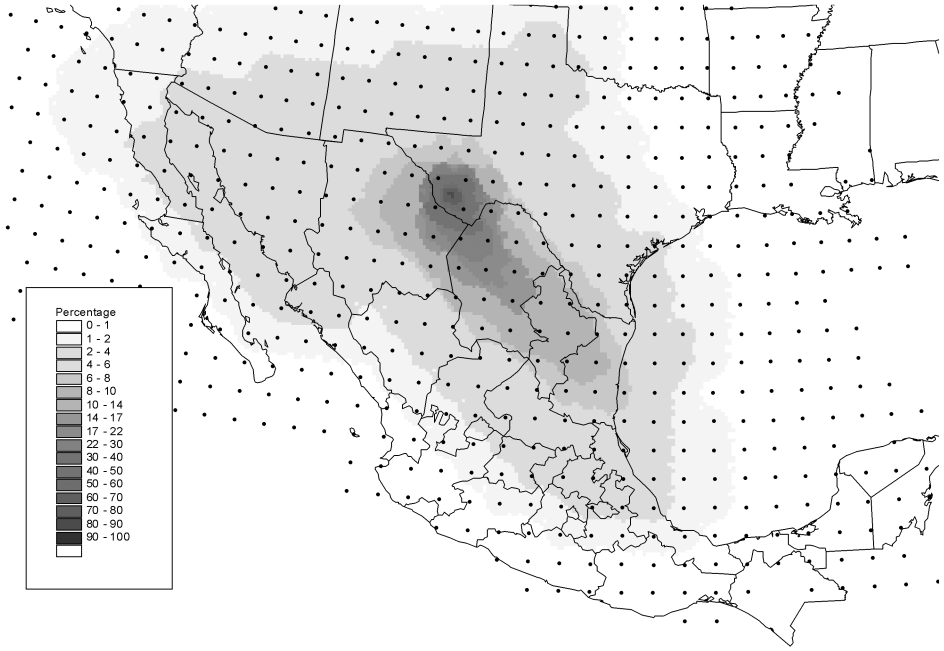


Figure 2-4 Annual trajectory frequency passing over cell.

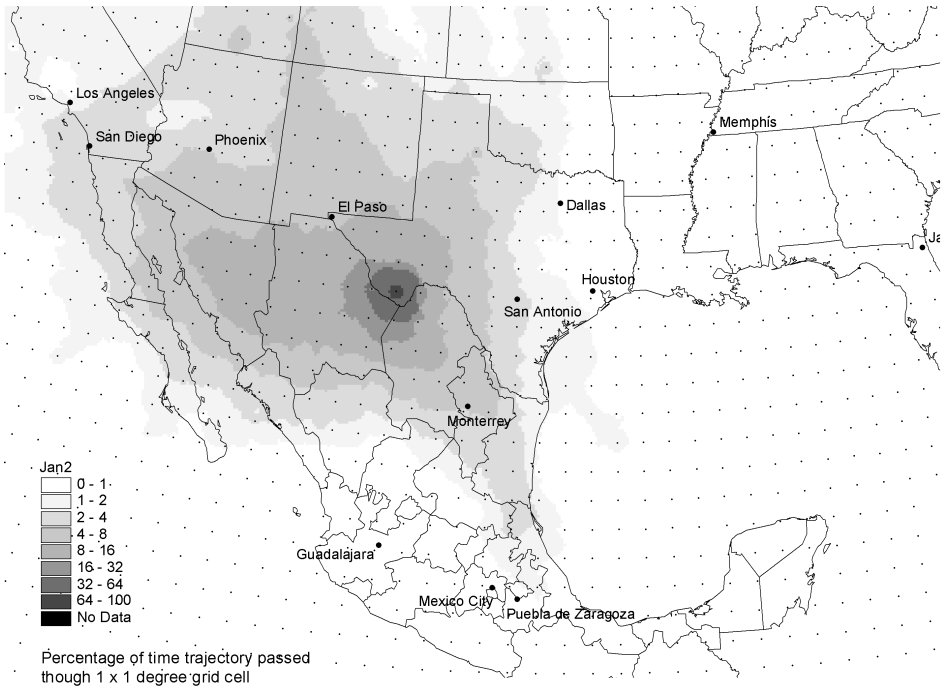


Figure 2- 5 Trajectory frequency for second half of January

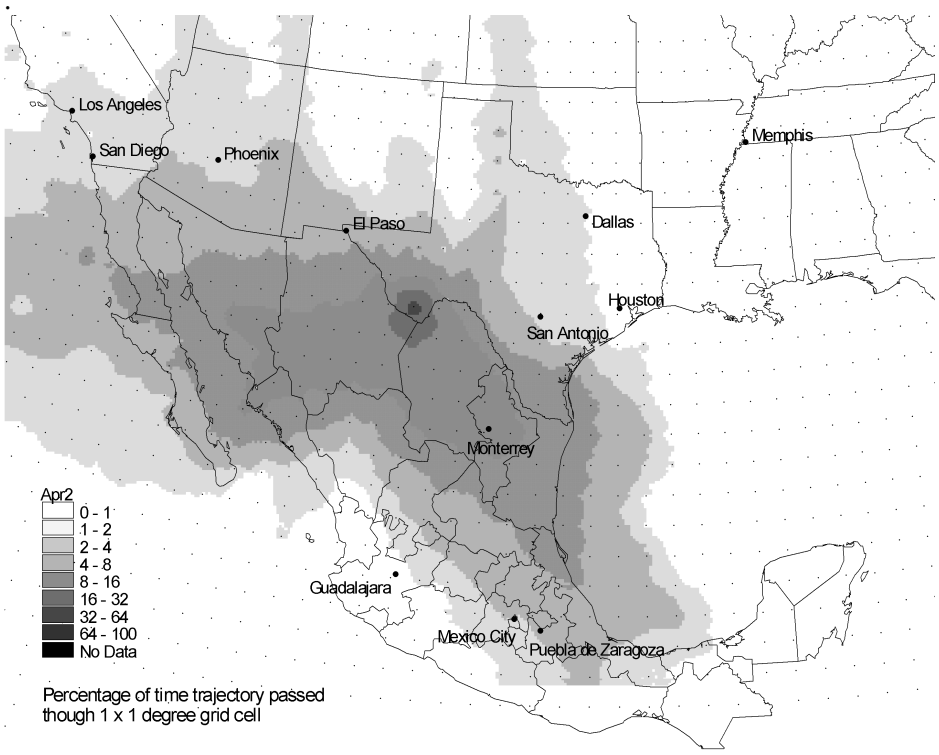


Figure 2- 6 Trajectory frequency for second half of April.

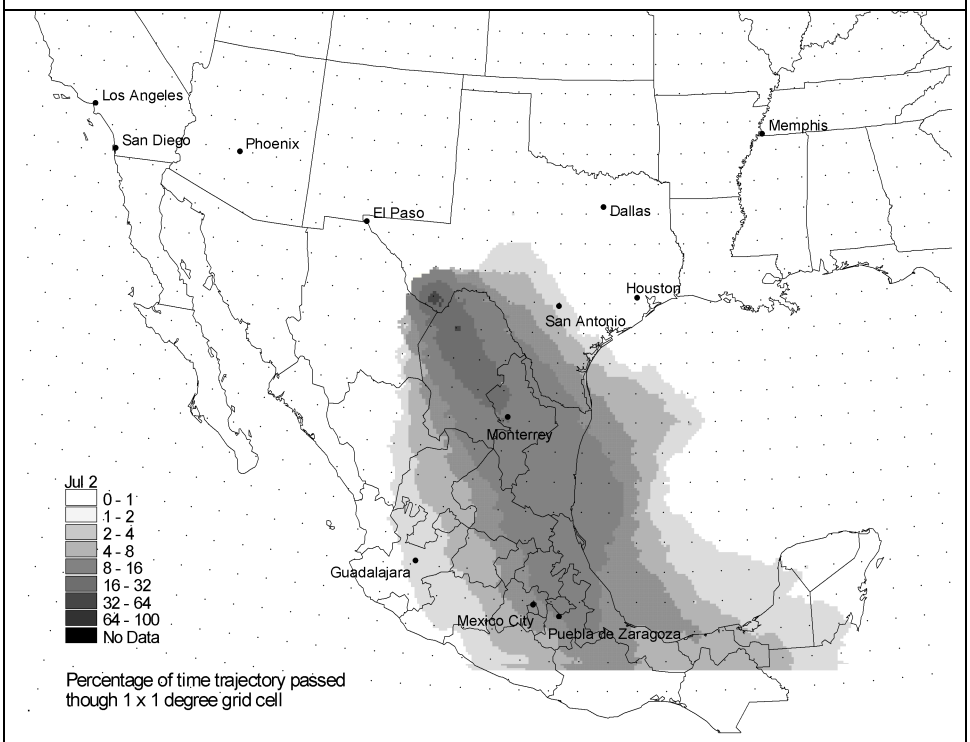


Figure 2- 7 Trajectory frequency for second half of July.

In late summer flows are still dominated by southeasterly backtrajectories, but trajectories from the east or northeast increase, reaching their annual peak frequency (Figure 2-8).

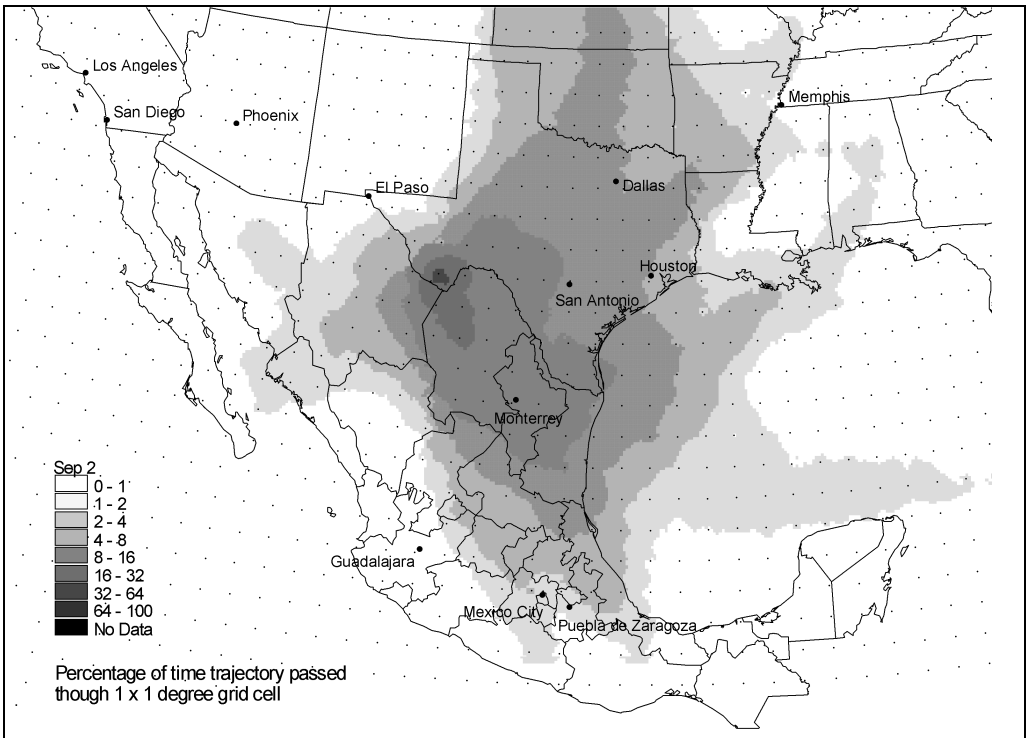


Figure 2- 8 Trajectory frequency for second half of September.

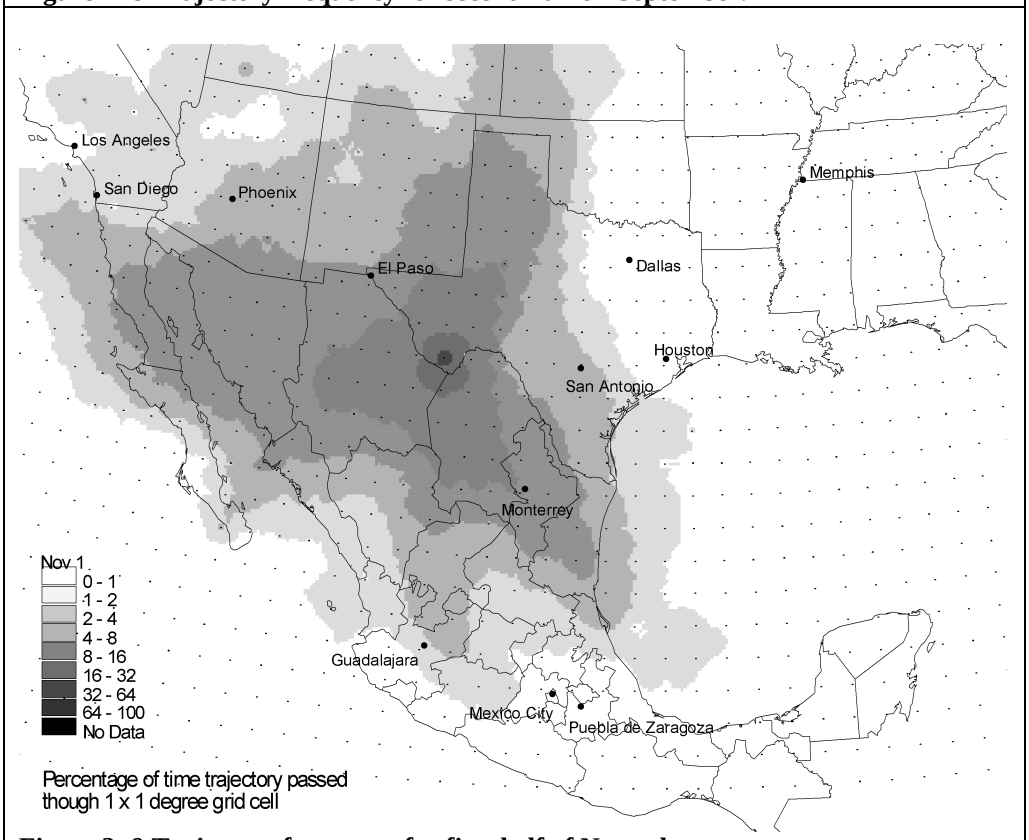


Figure 2- 9 Trajectory frequency for first half of November

By early November, a tri-modal distribution of backtrajectories from the north, west, and southeast is apparent (Figure 2-9). The pattern gradually evolves back to the west & northwest backtrajectories being most frequent in January, completing the annual cycle.

In summary, the backtrajectories in summer are very much dominated by south-easterlies. Easterlies, which are not very common overall, peak during late September. During winter months backtrajectories are mainly from the west and northwest, with few from far to the south. In the transition periods, flow is common from the west, north, and southeast.

Relative effects of transport from some specific source areas

Next we consider relative effects of transport from some specific source areas considering distance from Big Bend and frequency of transport. This assessment was not expected to accurately model the impacts from different source areas; rather it was used for study planning purposes. Figure 2-3 showed estimated SO_2 emissions from 1? latitude by 1? longitude cells. Emissions from sources at a greater distance from BBNP disperse more before reaching BBNP than emissions from more nearby sources. Emissions were weighted by distance (emission rate divided by distance) to account for this effect; the results are shown in Figure 2-10. The inverse distance weighted analysis shows less weighting of the Ohio River Valley sources and much greater weighting for the Carbon I/II powerplants. Other sources in northern and central Mexico and eastern Texas appear to be potentially significant as well. This analysis may give an indication of potential maximum impacts from an area, but does not consider how frequently there is transport and hence total potential impact from the various source areas.

SO_2 emissions were also weighted by the frequency of transport from the source areas to BBNP (Figure 2-11). Due to most frequent transport from the south and southeast and infrequent transport from the northeast, the Mexican sources (especially Carbon I/II, Tula-Vito-Apasco, and the Mexico City area) predominant using this method.

Figure 2-12 shows the frequency of flow by half month period from each selected source area to BBNP using the 12 years of ATAD backtrajectories. These sources included additional regions, such as San Antonio that may not be large SO_2 sources but are sizable area sources of various pollutants that potentially affect visibility. With the exception of locations to the west and north (Cananea , the Texas/New Mexico border, and Ciudad Juarez/El Paso), all of the areas are most frequently transported to BBNP during the period from the beginning of July through the end of October. During the early part of this period emissions from sources in Mexico to the southeast of BBNP are almost exclusively transported to BBNP. At the end of this period, the sources to the northeast (Houston, and the Texas lignite belt power plants) are also transported to BBNP.

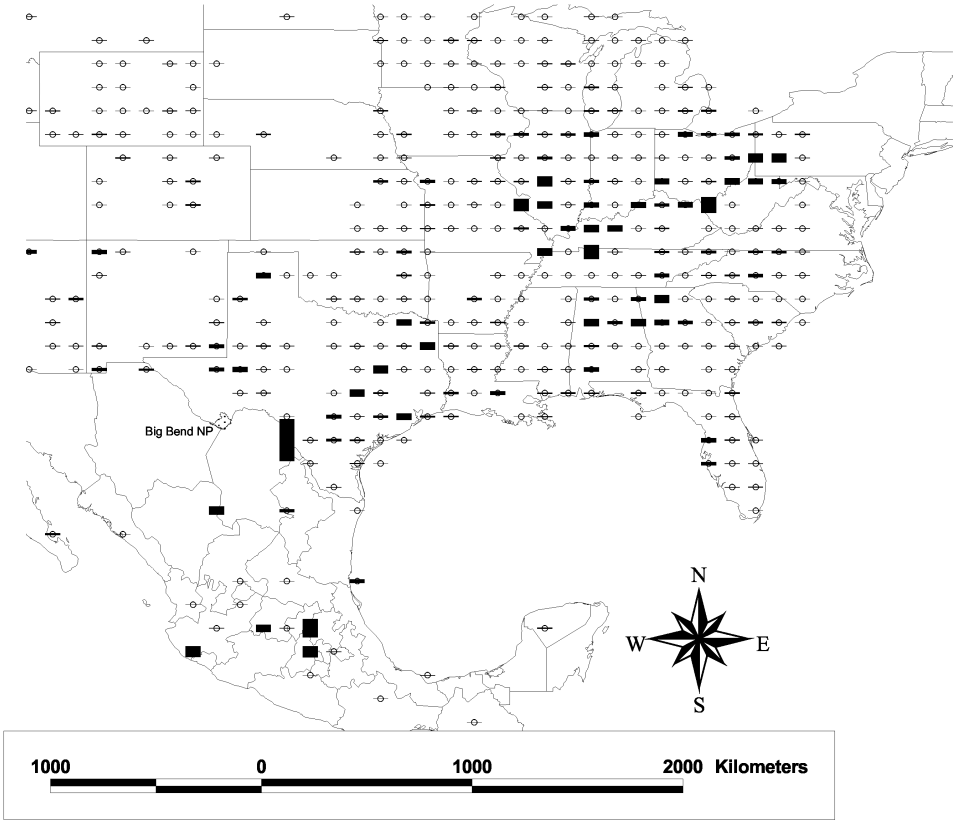


Figure 2-10. Emissions weighted inversely by distance from BBNP for 1? lat. by 1? long. grid cells.

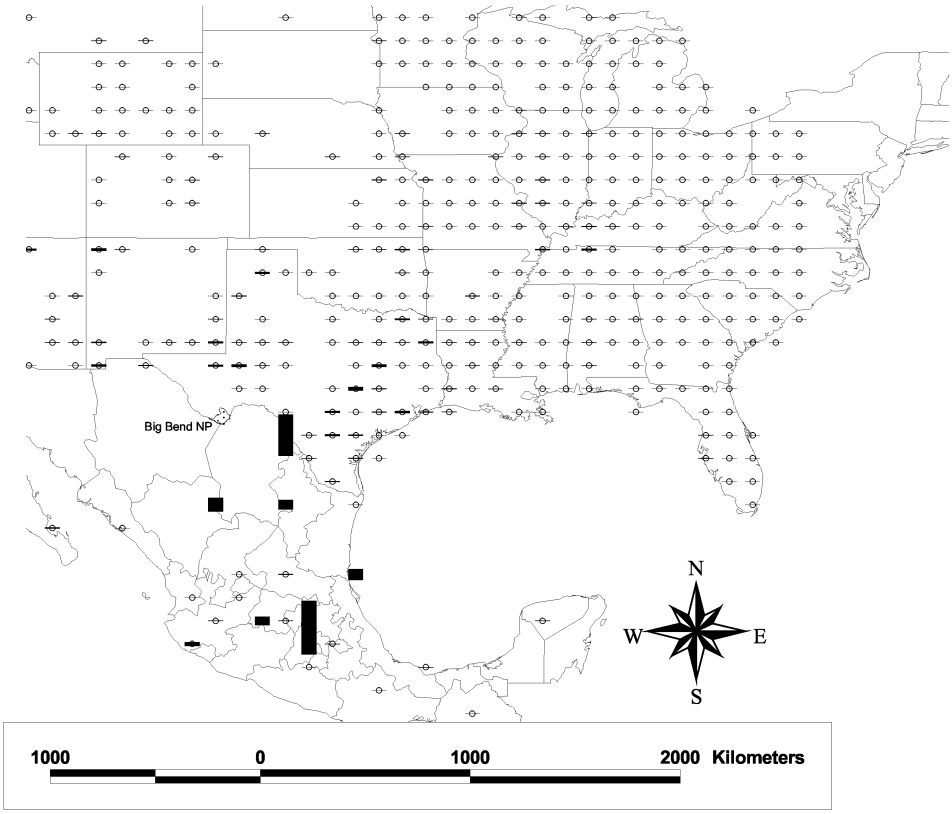


Figure 2-11. Emissions weighted by transport frequency for 1? latitude by 1? longitude grid cells.

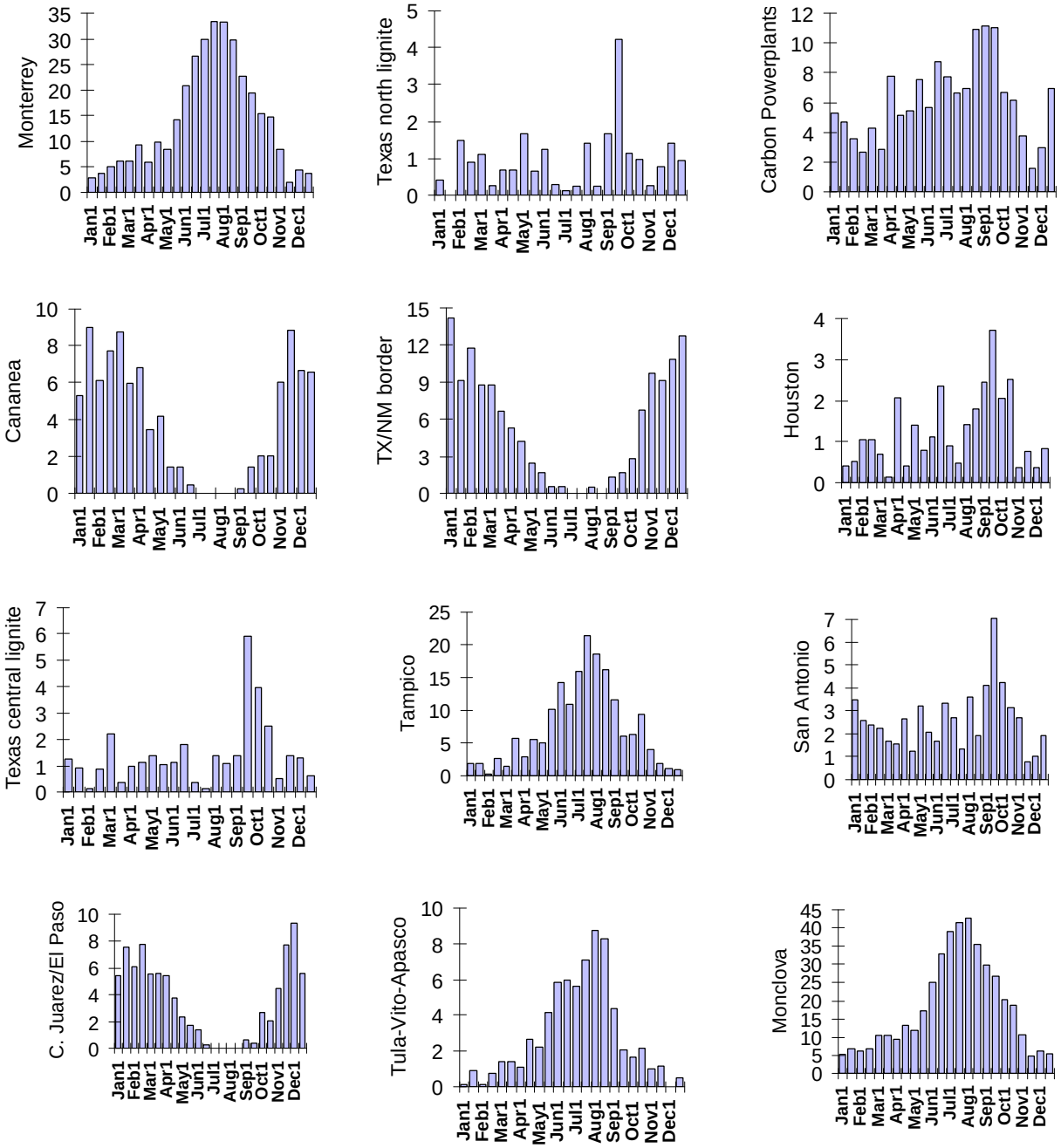


Figure 2-12. Frequency of flow by ½ month periods to Big Bend National Park from selected source areas. Frequency is the percentage of backward trjaectories from Big Bend that passed over the 1 degree latitude by 1 degree longitude cell containing the source area. The relative frequency by time of year is the parameter of interest. The absolute magnitude is an artifact of the grid size (1? x 1?) used.

2.4 Seasonality of light extinction and aerosol components

Figure 2-13 summarizes the tenth, fiftieth, and nintieth percentile levels of light extinction coefficient (b_{ext}) by month, averaged over the period December 1988 – August 1998. Figure 2-14 gives the same information, except that deciview is used in place of light extinction coefficient. Periods with relative humidity greater than 90% are not included. Data flagged for having hourly changes of bext > 10 Mm^{-1}, but not > 90% RH were included (this data represents about 20% of the observations). While there can be substantial variability from year to year, the average pattern shows highest median extinction in May. A rapid increase occurs from March to May (39-56) Mm^{-1}, representing a 60% increase in non-Rayleigh light extinction) and median b_{ext} remains within a few Mm^{-1} from May through September, after which extinction decreases. This pattern is similar for the tenth and ninetieth percentiles of extinction. At the 90th percentile, a relative minimum occurs in July. In summary, light extinction levels are lowest in winter (November-March), and highest in summer (May-September), with transition periods in the spring and fall. May 1998 had particularly high light extinction due to large fires in Mexico (Yucatan Peninsula, especially).

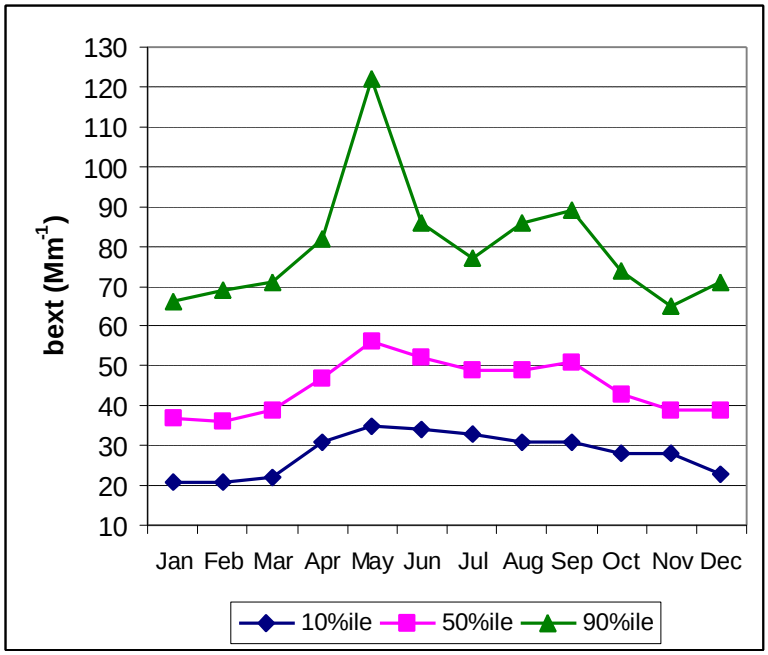


Figure 2-13. 10, 50, and 90 percentile b_{ext} values at Big Bend National Park (Dec 1988—August 1998). Data with relative humidity greater than 90% are not included.

Sisler, *et al.* (1996) used IMPROVE aerosol data to estimate the percent of aerosol light extinction from each of the major components for the period March 1992-February 1995. Their results (Table 2-1) show that sulfate is the most important contributor to light extinction at Big Bend, and organic compounds, light absorbing compounds, and crustal material are also important.

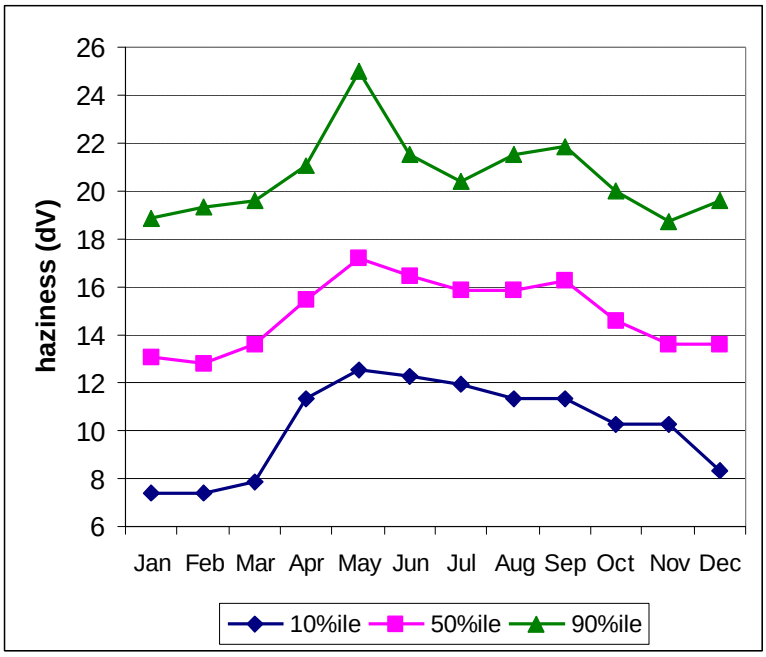


Figure 2-14. 10, 50, and 90 percentile haziness in deciview at Big Bend National Park (December 1988—August 1998). Data with relative humidity greater than 90% are not included.

Table 2-1
Average percent of reconstructed aerosol light extinction by component

Component	Percent of aerosol light extinction
Sulfate	41
Nitrate	3.8
Organics	19
Light absorption	21
Crustal	16

Table 2-1 shows that sulfate is the most important contributor to light extinction at Big Bend, and organics, light absorbing compounds, and crustal material are also important.

Variability in monthly averaged aerosol component concentrations for the period March 1988- February 1999 are shown in Figure 2-15. Elemental carbon (EC), organic carbon (OC) and fine mass all peak in May. This is the same month as the peak in b_{ext}. A few very high values of EC and OC in May suggest that fires (agricultural and wildfires) may be particularly important during this time of year (especially for May 1998).

Average monthly particulate sulfur is similarly high for May through October, except for a dip in concentrations in July. Fine soil is lowest in winter and shows a pronounced peak in July. The July peak is expected to result from transport of Saharan dust. Perry, et. al, (1997) demonstrated transport of Saharan dust into the southern and eastern United States, including Big Bend National Park. The Saharan dust is characterized by a deficit of calcium, leading to higher ratio of aluminum to calcium and silicon to calcium for periods with significant concentrations of Saharan dust present. Table 2-2 shows the monthly averaged silicon divided by monthly averaged calcium at Big Bend. For most months, the ratio is between 2 and 3; for July it is over 6 (also elevated in August). This suggests that Saharan dust is responsible for the peak in fine soil in July. Table 2-2 also shows monthly average fine soil divided by monthly averaged coarse mass. This increase in July and the fact that coarse mass (often associated with soil) does not show a peak in July (Figure 2-15) is consistent with the expectation that a significant fraction of the fine soil in July is transported from Africa.

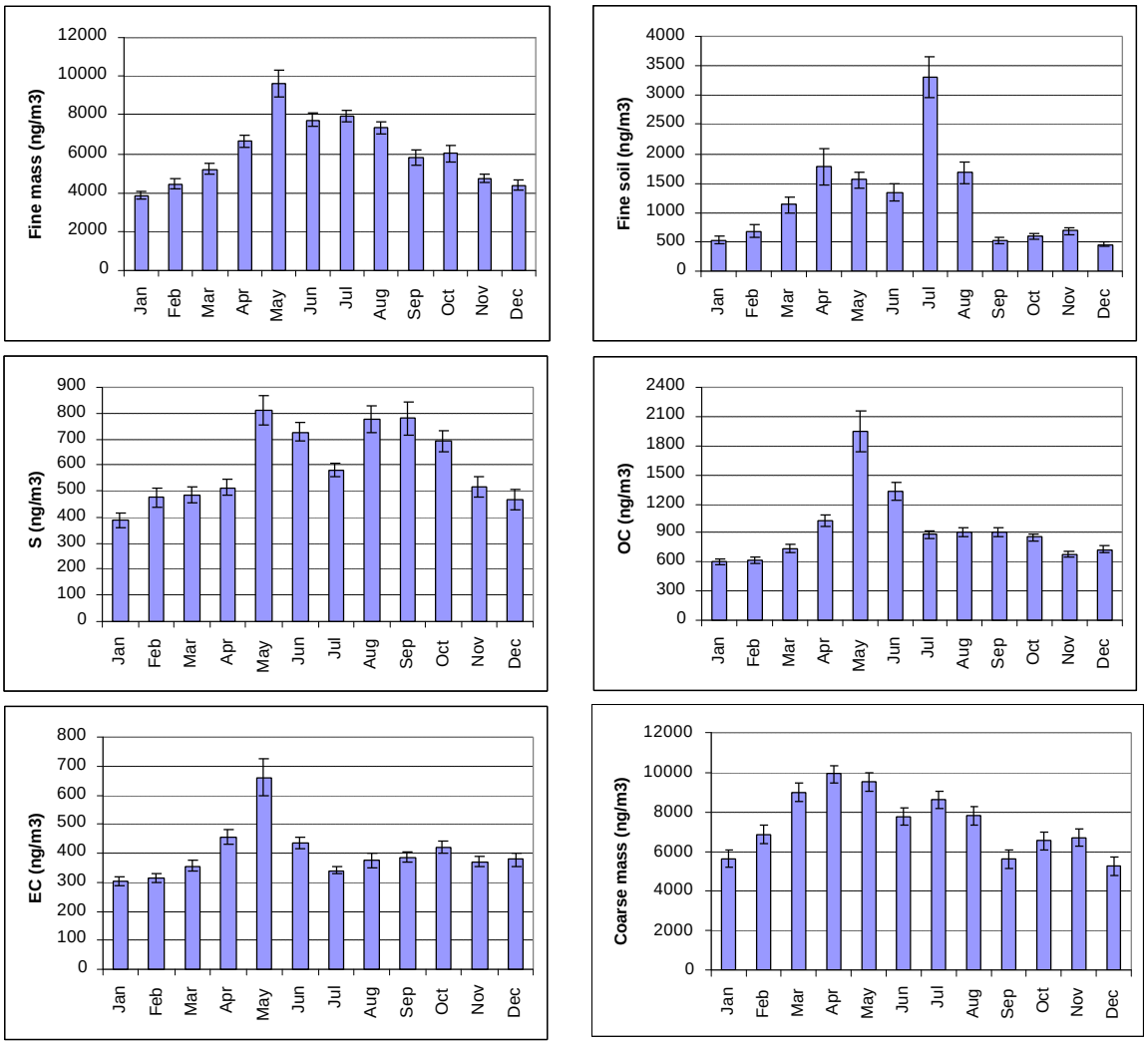


Figure 2-15. Monthly averaged concentration of aerosol components. Error bars show the standard error of the mean. Time period is from March 1988 – February 1999.

Table 2-2. Monthly averaged silicon divided by monthly average calcium and monthly average fine soil/ monthly average coarse mass: December 1988- February 1999.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Si/Ca	2.36	2.70	3.02	3.14	2.76	3.18	6.22	5.06	2.93	2.08	2.32	2.12
fine soil/CM	0.09	0.10	0.13	0.18	0.16	0.17	0.38	0.22	0.09	0.09	0.10	0.09

2.5 Relationship between light extinction, chemical components, and backtrajectories

The analyses presented here relate backtrajectories from Big Bend passing through each grid cell to b_{ext} and chemical components measured at Big Bend for the period December 1988- December 1994. These are presented in the form of conditional probability maps which give the probability that a condition is met for the backtrajectories passing through each grid cell. For light extinction coefficient (b_{ext}), particulate sulfur, organics, fine soil, organic carbon, and elemental carbon, the condition was that high (80 percentile or higher) concentrations occurred. It should be noted that these maps show the probability that high concentrations occurred when backtrajectories passed over an area; **they do not reflect average impacts of an area because some areas have much more frequent transport to Big Bend than other areas, as shown earlier.** It should also be noted that grid cells associated with a high frequency of certain conditions, such as high particulate sulfur at Big Bend should not be assumed to be contributing substantially to these conditions; rather, there are most likely sources somewhere along the trajectories passing over these cells that are contributing to the high concentrations.

Light extinction (b_{ext})

Figure 2-16 shows the frequency of backtrajectories passing through each grid cell for which b_{ext} at Big Bend was at the 80 percentile (57 Mm^{-1}) or higher. Figure 2-16 shows that areas to the northeast through south are relatively likely to be associated with high extinction when the air passes over these areas. Areas from the southwest through north are relatively less likely to be associated with high b_{ext} when the air passes over these areas.

Particulate sulfur

Figure 2-17 shows the conditional probability for high particulate sulfur concentrations (80 percentile = 929 ng/m^3). High sulfur concentrations are relatively likely for backtrajectories from areas northeast through south of Big Bend, with high concentrations unlikely to be associated with backtrajectories from the west-southwest through the north. Although they were not frequent, backtrajectories passing over east Texas and Louisiana were the most likely to be associated with high sulfur at Big Bend.

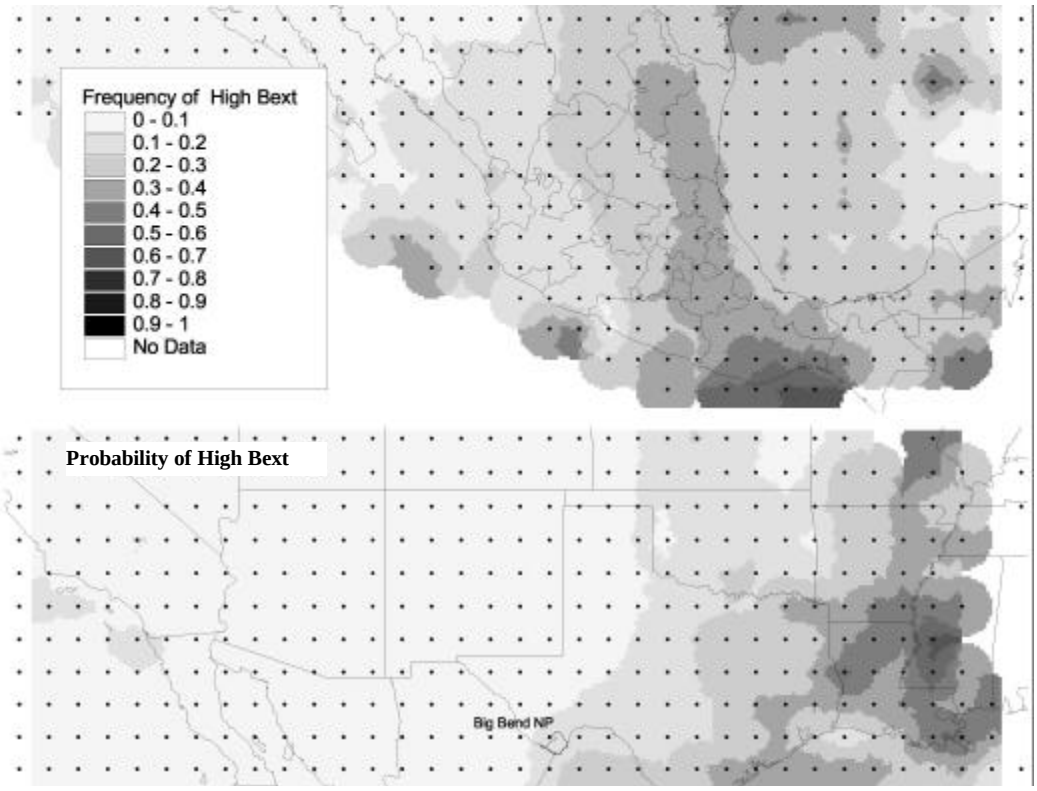


Figure 2-16: Probability that a trajectory passing over a cell will be associated with a b_{ext} value at BBNP above the 80 percentile value (57 Mm^{-1}).

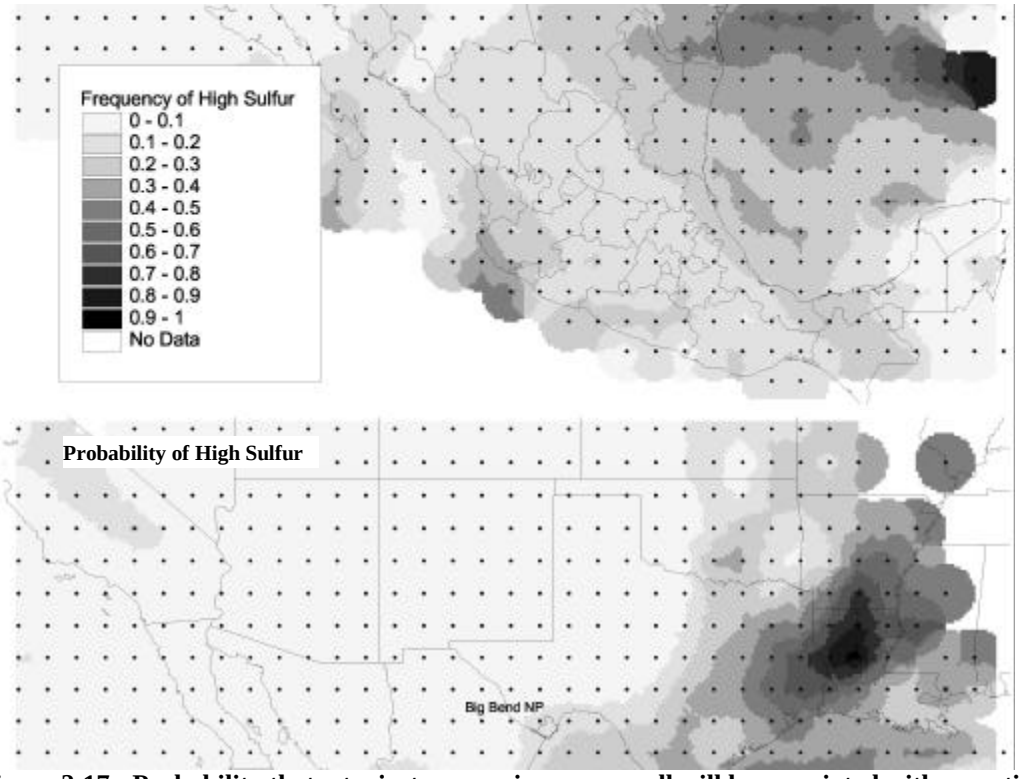


Figure 2-17: Probability that a trajectory passing over a cell will be associated with a particulate sulfur concentration at BBNP above the 80 percentile value (929 ng/m^3).

Light absorption (b_{abs})

Figure 2-18 shows that high levels of b_{abs} (80 percentile = 10.0 Mm^{-1}) are most likely for backtrajectories from the northeast clockwise through the west-southwest. The highest probability is associated with backtrajectories passing through east Texas and Louisiana.

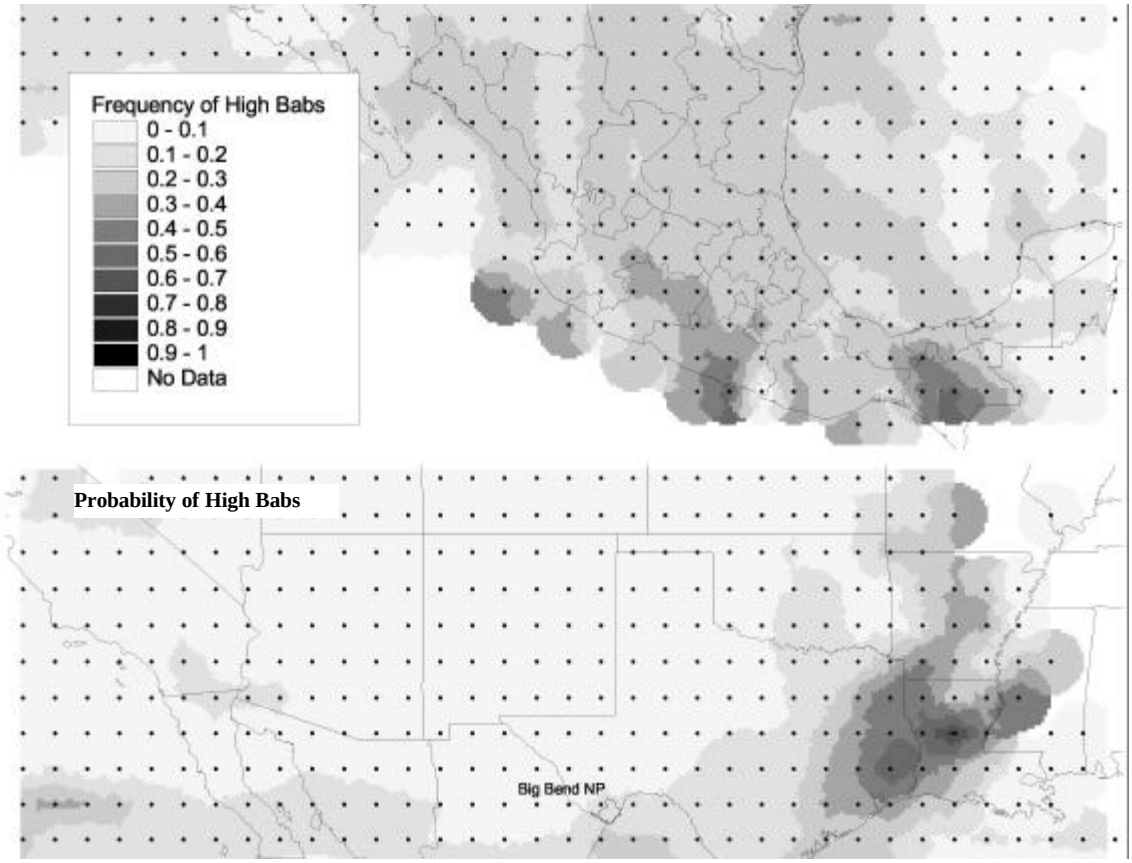


Figure 2-18: Probability that a trajectory passing over a cell will be associated with a b_{abs} value at BBNP above the 80 percentile value (9.96 Mm-1).

Elemental Carbon

Conditional probability for high elemental carbon (80 percentile = 555 ng/m3) is shown in Figure 2-19. Backtrajectories from the north-northeast clockwise through the west are relatively likely to be associated with high elemental carbon at Big Bend, especially backtrajectories passing over east Texas. Another area off the northern California coast is indicated to be associated with high elemental carbon; due to the small number of backtrajectories from this area, this result may not be meaningful.

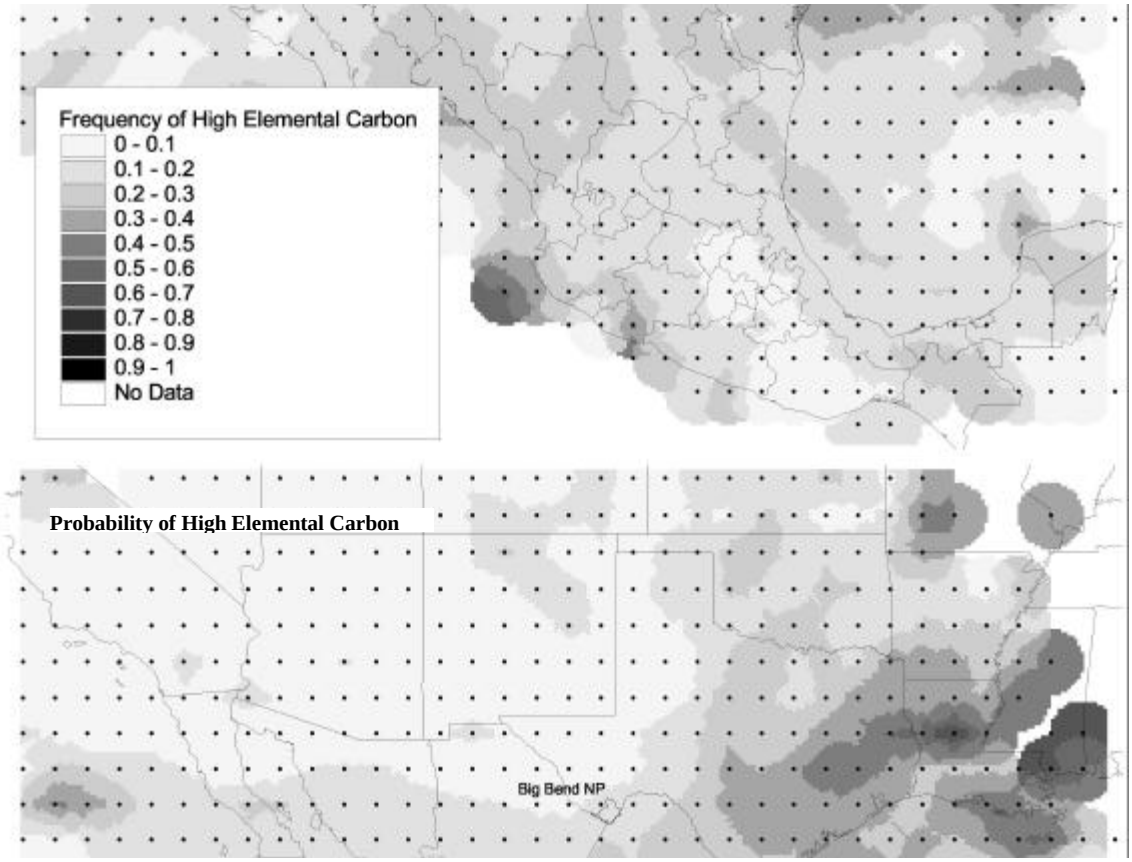


Figure 2-19: Probability that a trajectory passing over a cell will be associated with an elemental carbon concentration at BBNP above the 80 percentile value (555 ng/m^3).

Organic Carbon

High concentrations of organic carbon (80 percentile = 1208 ng/m^3) are most likely for backtrajectories passing over the coastal or near- coastal Gulf of Mexico in Mexico, Texas and Louisiana (Figure 2-20). High organic carbon concentrations are unlikely for backtrajectories from the northwest.

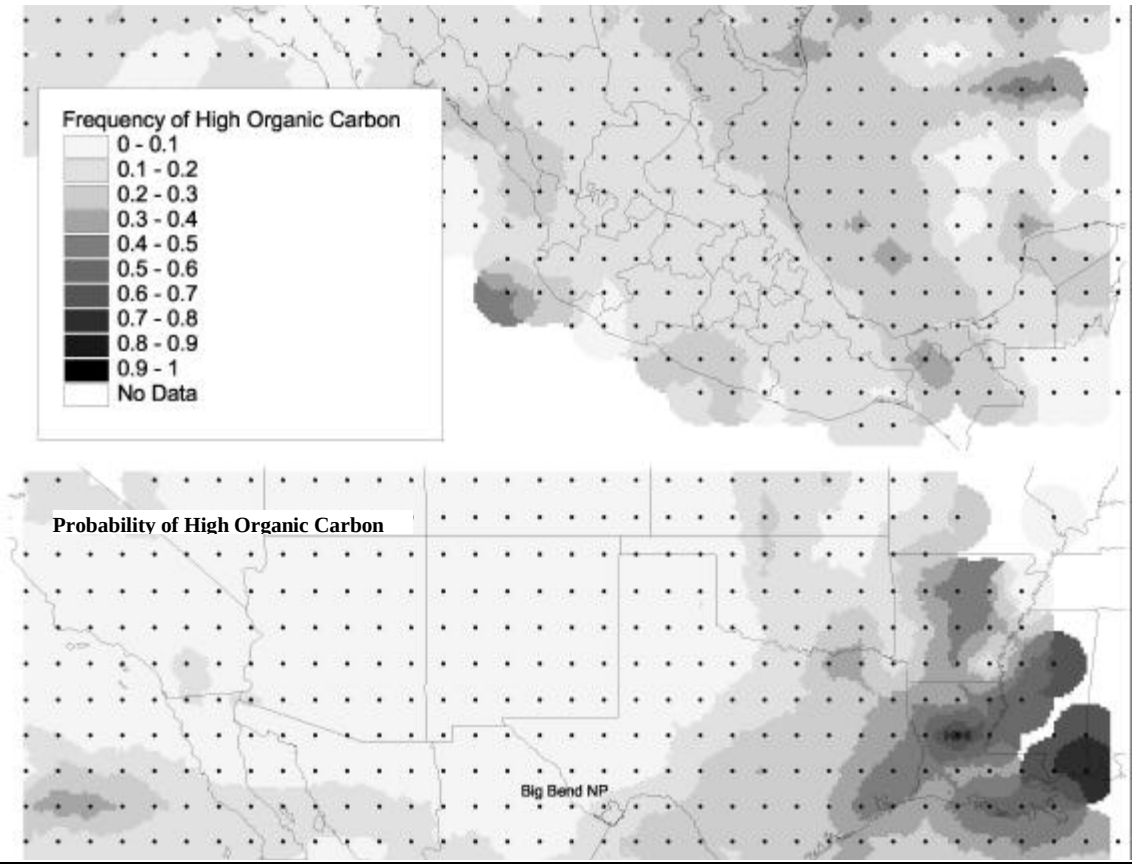


Figure 2-20: Probability that a trajectory passing over a cell will be associated with an organic carbon concentration at BBNP above the 80 percentile value (1208 ng/m^3).

Fine soil

Figure 2-21 shows the conditional probability for high concentrations of fine soil (80 percentile = 1690 ng/m^3). High fine soil is associated with backtrajectories from two areas: 1) southeast of Big Bend National Park and 2) long distances to the northwest. The areas far to the northwest are not likely the actual source of the fine soil; rather for backtrajectories to reach Big Bend during the 5-day backtrajectory, high wind speeds are required. Thus, flow from these distant regions is probably associated with high wind speeds, which would suspend soil materials from disturbed areas anywhere along the backtrajectory. We do see high fine soil associated with backtrajectories to the southeast over Mexico. The greater probability of high fine soil for distant backtrajectories from the southeast might be explained in terms of higher wind speeds, as discussed above. However, backtrajectories from the east may also include transport of Saharan dust into the area, as described above.

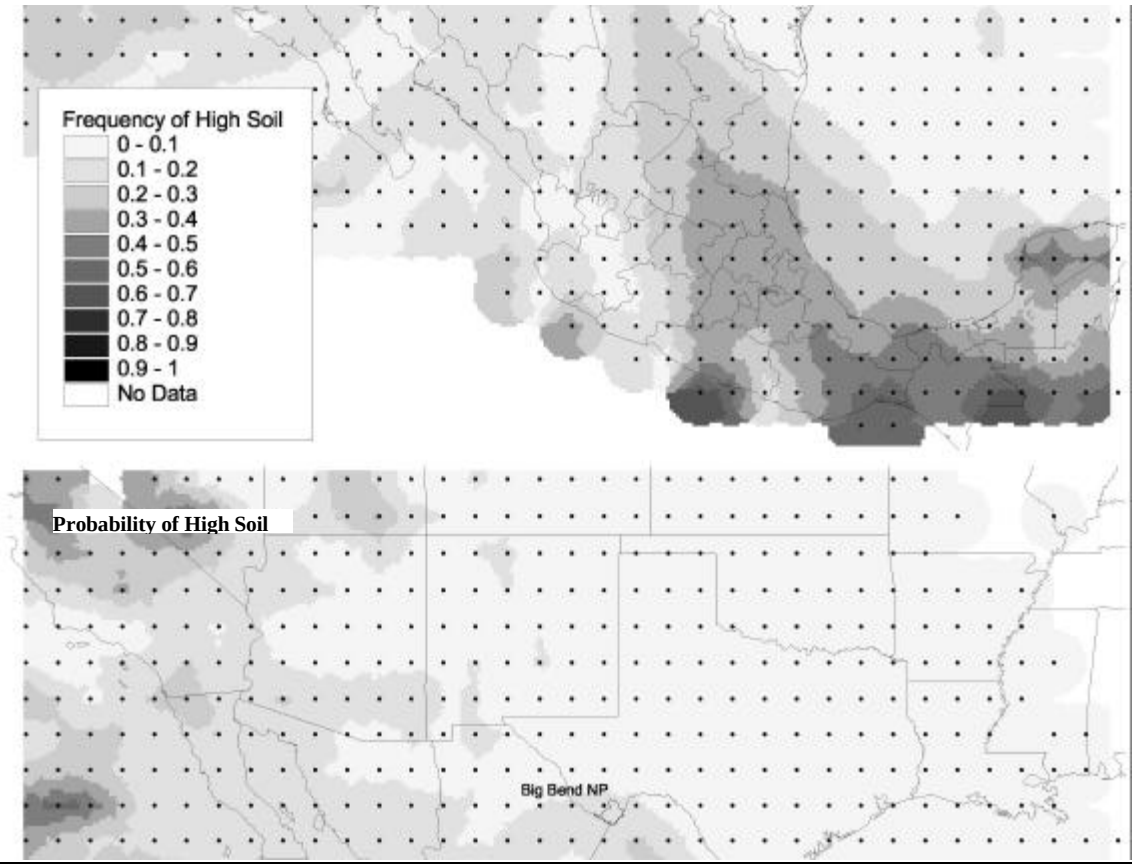


Figure 2-21: Probability that a trajectory passing over a cell will be associated with a fine soil concentration at BBNP above the 80 percentile value (1690 ng/m^3).

Relative Humidity

Because high humidity is required for water growth of hygroscopic aerosols, such as ammonium sulfate, and high humidity is often accompanied by clouds that enable rapid conversion of SO_2 to sulfate, it is informative to examine backtrajectory and relative humidity relationships. Figure 2-22 is a conditional probability that backtrajectories that passed through grid cells coincided with high (>70%) relative humidity at Big Bend. Overall, 19% of the backtrajectories from Big Bend met this criterion. The plot shows a clear division between backtrajectories with an easterly component which were likely to be associated with high relative humidity, and backtrajectories with a westerly component, which were unlikely to be associated with high relative humidity. Backtrajectories passing through the Gulf of Mexico to the east to southeast of Big Bend were especially likely to be associated with high RH at Big Bend. These areas have their peak transport toward Big Bend in September, which also has the highest average rainfall of any month along the south Texas coast. Thus, while the high RH and clouds associated with these backtrajectories will likely allow for high conversion and water growth of hygroscopic particles, offsetting effects of washout of particles may occur.

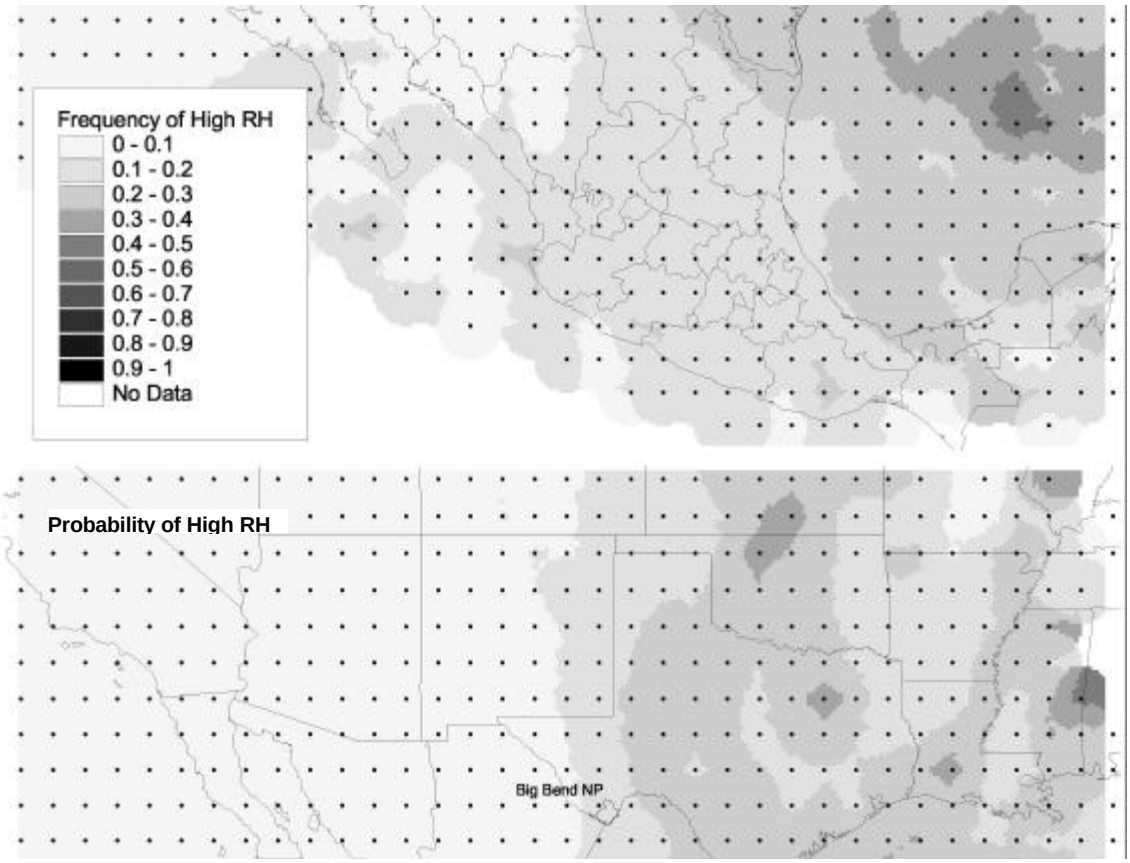


Figure 2-22: Probability that a trajectory passing over a cell will be associated with a relative humidity at BBNP above the 80 percentile value (70% RH).

2.6 Study Design Considerations

The material presented earlier in this section regarding monthly-summarized visibility and aerosol composition at Big Bend, transport patterns during periods of poor visibility, the spatial distribution of SO_2 emissions, and the frequency these emissions are transported toward Big Bend helped guide the BRAVO study design. Also helping to guide the BRAVO design was knowledge gained from previous studies, notably the preliminary Big Bend study and Project MOHAVE.

Particulate sulfate has been the compound that contributes most to visibility impairment at Big Bend National Park; thus sources of SO_2 are of particulate interest to BRAVO. Particulate carbon (elemental and organic) also contributes substantially to haze at Big Bend; the aerosol monitoring program (section 4.1) was designed to reveal more information regarding sources of carbonaceous aerosol at Big Bend.

On the average, visibility at Big Bend is most impaired during the May to September period. However, in October transport from the northeast is sometimes associated with very poor visibility. A four-month field program from July through October 1999 was selected to maximize the number of occurrences of flow from two regions of particular interest: northeast Mexico and eastern Texas. Backtrajectory analysis showed that this four month period would maximize the number of occurrences of flow from the significant source areas for SO_2 that are closest to Big Bend National Park. These periods would also be expected to give many episodes of transport from large SO_2 sources in central Mexico and would likely result in one or more cases of transport from large SO_2 source regions in the Ohio River Valley.

The use of tracers in Project MOHAVE showed that the current state of atmospheric transport and dispersion modeling in complex terrain is not sufficiently correct to draw reliable conclusions regarding source-receptor relationships on a day-by-day basis (Pitchford *et. al.,* 1999, Green and Tombach, 2000). This result argued for the release of artificial tracers for use in direct attribution methods such as TAGIT (Kuhns et al. 1999), to help evaluate and calibrate transport and dispersion models, and for use in receptor based models. The tracer program design is considered in more detail in section 3.

Previous studies also demonstrated the utility of a large network of particulate monitoring sites and chemical analysis of the filter samples. As discussed further in section 5, several analysis methods utilize this spatially resolved aerosol data. BRAVO design included a network of 37 aerosol monitoring sites. Purposes of the individual monitoring sites for BRAVO are described in section 4.1 (Table 4-2). Additional aerosol studies were conducted (mainly at Big Bend) to answer questions remaining after the preliminary study.

Additional upper air measurements were made to help evaluate and calibrate wind field models for input to air quality models (section 4.3). Extensive optical measurements at Big Bend National Park (section 4.2) were made to help characterize

effects of relative humidity on light scattering and the relative effects of fine and coarse particles on light scattering and light absorption. To help separate the effects from different sources, a source characterization program (sampling and chemical analysis of emissions) was conducted for several source types (section 4.4).

Unfortunately, the study design was constrained by the inability of the United States and Mexico to agree on the design for a joint U.S.- Mexico study. This resulted in a study design that included monitoring and source characterization only in the United States. Earlier versions of the proposed study plan included substantial aerosol and source monitoring and tracer release in Mexico. The final plan includes additional monitoring and tracer release along the U.S.- Mexico border to partly alleviate the limitations imposed from conducting a U.S. only study.

3 Tracer Release

3.1 Tracer Study Objectives

The objectives of the tracer study are to:

1) Tag (track emissions transport from) large individual sources with the potential for significant visibility impairment at Big Bend National Park
2) Tag source areas with the potential for significant visibility impairment at Big Bend National Park
3) Evaluate and improve performance of air quality models used for BRAVO.

For objective 1, tagging large individual point sources can be used in direct attribution analysis methods, such as TAGIT (Kuhns, et. al. 1998), which looks for gradients in particulate sulfur between source affected areas and areas outside the influence of emissions from the tagged source. The tracer can also be used to determine periods when the tagged source did not affect Big Bend National Park.

In objective 2, the tracer is used to give the general transport pattern and dispersion for emissions from a given source area. Because tracer is released from a point within an area of multiple sources, direct source attribution is not possible. The results are a qualitative demonstration of transport from the source region as well as information useful for objective 3. It identifies periods in which a source area is likely contributing to visibility impairment, but does not give a direct estimate of the impairment attributable to the source area.

Meeting objective 3 is useful for modeling the effects of tagged and non-tagged sources alike. This includes obtaining transport and dispersion, against which model results can be evaluated. Ideally, transport time would also be given. Model performance may be improved by adjusting dispersion parameters, etc. within a reasonable range that provides for improved model performance. As discussed in the following section, the tracer study is subject to constraints that affect the study design.

3.2 Tracer Study Constraints

The most significant constraint is that tracer release and sampling will not occur in Mexico. The conceptual study plan proposed tracer releases from the Carbon power plants in Mexico, about 20 km south of Eagle Pass, Texas. Also proposed was a tracer release from Tula-Vito-Apasco, a large Mexican area source for SO_2. The tracer study design described here reflects an attempt to mitigate the effects of this constraint.

Another political constraint on the tracer release study is that even though Mexico is not a participant in the study, the U.S. government desires a balanced study that is fair to Mexico. Thus the tracer study must be designed in a manner that does not unduly focus on Mexican sources while neglecting the effects of U.S. sources.

A physicochemical constraint is the availability of only four different perfluorocarbon tracers. This limits to four the number of sources or source areas that can be concurrently tagged.

3.3 Tracer Study Design

Emissions of SO_2 from the Carbon I and Carbon II powerplants are estimated to be on the order of 240,000 tons per year. The powerplants are located 1 km apart at a distance of 270 km east-southeast of Big Bend National Park. Because of the size of these plants and the closeness of the plants to Big Bend, relative to other large emission sources, tracking the emissions from these plants is the highest priority. Based upon dispersion estimates and reasonable SO_2 to sulfate conversion rates, there is a potential for the Carbon powerplants to, by themselves, cause a perceptible decrease in visibility at Big Bend. Other sources of substantial emissions of SO_2 and other compounds which may lead to visibility impairment are located in eastern Texas. These include many powerplants along the lignite belt, along with the cities of Houston, Dallas-Fort Worth and San Antonio. The Houston area contains numerous industrial sources and the nearby Parish powerplant. The San Antonio area is near powerplants in the southern lignite belt.

The most frequent wind flow patterns are from the southeast, which would take emissions from Mexican sources such as Tula-Vito-Apasco and Monterrey toward Big Bend National Park. However, as noted in the previous section, tracer releases cannot be done from these areas. Less frequently, but not uncommonly, transport from the Carbon powerplants is expected to be transported to Big Bend. Sources in east Texas are transported still less frequently toward Big Bend National Park. Transport from east Texas is rare in July and August, but increases in frequency in September and October. As a result of these emission and transport patterns and the constraints described earlier, the tracer study is designed to track emissions from the Carbon powerplants and sources in eastern Texas (more information on flow is given in section 2).

Because of the inability to gain access to the Carbon stacks, tracer will be released from Eagle Pass, Texas, approximately 20 km north-east of the Carbon plants. An

elevated (tower) release will be done at Eagle Pass to better simulate stack releases than would be possible with a near ground-level release. Tracer releases will also be done from a location in northeastern Texas to represent emission sources in that area, particularly from powerplants in the northern lignite area, the Houston area to represent urban and industrial emissions from east-central Texas, and San Antonio to represent powerplants and urban sources in the southern lignite area. The release in northeastern Texas will be from a powerplant stack to represent transport and dispersion of elevated releases that would be applicable to multiple plants in the area. Because flow from eastern Texas is uncommon in the first two months of the study (July and August), tracer releases from multiple Texas locations during these months is not the best use of resources. Providing information about the adequacy of the Eagle Pass tracer release to represent emissions from the Carbon plants is a more effective use of resources. Concern over the Eagle Pass releases arises from the facts that there is a horizontal separation of 20 km between Eagle Pass and Carbon I/II and a vertical separation of varying amount between any release location and the effective stack heights from Carbon I/II. The vertical separation is of concern especially at nighttime and early morning hours when the atmosphere is stable and significant vertical wind shear may occur. Radiosonde data from Del Rio indicates substantial vertical wind shear during the morning sounding (Figure 3-1).

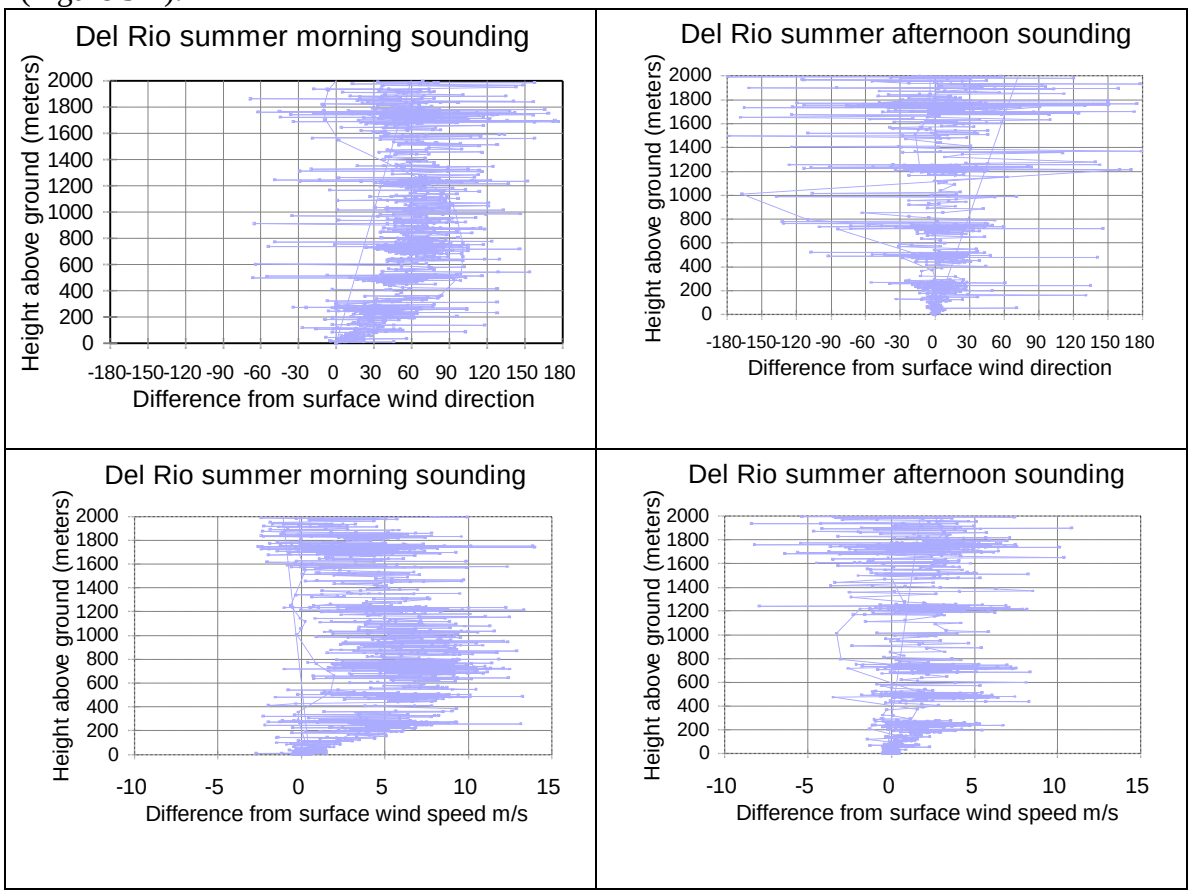


Figure 3-1. Differences from surface wind speed and direction as a function of height. Plot is for Del Rio, Texas radiosonde data, July to September 1992. Morning sounding taken at 6am CST. Afternoon sounding at 6 pm CST. Positive wind direction differences represent a clockwise direction of wind shear with height.

Composite virtual potential temperature soundings shown in Figure 3-2 illustrate the stable conditions in the morning and well-mixed conditions in afternoon.

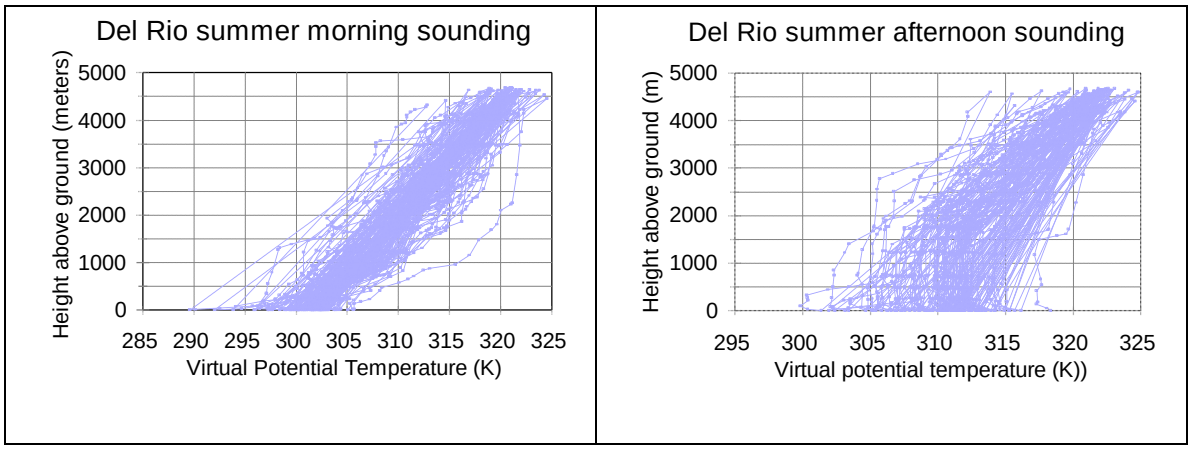


Figure 3-2. Virtual potential temperature as a function of height July -September 1992 for morning and afternoon soundings. Vertical line would indicate well-mixed conditions. A strong inversion is apparent throughout the soundings in the morning. For the afternoon, conditions are generally well - mixed through about 2 km AGL.

It might be expected that for tracer releases during periods of well-mixed atmospheric conditions Eagle Pass is a suitable surrogate for Carbon I/II emissions. Well-mixed conditions are likely to occur during daytime from about 1-2 hours after sunrise until approximately sunset. The tracer release program calls for continuous release of one tracer compound plus a separate tracer to be released during the daytime so that the concentrations measured at receptors can be designated as resulting from daytime, nighttime, or a known mixture of daytime and nighttime releases. A third tracer will be released on alternate days to provide information on which day the tracers were released and to help resolve ambiguities over the release time of the tracer. If the Eagle Pass releases are representing transport from Carbon I/II there should be significant relationships between SO_2 and tracer concentrations. Two months of release using 3 tracers should be sufficient to understand the conditions during which tracer releases at Eagle Pass are representative of emissions from the Carbon plants.

During the second two months of the study, only one tracer will be released at Eagle Pass. The two tracers previously used for timing will be moved to Houston and San Antonio. The September-October period is the time of year with most frequent transport from these source areas toward Big Bend National Park.

The four perfluorocarbon tracers used were oPDCH, PDCB, PTCH, and i-PPCH. Criteria for selection of the tracer compounds included background concentration, cost, and ability to separate the compounds during chromatographic analysis. Release rates were determined using estimated dispersion factors from the release locations to Big Bend (extrapolated from Project MOHAVE tracer data), and estimated precision for the new chromatographic system developed for BRAVO. Concentration uncertainty for 6 hour and 24 hour samples was estimated to be in all cases less than 10% of maximum concentration expected at Big Bend. Sample volume will be the same for the 6 and the

24 hour samples because the 6 hour sampler pumps 4 at times the rate as the 24-hour sampler. Concentration uncertainty for the 1-hour samples at Big Bend will be higher due to the lower sample volume. The sampling network is described in section 4.

Release rates for the first period of the study are shown in the Table 1. oPDCH and i-PPCH were released continuously. PDCB was released on alternate days from 8am to 8am CDT. PTCH was released every day but only from 8am to 8pm CDT.

Table 1. Tracer release schedule first phase of study.

Location	**Eagle Pass**	**Eagle Pass**	**Eagle Pass**	**Big Brown**
Tracer	**OPDCH**	**PDCB**	**PTCH**	**i-PPCH**
Release period	7/5/99-11/1/99	7/5/99-9/13/99	7/5/99-9/13/99	7/9/99-11/1/99
Release Rate (kg/hr)	0.155	0.525 alternate days (8am-8am) CDT	0.184 8am – 8pm CDT only	0.092

Release rates for the second period of the study are shown in Table 2. There was a hiatus of 4 days (8am to 8am) from terminating PDCB and PTCH at Eagle Pass and initiating release at San Antonio and Houston to allow these tracers to clear the study area. oPDCH at Eagle Pass and i-PPCH at Big Brown continued to be released during this interim period. In early September, PDCB and PTCH releases from Eagle Pass were terminated. Release at San Antonio and Houston began 5 days later at 8am and terminated at 8am CDT (7am CST) on November 1 along with the releases from Eagle Pass and the Big Brown power plant. Note that all tracers were released continuously during the second half of the study.

Table 2. Tracer release schedule for the second half of the study.

Location	**Eagle Pass**	**San Antonio**	**WA Parish**	**Big Brown**
Tracer	**OPDCH**	**PDCB**	**PTCH**	**i-PPCH**
Release period	7/5/99-11/1/99	9/17/99-11/01/99	9/17/99-10/25/99	7/9/99-11/1/99
Release Rate (kg/hr)	0.155	0.442	0.115	0.092

This program provides balance with 3 tracers representing Mexican emissions and 1 representing American emissions during the first half of the study when flow is more frequently from the south and 3 tracers representing American emissions and 1 representing Mexican emissions during the second half of the study when flow from the east is more likely.

Locations of tracer release and sampling sites are shown in the next section.

4 Data Gathering

The data gathering component of the study is from July 1- October 31.

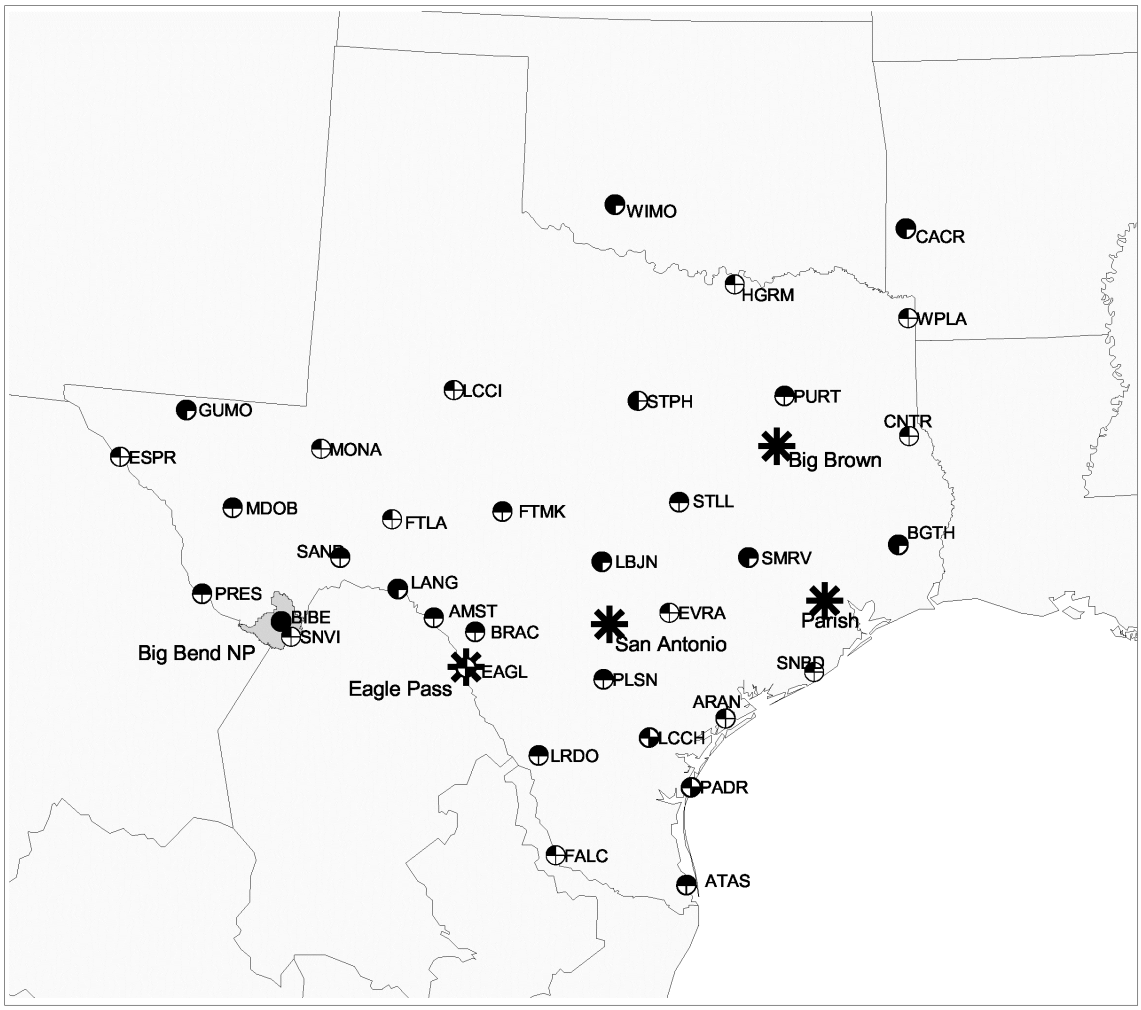
4.1 Aerosol and Gaseous (includes tracer) Data

The network for collection of aerosol and gaseous data includes 36 sites located throughout Texas, except for the panhandle area, and one site (Witchita Mountains) in Oklahoma. The IMPROVE sampler is used for collecting aerosol and SO_2 samples. All sites collect $PM_{2.5}$ on Teflon filters; many sites have additional measurements. Table 4-1 summarizes the number of sites for each type of measurement.

Table 4-1. Number of measurement sites by measurement type.

Measurement Type	Number of Sites
24 hour $PM_{2.5}$ elements (H, Na-Pb, mass, b_{abs}) (Teflon filter)	34
24 hour SO_2 and tracer	18
24 hour $PM_{2.5}$ carbon (quartz filter)	7
24 hour $PM_{2.5}$ ions (nylon filter)	4
6 hour $PM_{2.5}$ elements, SO_2, tracer	6
24 hour PM_{10} elements, ions, carbon	1
12 hour $PM_{2.5}$ elements, ions, carbon	1
Collocated 24 hour $PM_{2.5}$ elements, ions, carbon, SO_2, tracer	1
Collocated 24 hour PM_{10} elements, ions, carbon	1
Collocated 6 hour $PM_{2.5}$ elements, SO_2, tracer	1

Figures 4-1 and 4-2 show the locations of the monitoring sites and the parameters measured at each site. Table 4-2 gives this information as well, along with site names and latitude, longitude, elevation, and purpose of the site. The purposes of sites included: general gradient sites in Texas (about 100 km apart); border gradient sites at the Texas/Mexico border, Texas/other U.S. states border sites, coastal gradient sites, Big Bend area gradient sites, Class I areas, and sites predominantly downwind of tracer release locations. Additional aerosol and gaseous measurements are being made at Big Bend (K-Bar Ranch). These measurements are summarized in Table 4-3.



24 Hour BRAVO Network Configuration

- Fine Particles on Teflon Filter
- SO2 and Tracer
- Ion Balance
- Carbon
- Tracer Release Sites

100 0 100 200 Kilometers

Figure 4-1. 24 hour network of gas and aerosol sampling locations.

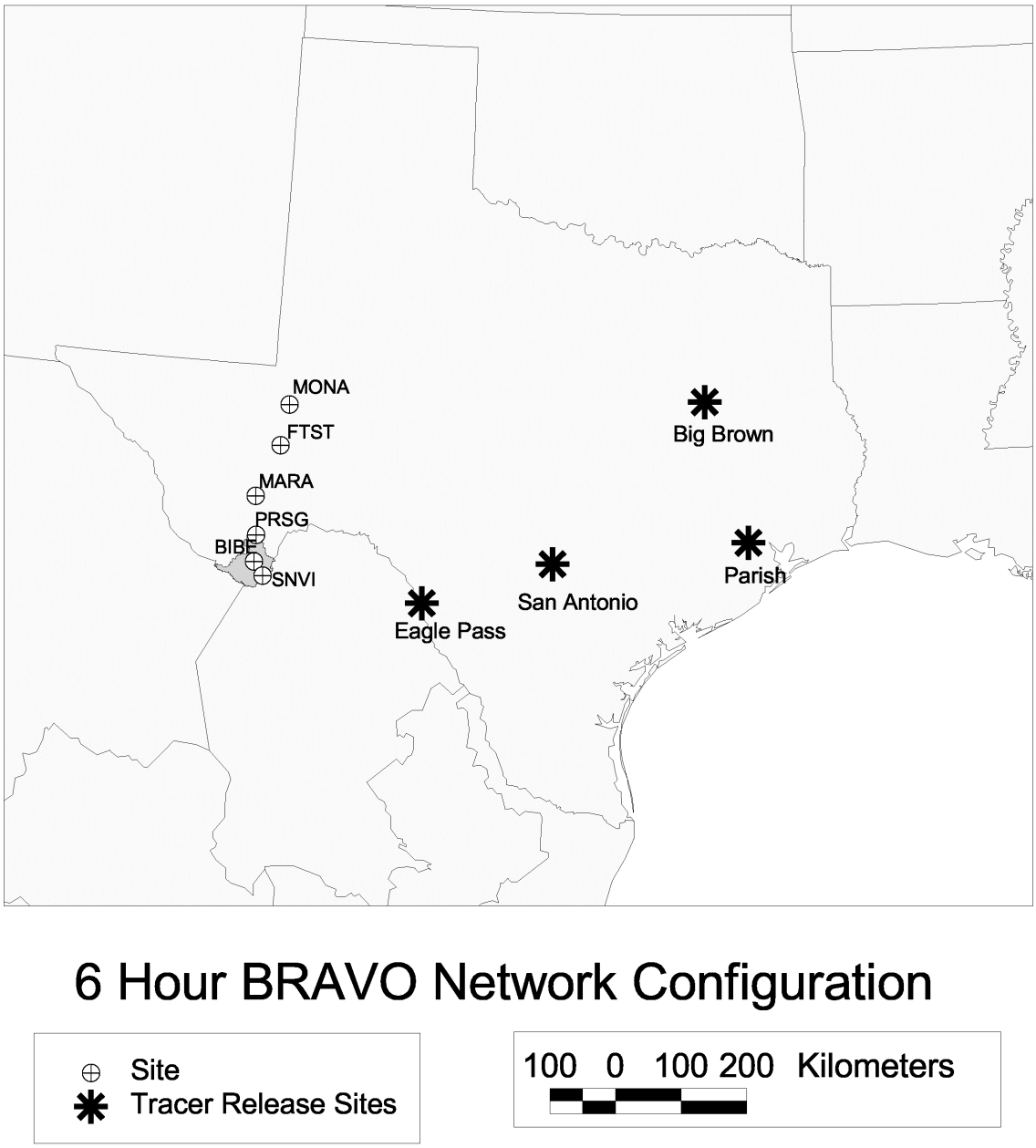


Figure 4-2. 6 hour network of gas and aerosol sampling locations.

Table 4-2. Aerosol and tracer monitoring site abbreviations, names, latitude, longitude, elevation, and purpose.

Site	Name	Latitude	Longitude	Elevation	Purpose
				m	
AMST	Amistad	29.47	-101.02	351	Downwind of Carbon/Eagle Pass
ARAN	Aransas	28.32	-96.83	0	
BIBE	Big Bend (K-Bar)	29.30	-103.18	1052	Receptor/Big Bend area gradient
BGTH	Big Thicket	30.48	-94.35	38	Texas/Louisiana border/gradient
BRAC	Brackettville	29.32	-100.42	335	Downwind of Carbon/Eagle Pass
CACR	Caney Creek	34.42	-94.15	646	Class I area
CNTR	Center	31.83	-94.17	24	Texas/Louisiana border/gradient
EPS	Eagle Pass	28.87	-100.52	274	Mexico border/near Carbon
ESPR	Esperanza	31.17	-105.72	1067	Mexico border gradient
EVRA	Everton Ranch	29.63	-97.65	244	Gradient
FALC	Falcon Dam	26.55	-99.17	61	Border gradient
FTLA	Fort Lancaster	30.67	-101.70	762	Gradient
FTMK	Fort McKavett	30.83	-100.10	671	Gradient
FTST	Ft Stockton	30.92	-102.90	983	Big Bend area gradient
GUMO	Guadalupe Mtns	31.83	-104.82	1659	Class I area
HGRM	Hagerman	33.73	-96.75	244	Texas/Oklahoma border
ATAS	Laguna Atascosa	26.22	-97.35	4	Coastal and Mexico border gradient
LCCI	Lake Colorado City	32.32	-100.90	640	Gradient
LCCH	Lake Corpus Christi	28.07	-97.90	91	Inland ion balance
LANG	Langtry	29.80	-101.55	396	Mexico border/downwind of Carbon
LRDO	Laredo	27.80	-99.45	148	Mexico border gradient
LBJN	LBJ	30.25	-98.63	518	Gradient/downwind of San Antonio
MARA	Marathon	30.20	-103.23	1280	Big Bend area gradient
MDOB	McDonald Observatory	30.67	-104.02	2043	Gradient
MONA	Monahans Sandhills	31.48	-102.80	831	Big Bend area gradient
PADR	North Padre Island	27.45	-97.30	0	Coastal/ion balance
PRSG	Persimmon Gap	29.67	-102.18	915	Big Bend area gradient
PLSN	Pleasanton	28.78	-98.57	122	Gradient
PRES	Presidio	29.57	-104.35	838	Mexico border gradient
PURT	Purtis Creek	32.35	-98.00	187	Gradient/downwind of Big Brown
SNBD	San Bernard	29.90	-95.58	0	Coastal gradient
SNVI	San Vicente	29.12	-103.03	549	Big Bend area gradient
SAND	Sanderson	30.18	-103.22	610	Gradient/downwind of Carbon
SMRV	Somerville Lake	30.33	-96.52	84	Gradient
STPH	Stephenville	32.27	-98.17	274	Gradient
STLL	Stillhouse Lake	31.02	-97.53	213	Gradient
WIMO	Wichita Mtns	34.70	-98.58	488	Class I area
WPLA	Wright Patman Lake	33.30	-94.15	9	Texas/Arkansas/Louisiana border

Table 4.3 Specialized aerosol and gaseous measurements at Big Bend.

Measurement	Averaging period
High time resolution, high sensitivity SO_2	1 hour
High time resolution particulate sulfate	12 minutes
Hourly tracer sampling	1 hour
$PM_{2.5}$ carbonaceous aerosol	24 hours
Carbon speciation by GC/MS for selected periods	24 hours
Gaseous nitric acid	24 hours
Gaseous ammonia	24 hours
MOUDI size resolved aerosol	24 hours
Various particle size measurements differential mobility analyzer, optical particle counters, aerodynamic particle sizers	Seconds
Gaseous hydroperoxides	1 hour
Scanning electron microscopy (SEM) analysis	24 hours

Many of the specialized aerosol measurements at Big Bend are to support an ion balance study, carbon apportionment, and a size distribution study. The goals and expected information from these studies are briefly summarized below.

Ion balance study goals

- Determine what form(s) aerosol sulfate is found in at Big Bend National Park (BBNP) (e.g., H_2SO_4, NH_4HSO_4, $(NH_4)_2SO_4$, Na_2SO_4, etc…)

- Determine whether previously observed correlations between BBNP sulfate and sodium reflect the presence of sodium sulfate aerosol

- Determine changes in sulfate content and speciation during transport of air from the coast to BBNP

Expected information from planned ion balance measurements

- H^+ measurements will reveal whether BBNP aerosol is neutralized or acidic

- $PM_{2.5}$ ion measurements will indicate whether sulfate is present in ammonium salts or whether a significant portion is probably associated with sodium ion.

- MOUDI size-resolved aerosol samples will reveal if sodium ion and sulfate are found in the same particle size range(s)

- SEM single particle measurements will reveal if sodium and sulfur are found in the same particles

- Measured aerosol and gas compositions at BBNP can be used to predict how $PM_{2.5}$ mass and scattering properties might change in the event of changes in ambient concentrations of sulfate, nitrate, or ammonium

- Comparison of BBNP results with results from upwind coastal and inland sites will reveal if sulfate is added to sea salt particles as they are transported to BBNP from the coast

- Peroxide measurements will reveal the potential for rapid oxidation of SO_2 to sulfate in the presence of clouds

- Measurements of sodium ion can be compared with measurements of elemental sodium (from the Davis IMPROVE samples) to determine the fraction of sodium present in ionic form

Carbon study goals

- Determine dominant source types contributing to carbonaceous aerosol at Big Bend National Park (BBNP)

- Determine whether dominant source types change with transport conditions or season

Size distribution study goals

- Measure the dry atmospheric aerosol size distribution from ~0.02 µm to >10 µm, with particular focus on characterizing the coarse mode aerosol

- Estimate water content of optically-important particles (> 0.1 µm)

- Use optical measurements to detect shifts in aerosol composition

- The set of size distribution measurements will enable construction of the complete size distributions at BBNP, given some assumptions regarding the aerosol properties such as density and refractive index.

  - Dry size distributions can be used to compute the aerosol extinction and compared with dry nephelometer and aethalometer measurements made by other investigators.

  - The coarse mode data can be used to estimate the severity of errors in the nephelometer response at larger particle sizes.

Expected information from size distribution study

  - The ambient size distributions can be used to compare with impactor measurements (DRUM, MOUDI) to help constrain the mass distributions.

- The estimates of the number concentrations of particles of all sizes can be used to estimate the age of the various size fractions, using lifetime estimates for particles against dry deposition and other loss mechanisms.

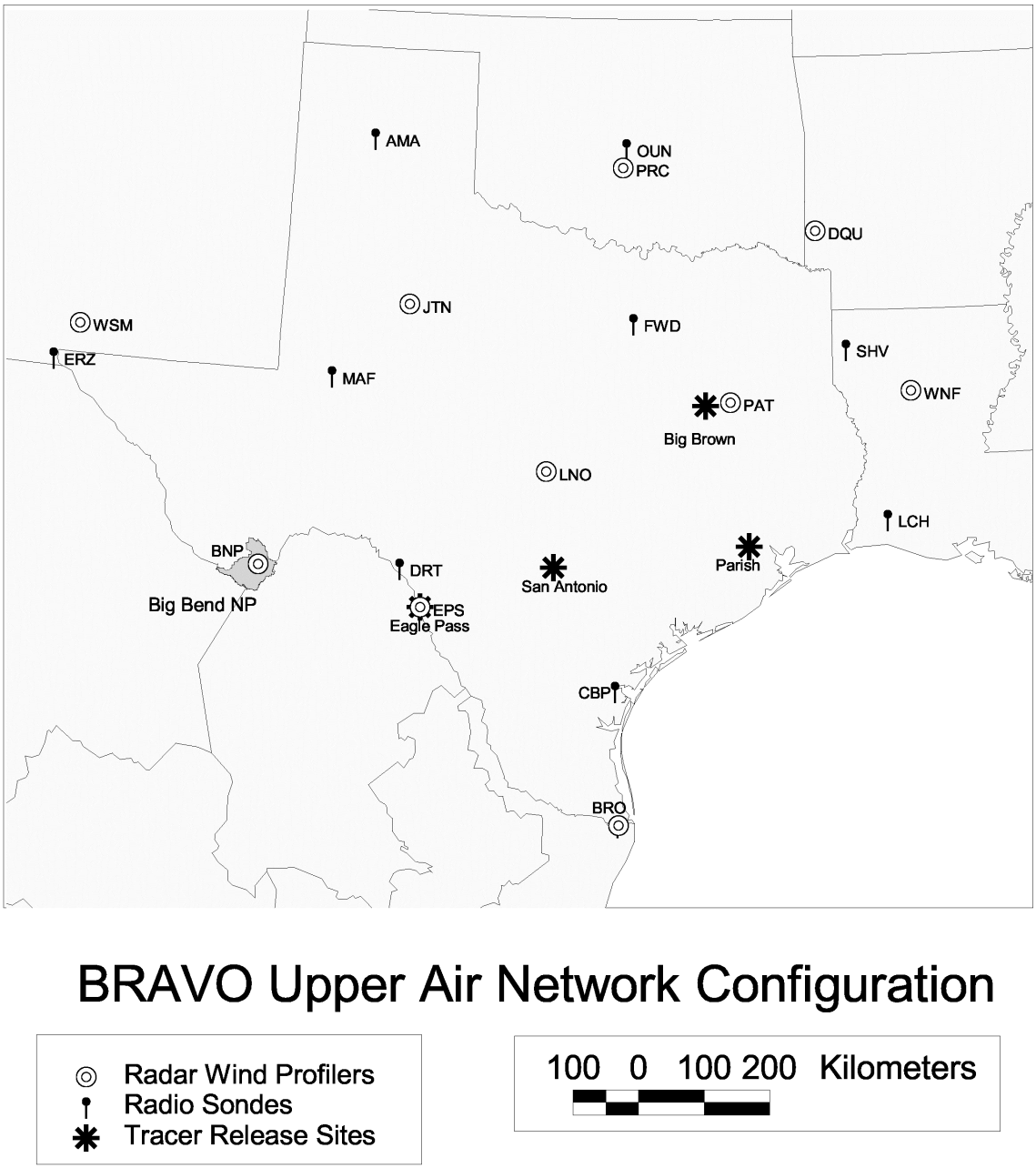
4.2 Optical Data

Optical data collected at Big Bend National Park includes transmissometer and ambient nephelometer data at a site about 5 Km north of the main BRAVO monitoring location at K-Bar Ranch. For the BRAVO study, additional optical data are collected. These include 2 additional transmissometers , 2 open air Optec nephelomters, two ambient $PM_{2.5}$ Optec nephelometers, one ambient PM_{10} Optec nephelometer. The additional transmissometers are located about 0.5 Km southwest of the K-Bar Ranch site. The additional nephelometers are all located at the K-Bar Ranch site. There are also five 35mm cameras and two 8mm time-lapse cameras at the south end of the new transmissometer path. The cameras give views from the Rio Grande River Basin to the existing transmissometer site path.

Additional optical instruments at the K-Bar Ranch site include two $PM_{2.5}$ Radiance Research nephelometers for which relative humidity is controlled, an aethalometer (operated with no-cut, 2.5 ?m cut and 1 ?m cut), and a photoacoustic light absorption instrument. The additional nephelometers were used to investigate the effects of relative humidity changes upon particle size and to quantify the light scattering by fine and coarse particles.

4.3 Meteorological Data

Upper air meteorological data sites are shown in Figure 4-3 and listed in Table 4-4. Radiosonde sites collect altitude, pressure, wind speed, wind direction, temperature, and dew point temperature, usually twice per day at 0 and 1200 Greenwich Mean Time (7 am and 7 pm CDT). Radar wind profilers collect wind speed and direction as a function of height – data is generally reported hourly. Radar wind profilers equipped with a radio acoustic sounding system (RASS) also obtain vertical profiles of virtual temperature, although usually only to 500-1500 meters.



BRAVO Upper Air Network Configuration

Radar Wind Profilers
Radio Sondes
Tracer Release Sites

100 0 100 200 Kilometers

Figure 4-3. Upper air meteorological sites.

Table 4-4. Upper Air Meteorological Monitoring Site locations and type.

Station	Location	Lat	Lon	Type
AMA	Amarillo, TX	35.23	-101.70	Rawinsonde
BBNP	Big Bend, TX	29.30	-103.25	BRAVO Profiler
BRO	Brownswille,TX	25.90	-97.43	Rawinsonde and NOAA Wind Profiler
CBP	Corpus Christi, TX	27.77	-97.50	Rawinsonde
DQU	Dequeen, AR	34.11	-94.29	NOAA Wind Profiler
DRT	Del Rio, TX	29.37	-100.92	Rawinsonde
EPS	Eagle Pass	28.87	-100.57	BRAVO Profiler
ERZ	Santa Teresa, NM	31.87	-106.7	Rawinsonde
FWD	Fort Worth, TX	32.83	-97.30	Rawinsonde
JTN	Jayton, TX	33.01	-100.98	NOAA Wind Profiler
LCH	Lake Charles, LA	30.12	-93.22	Rawinsonde
LNO	Llano, TX	30.79	-98.66	BRAVO Profiler
MAF	Midland, TX	31.95	-102.18	Rawinsonde
MONT	Monterrey, MX	25.70	-100.25	Rawinsonde
OUN	Norman/Westheimer, OK	35.22	-97.45	Rawinsonde
PAT	Palestine, TX	31.77	-95.71	NOAA Wind Profiler
PRC	Purcell, OK	34.97	-97.51	NOAA Wind Profiler
SHV	Shreveport, LA	32.47	-93.82	Rawinsonde
SNAN	San Antonio, TX	29.47	-98.50	BRAVO Profiler
WNF	Winfield, LA	31.89	-92.78	NOAA Wind Profiler
WSM	White Sands, NM	32.40	-106.34	NOAA Wind Profiler
MCV	Chihuahua	28.70	-106.07	Rawinsonde

4.4 Source Characterization

The relative abundance of chemical components in an ambient particulate sample reflects the mixture of emissions from multiple sources, each with their own chemical composition. Chemical source profiles are the fractional mass abundances of measured chemical species relative to primary $PM_{2.5}$ mass in source emissions. These profiles are obtained by extracting samples from specific emitters that are believed to represent the larger population of similar emitters that might contribute ambient $PM_{2.5}$ concentrations. Archived profiles of mobile, area, and point sources derive from regions of the United States and time periods that may not represent the sources in Texas, neighboring states, and northern Mexico that might affect visibility in Big Bend National Park. Representative emitters for sources of directly emitted $PM_{2.5}$ and precursor gases such as sulfur dioxide will be tested to develop source profiles specific to the BRAVO region and study period and to evaluate their similarity to source profiles derived from other times and places.

The objectives of the BRAVO source characterization program are to:

?? Identify and sample $PM_{2.5}$ from representative emitters from within the study domain

?? Analyze these samples for the same chemical components measured at receptor sites.

?? Create chemical source profiles for use in subsequent source apportionment and data analysis activities.

Accomplishment of these objectives will provide input data to receptor models such as the Chemical Mass Balance, Tracer Mass Balance Linear Regression, and Differential Mass Balance Receptor models. The derived profiles will also assist in the evaluation of meteorological trajectory models that determine relative impacts from different source areas when coupled with an emissions inventory that will be compiled for the BRAVO field study period.

Source Types

The Big Bend preliminary study showed that suspended dust, organic and elemental carbon, and ammonium or sodium sulfate were the largest contributors to light extinction. Several trace metals, such as vanadium, nickel, selenium, arsenic, and lead, were also quantified; these metals are often found in industrial source emissions. Nitrate levels were negligible. Geological material, trace metals, and carbon are directly emitted by sources, while most of the sulfate forms in the atmosphere from directly emitted sulfur dioxide. Atmospheric geological material derives from paved road dust, unpaved road dust, and natural soils. Mobile source emissions are dominated by gasoline and diesel cars and trucks. Vehicle exhaust is a large contributor to $PM_{2.5}$ carbon in most areas and these emissions derived from a variety of conditions. Vegetative burning consists of accidental fires, planned agricultural burning, trash burning, and residential wood combustion. Residential wood combustion for heating is not a major source in the area during the summertime study period owing to high ambient temperatures. Meat cooking, either over coals or with compressed or natural gas, has a similar profile to vegetative burning unless specific organic compounds are measured.

A subset of point sources that can reasonably represent those that might contribute to particulate concentrations at Big Bend National Park will be tested. Variations for three separate power plant units using the same coal show the need to test several coal-fired boilers in an emissions area that have different combustion and pollution control configurations. In addition to power stations, coal is also combusted in steel and some cement operations for process heat and power generation. Residual oil is burned in power stations as well as for oil extraction, in ships at sea, and for petrochemical production. Steel production emissions are result from several different sources, including furnaces, sintering, and coking.

The types of industrial point sources that emit the most sulfur dioxide accompanied by particles with trace metals that can be determined at receptors for the study domain are coal combustion in power stations, cement kilns, and steel mills and residual oil combustion in power stations, petroleum extraction, cement kilns, ships, and

refineries. The major industrial source of carbon is from coking emissions in steel mills; these may also be accompanied by trace metals in the coal ash.

Chemical Analyses

At a minimum the source samples need to be analyzed for the same species that will be obtained at the receptor sites. These includes mass concentrations to which other chemical components can be normalized, the elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U by proton induced x-ray emission spectrophotometry and x-ray fluorescence (XRF), sulfate, nitrate, and ammonium by ion chromatography, and organic and elemental carbon by thermal optical reflectance. Teflon membrane and quartz fiber filters are used in parallel for these analyses.

In additional, carbon speciation for sources can be helpful for use in CMB modeling at receptor sites for which carbon speciation of ambient samples is done.

Criteria for Selecting Specific Sources

It is not possible to obtain source profile samples from every source within the BRAVO domain. Several criteria are set forth to select the source types and specific sources that need to be tested.

The first criterion is source types that are likely to contribute to $PM_{2.5}$ carbon, suspended dust, and sulfate. These are the largest contributors to excessive light extinction at Big Bend National Park. The largest source types with these components are: 1) gasoline vehicle-exhaust for carbon and some sulfate; 2) diesel vehicle exhaust for carbon and some sulfate; 3) vegetative burning for carbon; 4) cooking for carbon; 5) coking for carbon; 6) road dust for suspended dust; 7) windblown dust from deserts and playas for suspended dust; 8) coal combustion in a variety of industries for sulfate; and 9) residual oil combustion from a variety of industries for sulfate.

The second criterion is representatives of these source types that allow an average and standard deviation for chemical abundances to be estimated. For a limited number of samples, these representatives should be selected to maximize, rather than minimize, the conditions under which variability in fractional abundances are expected. As noted above, these will depend on fuel type, combustion process, and pollution controls.
The third criteria for industrial point sources is source types that have high sulfur dioxide emissions accompanied by high particulate emissions. The majority of sulfur emissions are accompanied by reasonably high particle emissions. The profiles derived from these tests may be more specific to the type of fuel burned (e.g. coal) than to the type of industry in which it is burned. The magnitude of these differences cannot be ascertained until after the tests are made.

The fourth criterion is access to effluent streams. For area sources such as open fields, playas, and roadways dust, different geological formations need to be visited and

sampled. This requires areas that are reasonably close to roadways. Paved road dust sampling requires permission to stop traffic for the short period necessary to acquire the sample. For mobile sources, locations are needed with permission to use them for locating source samplers and the generators to power them. For ducted emissions such as smoke stacks, a sampling platform of at least 3 m x 3 m is needed to accommodate the dilution sampler and personnel. Sampling ports of at least 7.5 cm diameters are needed to insert sampling probes, as is at least 20 amps of electrical power. Permission is needed for industrial sources as is a stairway or elevator to access the sampling platform.
The fifth criterion is cost-effectiveness. After the first four criteria are met, representative sources should be located in close proximity to each other to minimize travel, setup, and takedown time for the source testing technicians.

Source Sampling Selection

The following list of sources will be sampled as part of the BRAVO source characterization program.

Motor Vehicles: Roadside sampling will take place at several sites in both San Antonio and Laredo. A ground based sampling method will be used at intersections and overpasses to sample the cooled emissions from both cars and trucks. Proper site selection may permit the collections of profiles representing only diesel and only gasoline vehicles.

Vegetative Burning: Ground level source sampling of a prescribed burn will take place near Big Bend National Park. Fallen trees and vegetative debris will be assembled into a pile and set on fire. Either a mobile sampler or multiple samplers will be operated near the fire to collect the emissions. The mobile sampler will be moved during the burn so that it is always downwind of the fire. If multiple samplers are used, they will be configured to sample the plume over a range of likely wind conditions that occur during the burn.

Coal Fired Power Plants: Two coal fired power plants and an aluminum smelter that generate power via coal combustion will be sampled. These sources burn a variety of coal types and use multiple types of controls to reduce their emissions of both particulate matter and sulfur dioxide. The dilution tunnel will be used to sample these coal combustion sources. The samples collected will provide a range of source profiles that should be representative of most coal combustion facilities in the BRAVO study domain.

Cement Kilns: Cement Kilns use a variety of fuel sources to process limestone into cement. The most common fuel types include coal, hazardous waste, and tires. Two cement kilns will be sampled using the dilution tunnel to produce source profiles representative of this industry.

Refineries: Four crude oil refineries will be sampled using the dilution tunnel. The refineries are located across the state of Texas. These sources can be substantial emitters of SO_2, organic and elemental carbon particulates, VOC's, and NO_x. The source samples

will assisting in distinguishing these sources from motor vehicle and other combustions sources.

Carbon Black: Texas is a major producer of carbon black which is used for manufacturing paints, plastics, and tires. The process involves the quenching of hydrocarbon fuel combustion to produce elemental carbon. Fugitive emissions of elemental carbon along with organic carbon are expected from this source. The dilution tunnel will be used to sample emissions at two carbon black facilities.

Cooking: Food preparation source samples will be collected for several types of cuisines including Mexican food, Chinese food, and Wood Smoke Barbeque. Caterers will be hired to prepare food at a special laboratory kitchen at the CE-CERT facility at the University of California, Riverside. A large platform with a fume hood mounted overhead is used to collect emissions from the food preparation activities. The dilution tunnel will be attached to the fume hood to samples these emissions. These source profiles will be added to an existing library of food preparation profiles that already include hamburger, steak, and chicken cooking sources.

4.5 Emissions Inventory

An emissions inventory (EI) is a critical component to air quality studies. The EI database stores the location, type, and rate of emissions for sources throughout the study domain. This database is used as input to air quality models that simulate the dispersion and chemical transformation of pollutants.

A comprehensive emissions inventory will be compiled for air pollution sources within the BRAVO study domain which includes Texas, New Mexico, Oklahoma, Arkansas, Louisiana, and sources in Mexico north of Mexico City. The emissions inventory database will be spatially resolved in order to identify the location and density of sources. The inventory will document emissions of SO_2, NO_X, PM_{10}, and VOC's. Within the database, all emissions data will be linked to the data provider so that the information can be traced back to its origin. Generally source types in the emissions inventory will be grouped as:

?? Point Sources: Large, stationary, identifiable sources with total annual emissions greater than some predefined cutoff. Sources include both stack emissions as well as unconfined fugitive emissions. Examples include large manufacturing or production plants.

?? Area Sources: Smaller sources that do not qualify as point sources under the relevant emissions cutoffs. Emissions are estimated as a group rather than individually. Examples include dry cleaners, residential wood burning, and consumer solvent use.

?? Mobile Sources: All non-stationary sources such as automobiles, trucks, aircraft, trains, construction, and farm equipment.

Data for the EI will be compiled from the following list of data providers:

Texas Natural Resource Conservation Commission (TNRCC)

TNRCC has assembled an EI for the state of Texas using 1996 as the base year. The EI is divided into point, area, and mobile sources. Area and mobile sources are aggregated by county and quantified by individual source types (e.g. light duty gas vehicles, dry cleaners, restaurants, etc.). Emissions of VOC's, NO_X, and CO are reported for the area and mobile sources. Emissions estimates reported are actual emissions as opposed to the permitted emissions.

The point source EI catalogs emissions from point sources in Texas for TSP, PM_{10}, SO_2, NO_X, NMOC, CO, and Pb. Both permitted and actual emissions are reported. The base year of this inventory is 1997. All sources with criteria pollutant emissions (including VOC's) greater than 100 tons per year are required to be included in the EI. In ozone non-attainment areas, the criterion for a source to report emissions to TNRCC is less than the 100 tons per year limit. Therefore, smaller sources are also included in the EI in the ozone non-attainment areas.

Minerals Management Service

An emissions inventory MOAD3 (Minerals Management Service Outer Continental Shelf Activity Database) was created using 1993 as a base year. The EI catalogs emissions from the development of petroleum resources in the Gulf of Mexico. Sources include platform, crew/supply vessel, and helicopter emissions. Emissions of CO, SO_X, NO_X, PM, and VOC's are reported for activities in the gulf. An updated emissions inventory is currently being prepared using a more recent base year. These results will be incorporated with the BRAVO EI database if the data can be obtained in a timely manor.

Environmental Protection Agency: AIRS Facility Subsystem

The AIRS facility subsystem (AFS) archives emissions data for all permitted facilities operating in the United States. Data is submitted to AIRS from the state regulatory offices on an annual basis. AFS archives emissions of all criteria pollutants including VOC's as well as the facilities geographic coordinates, street address, facility type, and point of contact. A point source EI will be downloaded from AFS for all facilities operating in Texas, New Mexico, Oklahoma, Louisiana, and Arkansas.

Environmental Protection Agency: National Emissions Trends Database

The Office of Air and Radiation produces the National Emissions Trends (NET) database. Emissions estimates of criteria pollutants are derived from many factors, including the level of industrial activity, technological changes, fuel consumption,

vehicle miles traveled, and other activities that affect air pollution. As of 1994, the annual NET EI incorporates NO_X and SO_2 data from the Continuous Emissions Monitors operating at electric utility facilities.

Environmental Protection Agency: Continuous Emissions Monitors

Under Title IV of the 1990 Clean Air Act, electric utilities must report hourly emissions of SO_2 and NO_X to EPA on a quarterly basis. Continuous Emissions Monitors (CEM's) are installed at these facilities and provide accurate high time resolution data suitable for use in air quality modeling. Hourly data from all CEM's operating in the study region will be included into the BRAVO EI database.

Western Governor's Association: Visibility Assessment of Regional Emissions Distributions

An EI was developed for the Grand Canyon Visibility Transport Commission to assess the sources of haze observed at Grand Canyon National Park. The EI compiled data from EPA's 1990 Interim Inventory with data from the AFS. Addition emissions from large sources in Mexico were also included. The primary study domain includes the 11 western states, Texas, southwestern Canada, and northern Mexico. Emissions of SO2, VOC, NO_X, NH_3, $PM_{2.5}$, CO, and organic and elemental carbon particulates were reported for point sources and mobile and areas sources aggregated by county. The base year of the inventory is 1990. Emissions are summarized as seasonal average weekday emissions and annual average emissions.

Instituto Nacional de Ecologia (INE)

A comprehensive emissions inventory for Mexico is currently being prepared in a bi-national effort with Mexico and the United States. The inventory will not be completed for several years and therefore the emissions data will not be available for inclusion in the BRAVO inventory. Emissions data that is available for Mexico includes point, area, and mobile emissions for the cities: Mexico City, Toluca, Guadalahara, and Monterrey. Additional data from industrial and mobile sources are also available from 16 other cities. Emissions inventories are quantified for PM, SO_2, CO, VOC's, and NO_X with at a base year of 1994. Emissions from major SO_2 point sources outside of these cities (e.g. Carbon I/II Power Plant and Nacozari and Canenea Copper Smelters) are not publicly reported by INE. This is a limitation of the emissions inventory for Mexico. As a result many Mexican sources may not be cataloged in the BRAVO EI database.

Environmental Protection Agency: Atmospheric Modeling Division

A computer model Biogenic Emissions Inventory System (BEIS) incorporates land use and meteorological data to estimate emissions of VOC's from plants (Pierce and Waldruff, 1991). The model has since been updated (BEIS2) to also account for NO emissions from soils. BEIS was applied for the 1997 base year and aggregated by county for the contiguous United States. Emissions are estimated on a daily basis.

National Interagency Fire Center

The National Interagency Fire Center tracks the location and size of both prescribed and wild fires in the United States. A database of the dates, location, area (for wild fires), and fuel mass (for prescribed fires) of all recorded fires in Texas, New Mexico, Oklahoma, Arkansas, and Louisiana will be obtained for dates corresponding to the BRAVO study period. The U.S.E.P.A. emissions estimation protocol in AP-42 publishes prescribed and wild fire emissions factors for CO, VOC's, NO, and PM (i.e. $PM_{2.5}$). These factors are likely to be highly uncertain since other parameters such as wind speed, moisture content, fuel type, and fuel loading may not be well characterized for each fire

Data Processing

All emissions data will be processed into a spatially and (where possible) temporally resolved database. These database will be displayed as individual coverages in ArcView GIS software. When inventories are redundant (i.e. point sources in Texas are listed in both the TNRCC EI and the AFS EI), a judgment will be made to use data from the source that originally collected the data. Only the most recently collected emissions data will be used for the final BRAVO EI. The final database will list each pollution source along with the data provider so that all data may be traced backed to its source. When complete, the EI will be in a format that can be gridded so it may be used as input for dispersion modeling.

4.6 Aircraft Measurements

Aircraft measurements will be made by Baylor University in coordination with TNRCC. The flight paths of interest for BRAVO include transport of continental haze over Texas toward Big Bend National Park (over Texas Gulf coast and east Texas interior areas), and Transport along and across the US Mexico border towards Big Bend. Flights will be schedules when forecast back-trajectories show the conditions of interest likely to occur. Flights will occur on 2- 3consecutive days tracking air masses of interest as they approach Big Bend National Park.

The Baylor Aircraft will measure the following variables:

- ?? Light scattering (nephelometer) 5 second data
- ?? SO_2 1 second
- ?? Sulfates 1 second
- ?? NO, NO_2, NO_Y (1 second)
- ?? temperature, relative humidity, barometric pressure (1/5 second)
- ?? Altitude, location (1/5 second)

5. Assessment Approaches

5.1 Overview

Assessment includes all systematic uses of data and other information to meet the BRAVO Study objectives. Some of the assessment methods provide results that directly address one or more of the study objectives, while others provide information useful or required as intermediate results in the overall process of assessment. Among the latter reasons for assessment is to check the plausibility of the data (i.e. a form of data validation) and to familiarize data analysts with conditions in the study region. The assessment approaches that will be used range from very simple data summary and display methods that are applied to parameters one at a time to sophisticated models that require dozens of parameters and numerous assumptions.

A major product of the BRAVO Study is the development of a conceptual model of the important physical and chemical processes that are responsible for haze conditions in Big Bend National Park. The conceptual model is a plausible descriptive explanation of the causes of impairment that is supported by the measurement data. It includes the identification of the important sources (i.e., individual major sources, source types, and source areas), and a description of the meteorological conditions under which these sources contribute to Big Bend haze. Case study analyses are narrative histories of individual haze episodes that illustrate the measured and modeled components of a conceptual model.

Attribution analyses are quantitative assessments of the contributions by important sources. Attribution methods are typically divided into two broad categories: predictive air quality models and receptor models. Air quality models use meteorological measurements, pollutant emissions data, and calculated or assumed boundary conditions to calculate the transport, dispersion, deposition and chemical transformation of pollutants emitted into the atmosphere at specific known emission source locations. Receptor models rely on the ambient air quality measurements made at monitoring site and the characteristics of the likely emission sources to infer the contribution of those sources. Another category of attribution analysis is a hybrid of these. For example a wind field model could indicate the transport path of the pollutants measured at a site and receptor methods used to apportion among the sources along that path, or a unique tracer for a source (a receptor method) could be used to determine the transport and dispersion of primary pollutants while production of the secondary aerosol is estimated with the atmospheric chemistry portion of an air quality model.

One of the design strengths of the BRAVO Study is the planned use of multiple attribution analyses methods. Comparisons of results from various attribution methods that utilize different assumptions and data sets can provide insights not otherwise achievable by any single attribution method. If the results tend to agree, credibility is enhanced. If they are inconsistent, a reconciliation process is applied which may uncover inappropriate model assumptions or questionable input data, or in the worst case be used

to determine a suitable range of uncertainty for the study findings. A corollary to the use of multiple attribution methods is the involvement of multiple individual data analysts/modelers often working for different organizations. Generally, those who conduct the analysis or modeling are proponents of the methods they apply who champion them in an almost competitive atmosphere that drives them to do all they can to make their approach successful. In other words experts motivated to have them succeed vigorously apply each method.

Of the various attribution methods that will be applied, only regional air quality modeling can be used to address all of the important emission sources in the region for any time period, including times outside of the BRAVO Study period. A major product of the study is the evaluation, and fine-tuning (if needed) of a regional air quality model for uniform application to all of the important emission sources in the region. The reconciliation process will determine if air quality modeling produces results that are consistent with the best of the other methods and if not whether they can be made more consistent by modifying the assumptions within acceptable ranges or changing which input data are utilized. The best of the regional air quality models that are evaluated in the BRAVO Study will be applied to all of the important emission sources as a means to ensure consistent evaluation of each source's contribution to haze at Big Bend.

The remainder of this section of the plan is organized into subsections by the types of assessment methods, beginning with the simple descriptive assessment and ending with the development of overall BRAVO Study findings as a result of the reconciliation process.

5.2 Descriptive Analysis

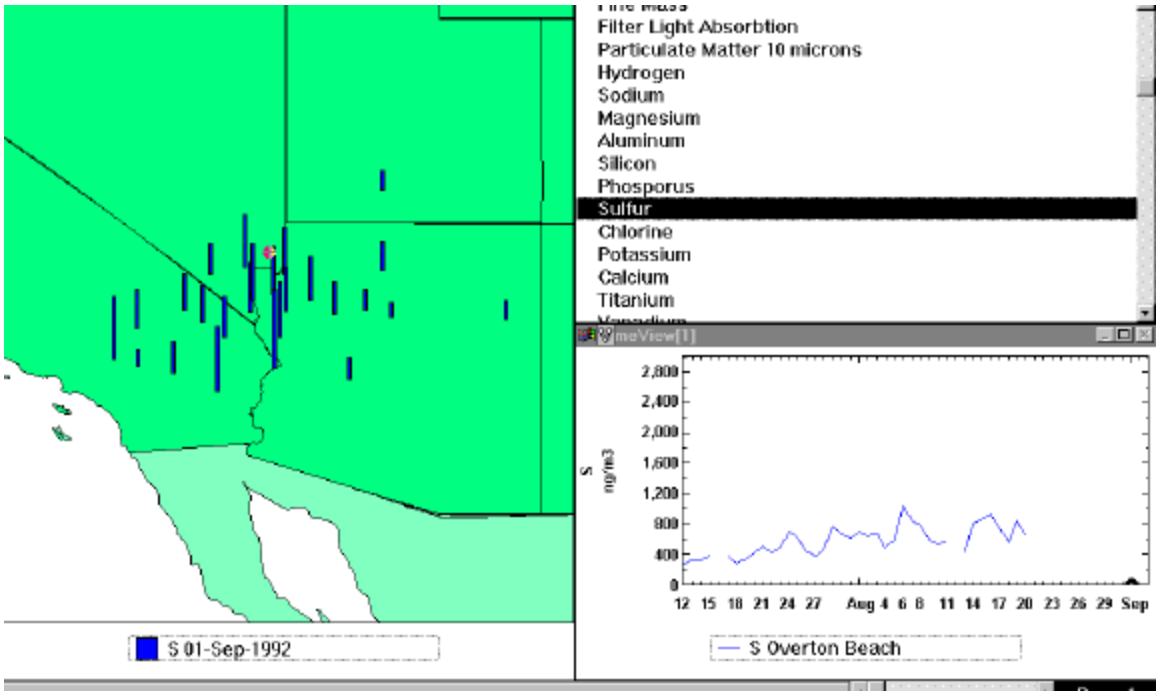
Several purposes are served by descriptive analysis including data quality assurance and validation, data familiarity, and a means of testing the plausibility of some aspects of prospective conceptual models.

The initial steps in determining data quality assurance and validation are the primary responsibility of the organizations that made the measurements. These usually include checking for outliers (values beyond physical or typical limits), and spatial and temporal trends that are too large to be believed (maps of data values by time period, and time plots or limits on a change from one period to the next). Data with substantial inconsistencies are then the subject of further investigation to attempt to identify the cause, correct the data if possible and flag it if necessary.

The measurement organizations are fully responsible for the first of these three activities, and often will conduct some of the second and third activities. Independent data analysts will supplement the activities of the data collection organizations were necessary to look for suspect data based upon unlikely spatial and temporal trends. It is essential that all measurement organizations identify the data validation steps that they intend to conduct so that others can apply the required additional validation steps. Data

will not be submitted to the database until it has reached validation level 1A (see discussion of data validation levels in section 6.4).

The enormous amount of data collected in a study like BRAVO makes the use of summary statistics and displays essential for the analysts to gain familiarity with it. Data analysts will want to become familiar with those subsets of the data that they intend to use or that may be pertinent to the conceptual model that justifies the assessment methods they are promoting. While data analysts will have the ability to download any data they wish and apply their favorite statistics and graphics programs, a specific set of data summary tables and display figures will be provided to all of the analysts to minimize duplicative efforts. To further facilitate efficient familiarization with the data, many of the key ambient measurement values (e.g. aerosol species, major components & mass, tracer concentration, optical parameters, wind data, etc.) will be put into Voyager? format so that spatial maps and time plots of the data can be very quickly generated by the analysts using the Voyager? program. Figure 5-1 shows an example of a VOYAGER data plot from Project MOHAVE.



Example VOYAGER data plot from Project MOHAVE. The map view shows relative particulate sulfur concentrations for September 1, 1992. The time series plot shows sulfur concentrations each day of the study for an individual site. By clicking on another site on the map, time series is then shown for that site. Similarly, by clicking on another day on the time series, the map shows the spatial pattern for that day. Finally, clicking on another variable in the variable list changes the variable that is mapped and shown as a time series.

Often a data analyst recognizes a significant aspect of the data that was not noticed by the other analysts. To promote the sharing of these often-important insights, frequent (e.g. quarterly) data analysis meetings will be scheduled with briefing by all of

the active data analysts. Email and other telecommunications will be promoted between the data analysis meetings to ensure timely sharing of information.

A primary means of testing the credibility of a conceptual model is by determining if it is consistent with the validated data. Experienced data analysts in the initial stages of a complex study such as BRAVO bring to the study a number of possible simple conceptual models based upon findings in earlier studies. Much of the process of data familiarization is in fact informal checking of consistency between the possible conceptual models and the data. When an analyst indicates that the data seem reasonable or makes sense, in fact he (she) is indicating that it fits satisfactorily with some elements of a conceptual model of the important phenomena. For example if the sulfate concentrations are similar over a large areas it confirms the widely held belief that as a secondary component (produced in the atmosphere over many hours) sulfates should be regional in scale. If nearby monitoring sites have at times very different sulfate concentrations, one or more of the sites might be impacted by a source of primary sulfate emissions (a very different conceptual model for the sulfate source).

Descriptive data analysis methods will also be applied to data from short-term and special studies done as part of or in conjunction with the BRAVO Study. These include any measurements made on a non-routine basis (e.g. microscopy and carbon speciation of select aerosol samples, or relative humidity growth studies) or by mobile platforms (e.g. aircraft measurements). However, the specialized nature of these efforts makes it difficult to include in a general description of assessment analyses. The organizations that conduct these measurements are expected to produce separate reports of their results. They may be asked to provide specific additional data analysis as needed to help in developing or confirming a conceptual model or to provide needed inputs to other assessment methods.

Validation checks will need to be applied to all of the data before they are entered into the database. The timing for data availability in the database will vary depending on the type and source of the data. Generally data generated by subsequent laboratory analysis of samples collected at monitoring locations (e.g. particle filter samples and tracer samples) will require longer than instrumentally measured data (e.g. optical and meteorological data). The former may not be all incorporated into the database before the end of March 2000, while the latter may be available by the end of December 1999. Except for data validation checks, most of the analyses will not be applied to data prior to its availability in the BRAVO Study database.

Table 5-1 summarizes the various descriptive analysis methods, the data they will be applied to and which organization are responsible for conducting the analyses.

Table 5-1. Application of descriptive analyses methods to various data types and the organizations responsible for conducting the analysis.

Analysis Methods Types of data	Validation checks	Time plots	Maps by time period	Univariate statistics
Aerosol mass & major components & size dist.	UCD & CSU	CSU	DRI & TNRCC	DRI
Aerosol trace elements (by PIXE & XRF)	UCD & CSU	Voyager? [1]	Voyager?	DRI
Optical data (b_{ext}, b_{scat}, b_{abs})	ARS & DRI	Voyager?	N/A[2]	DRI
Ambient tracer data (24-, 6-, & 1-hour)	BNL & EPRI	DRI	Voyager?	DRI
Tracer emission rates	NOAA-FRD	NOAA-FRD	N/A	DRI
Surface meteorological data (ws, wd, T, & RH)	N/A	Voyager?	Voyager?	DRI
Upper air meteorological data (ws, wd, T, & RH)	NOAA-ETL	DRI	Voyager?	DRI
Annual emission rates – point & area sources	N/A	N/A	DRI	DRI
Continuous emission rates—select point sources	N/A	DRI	N/A	DRI

5.3 Association Analysis

Association analyses are similar to descriptive analyses except that more than one parameter is considered at a time. Like descriptive analysis, association analysis is an important step in data quality assurance and validation, promotes data familiarity, and is a means to test conceptual models. In addition association analysis allows precision (and other quality descriptors) to be directly determined from collocated measurement, permits assessment of aerosol and optical closure at some of the more complete monitoring sites, and may reveal insightful relationships concerning the conditions associated with and causes of haze.

In cases with collocated measurement of the same parameter, measurement approach, and organization a direct determination can be made of data precision, uncertainty, and lower detection limit. Correlation analysis and scatter plots of the paired data are inspected to identify data outliers or systematic differences between the two samplers (e.g. flow inconsistencies). Standard algorithms to calculate precision, uncertainty and detection limits are used (see quality assurance- section 7). Such determinations are the responsibilities of the measurement organizations.

Comparisons of coincident similar measured parameters (e.g. elemental sulfur and sulfate, or use of different samplers or laboratories to obtain nominally the same measurement) can be used to identify periods with outliers and/or systematic

[1] Except for some specifically requested plots, these analyses will not be done centrally but will be left to individual data analysts using Voyager? or some other graphic/statistics software.
[2] N/A is not applicable or not attainable.

inconsistencies. As with collocated measurements, the usual method is to examine scatter plots and conduct regression analysis. In cases where the related measurements are made by the same organization, they are responsible for the assessments. If the related measurements are by different organizations, another organization will typically do the assessment.

A series of simple closure determinations are possible using association analysis of some of the measurements. In essence, closure is a consistency check involving measured data and simple conceptual models. The following are the principal closure exercises for the BRAVO Study:

?? Fine mass closure – compare the sum major of measured species combined with the mass of the assumed common oxides and other non-measured components (ammonium ion for sulfate and nitrates, etc.) with the gravimetric fine mass;
?? Optical closure – compare the sum of the measured light scattering and light absorption with the total measured light extinction; and
?? Extinction budget – compare the sum of the calculated extinction for the major aerosol components (component concentration multiplied by an extinction efficiency that may be a function of relative humidity) with the measured total light extinction.

The Big Bend monitoring site is the only one with sufficient measurement to check closure for each of these. Comparisons would include scatter plots and regression analysis of the sum of the measured or derived components with the measured total. Time plots of the components and totals are also useful to look for temporal patterns when closure may be a problem (e.g. optical closure problems during a certain time of day might result from sunlight interfering with the transmissometer). Figure 5-2 is an example of fine mass closure from the Project MOHAVE final report. Figure 5-3 is an example of optical closure from Project MOHAVE.

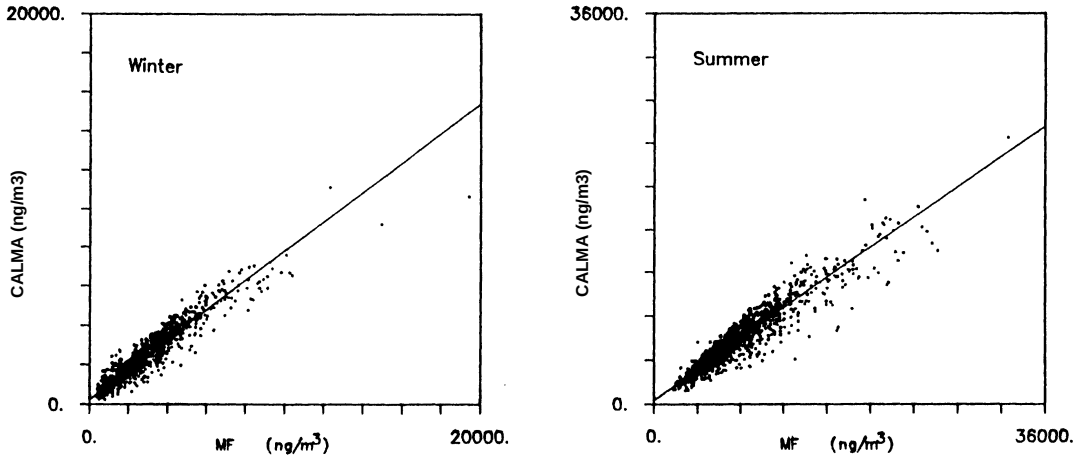


Figure 5-2. Comparison of gravimetric mass (MF) and calculated mass (CALMA) at all Project MOHAVE IMPROVE sites. The left plot is for winter and the right plot is for summer. The slopes are 0.76 (winter) and 0.70 (summer). The correlation coefficients (r^2) are 0.89 (winter) and 0.89 (summer). The number of data pairs are 1102 (winter) and 1533 (summer).

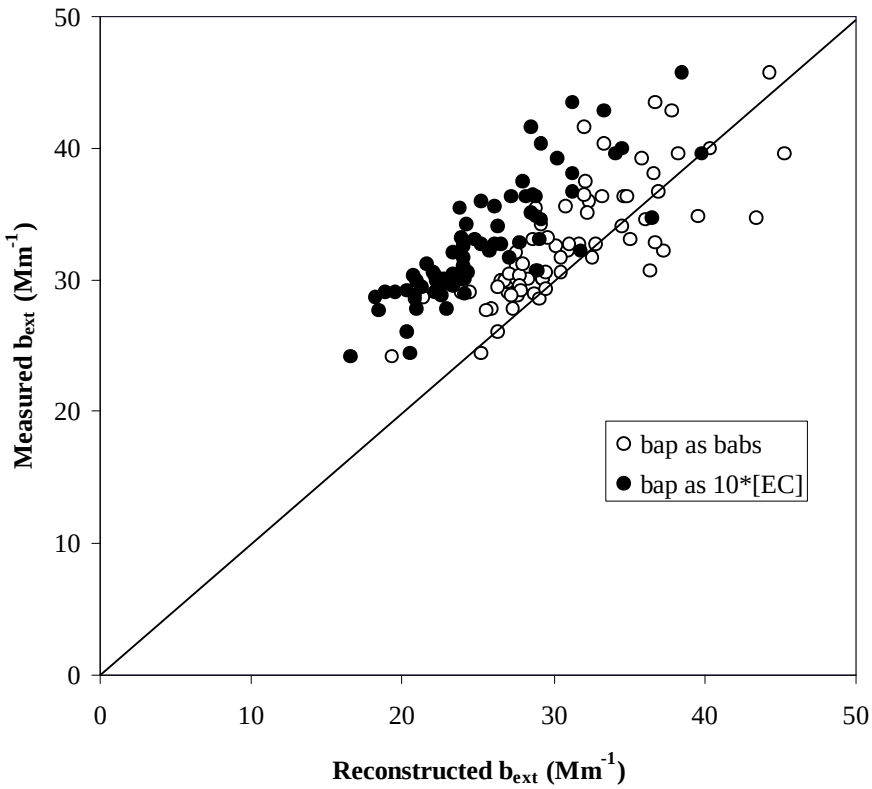


Figure 5-3. Comparison of measured extinction with calculated extinction ($b_{sg} + b_{sp}$ + CMS/2 + b_{ap}). The open circles were calculated using $b_{ap} = b_{abs}$. The closed circles were calculated using b_{ap} = 10 [EC]. The line is the 1:1 line.

Using association analysis methods data analysts can explore possible relationships between any of the measured parameters to help develop or evaluate conceptual models, to identify the conditions that are conducive to haze events, and to identify the aerosol components that are significant contributors to the haze. For example a positive correlation between the fraction of sulfur that is particulate and the presence of low clouds might indicate that aqueous chemistry is an important mechanism for converting the SO_2 to sulfate during the study. An association between wind speed beyond some threshold and increased soil aerosol component concentration could be used to identify locally suspended dust as a principal source of the soil component. Extinction budget analysis will permit an estimate of the extinction contribution by the major aerosol components for each sample period. Combining these with wind direction in a wind rose analysis could indicate that some aerosol extinction components are enhanced during local flow from certain directions.

There are an incredibly large numbers of possible combinations of data that could be examined for associations for exploratory purposes, most of which would not yield productive results. Experienced data analysts narrow the choices to a manageable effort by having specific conceptual models that they explore in an effort to better understand the important processes for this study. Another approach to narrowing the choices is to reduce the dimensions of the data matrix by any one of several statistical analyses methods known as factor analysis. These include factor analysis, principal component,

eigenvector analysis, and empirical orthogonal function analysis methods. These methods attempt to simplify the description of the system by determining a minimum set of vectors that spans the data space to be interpreted. In other words, a new set of variables is found as linear combinations of the measured variables so that the observed variations in the system can be reproduced by a smaller number of these causal factors.

Table 5-2. Application of association analysis methods (i.e. scatter plots and regression analysis) to various data types and the organizations responsible for conducting the analyses.

Analyses Types of data	Validation checks	Quality assurance parameters	Closure assessment	Exploratory (compare to any data)
Aerosol mass & major components & size dist.	UCD & CSU	UCD & CSU	NPS & UCD	Any analyst
Aerosol trace elements (compare PIXE & XRF)	UCD	UCD	N/A	Any analyst
Optical data (b_{ext}, b_{scat}, b_{abs})	ARS & DRI	ARS & DRI	NPS	Any analyst
Aerosol extinction	N/A	N/A	NPS, UCD	Any analyst
Ambient tracer data (24-, 6-, & 1-hour)	BNL & DRI	BNL, DRI, & EPRI	BNL, DRI, & EPRI	Any analyst

5.4 Study Period Representativeness

In order to know how applicable BRAVO Study results are to other periods of times (other times of the year and other years), the representativeness of the study period must be determined. If the study period is found to be significantly unusual compared to typical years or long-term composite conditions, the results should be interpreted in light of this finding.

The approach used to determine representativeness of the study period starts by comparing meteorological and air quality data during the study period with similar data for other times during the year and for the same period of time in previous years. Simple statistical tests and comparisons of frequency distribution plots for the study period and other periods show the degree of similarity of the study period to those other periods for each parameter. For example, the frequency distribution of the light extinction coefficient at Grand canyon National park for the Project MOHAVE summer (1992) is compared to other years in Figure 5-4. The study period will undoubted be quite different in many respects from other time of the year, since that period was chosen for its association with high haze levels and flows from know emission source areas. However it is not so likely that for many of the parameters this analysis will indicate that the study period was particularly unusual compared to the same period in previous years (because by definition unusual events rarely happen). These preliminary representativeness comparisons can begin as soon as the BRAVO Study data is available in the database.

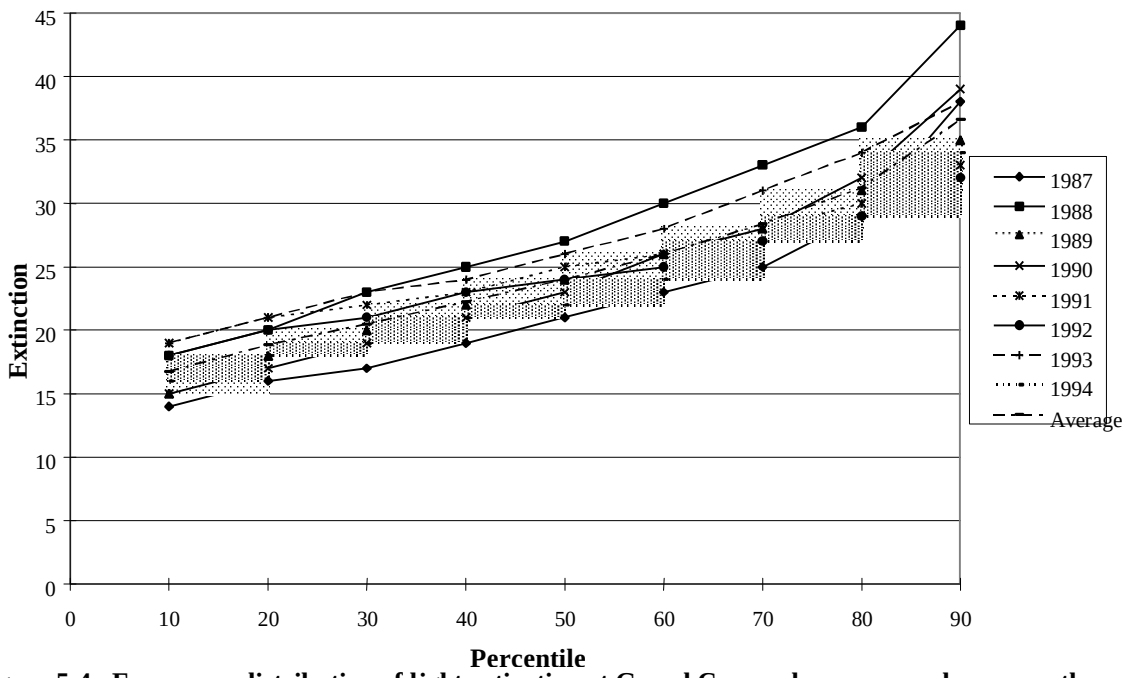


Figure 5-4. Frequency distribution of light extinction at Grand Canyon by season and year: south rim, summer (May – October).

Undoubtedly the frequency distribution for some parameters will be significantly different compared to the corresponding distributions for some of the previous years. The question of how significant these differences are can be best addressed in the context of the conceptual model that will be developed as a major product of the BRAVO Study. For example, the conceptual plan may indicate that sulfate particulate concentrations are much higher when transport is from a specific SO_2 source region if low clouds that promote rapid atmospheric chemistry accompany them. An unusual joint frequency of the two conditions (i.e. clouds and transport from the source region) during the study period would be considered significant to the findings of the study. In this circumstance one would expect unusual sulfate concentration, which would give further support to the validity of the conceptual model. Representativeness comparisons guided by conceptual models must be done towards the end of the data assessment process when conceptual models are well developed.

If significant differences are found between the study period and the same periods in other years, data analysts can attempt to reconstruct the results that might by found in a typical year. This would be accomplished by generating a weighted frequency distribution of study results using the long-term average frequency of conditions to determine the weighting factors. For example, a source area might be found to contribute 5% of the study-periods sulfate, but the study was done in a year where flow from that source region was three times as often as during the long-term average. The contribution could be recalculated with one-third the frequency of impact by that source area and a corresponding increase in the frequency of impacts from the under-represented areas during the study period. The reconstructed contribution by the example source would be much reduced. Another approach that could be used to reconstruct results for a

typical year is to use the most credible of the air quality models with current emissions but using meteorology that is more typical of the long-term average conditions. The steering committee will determine whether there is a need to reconstruct the findings to adjust for unusual study period conditions near the end of the data analysis process.

Desert Research Institute will be responsible for all of the preliminary representativeness analyses. UC-Davis and Colorado State University will also consider the representativeness of aerosol concentrations during the study period. Subsequent work to determine the significance of differences between the study period and other periods, and to reconstruct the results will only be conducted as needed. They may be done by any of the data analyst or modeling organizations depending on the nature of the effort. Data analysis meetings are the appropriate forums for making these decisions.

5.5 Source Attribution

The principal purpose of source attribution analyses is to estimate magnitude, duration, and frequency of visibility impairment at Big Bend by major sources or source categories. These analyses should also result in a better understanding of the conditions and causes of impairment (conceptual models) and some of the methods could subsequently be used to predict the visibility response to emission changes (not considered part of the BRAVO Study).

Attribution assessment is the most difficult of the data assessment tasks, its results are likely to spark the liveliest debates, and it will consume the majority of the BRAVO Study data analysis resources. All source attribution methods require the use of numerous critical assumptions many of which can be reasonably challenged. The practitioners of the various attribution methods are usually strong proponents of their approach while often are highly critical of the capabilities of competing methods. The inner workings of many of the methods range from complex to obscure with the result that it is often difficult for those who are not expert in the method to understand the sensitivity of the results to input data and assumption uncertainties.

Often studies will employ only one attribution method, which has the advantage of minimizing the cost and internal controversy of the assessment results. The disadvantage of the one-method approach is that there may be very vocal external critics of the final study findings who are proponents of alternative approaches. BRAVO Study technical management has chosen to include numerous distinct methods applied by their proponents so that any voices of dissent can be heard at data analysis meetings when there remains time to reexamine, refine, and reapply approaches that are accused of deficiencies. The obvious disadvantage of the multiple-method attribution approach is the additional time and cost required, plus the need for a results reconciliation effort (discussed in the next section) to develop study findings that reflects the overall judgment of the technical committee.

Attribution methods are typically divided into two broad categories: air quality simulation models and receptor models. The first method – receptor data analysis or receptor modeling – is an analysis of concentrations and chemical composition data collected at one or more receptor locations, sometimes in combination with meteorological information, and comparison of the receptor data with the composition of emissions from sources of interest. Receptor modeling is a diagnostic approach that analyzes measurements to derive a plausible accounting of the emissions that produced measured concentrations and compositions. Although conceptually straightforward, receptor modeling depends on accurate measurements of ambient concentrations and, in many cases, on accurate characterization of the compositions of emissions from major source categories. In practice, some receptor analysis methods can be statistically complex. Receptor analysis can only be used to analyze conditions at the times and locations for which measurements exist: it has no predictive capability for other times and locations.

Many receptor methods are also limited to attributing sources for which there are distinctive chemical signatures. Most prior information on emission source composition profiles is from measurements made years ago of sources outside of the study region. The BRAVO Study included a substantial effort to make new measurements of source characteristics from many types of industrial, commercial, transportation, agricultural, and natural sources (section 4.4 summarizes the source types that were included). It was not possible to characterize all of the larger sources in the study region; so composite source profiles by source type will be developed and made available to analysts in the BRAVO Study database.

A fundamental assumption for many receptor model approaches is that the ratio of the species of interest and the unique source characteristic that is used to identify the source is preserved during transport from the source to the receptor sites. This is not the case for sulfate formed in the atmosphere by conversion of SO_2. Hybrid receptor models that add a parametric representation of the chemical conversion and/or deposition processes to the basic receptor model are used to overcome this limitation.

The second method – source emissions simulations or simulation modeling – uses mathematical models of the transport, diffusion, deposition, and chemical conversion of the emitted pollutants to predict ambient concentrations resulting from emissions. Such models, which rely on our understanding of the physics and chemistry of the atmosphere, are conceptually able to predict air quality impacts at all locations and time. Because of limitations in our knowledge of atmospheric behavior, or ability to portray that knowledge mathematically, and the ability of computers to carry out the needed calculations in a reasonable amount of time, all models require some input data on meteorology and air quality, in addition to the obvious requirement of emissions information.

Past mesoscale tracer studies (Project MOHAVE, WHITEX, NGS Study, etc.) have shown that air quality simulation models perform poorly in their ability to predict tracer concentrations in regions dominated by complex terrain. Limited computational

resources force modelers to compromise between the overall domain of the modeled area and the grid size that is considered. Large study regions in complex terrain usually result in modeling that cannot spatially resolve many flow influential terrain features (e.g. canyons, ridge lines, etc). Nested grid models allow modelers to increase the spatial resolution at some locations in the domain. However, for studies like BRAVO where the domain is of the order of a thousand kilometers the smallest grid in a nested model may be of the order of ten kilometers, which is still too coarse to adequately resolve the Rio Grand River Canyon at Big Bend.

The BRAVO Study tracer data will be used to evaluate the performance of both types of attribution models used in the study and will also be available for direct or indirect use to enhance model performance. Air quality simulation models' predictions of the tracer compounds released during the BRAVO Study will be compared to the measured concentrations to evaluate their ability to simulate transport and dispersion. Modelers may change certain aspects of the air quality model (e.g. selection of input data, boundary conditions, etc.) to improve their ability to predict the tracer concentrations. Receptor models that can predict the pollution contribution from sources that have been tagged by tracer can also predict the tracer concentrations by appropriate scaling of the predicted pollution concentration by the ratio of tracer to pollutant release rates. Some receptor models may use the tracer data as input to predict the contribution of the tagged sources and must be evaluated in other ways.

Tracer data will be divided into two subsets by time periods. One of the subsets will be placed in the database relatively early in the assessment phase of the study so that it can be used as input to or to fine-tune attribution models. The second subset will be submitted to the database after the attribution models have been documented and will be used to openly evaluate their performance. Schedules and procedures for subdividing and use of the tracer data will be developed in consultation with the data analysts during data analysis meetings.

Receptor and air quality simulation models that will be used during the BRAVO Study are described below starting with the receptor methods. Most of the methods described were used in Project MOHAVE to assess the particulate sulfate contribution to haze from the Mohave Power Project (MPP). Many of these methods can be adapted to assess primary particulate (e.g. crustal components and soot) and perhaps other secondary particulate (e.g. secondary organics and nitrates).

Tracer Scaling (also called Tracer Max)

Tracer scaling is a simple method employed in Project MOHAVE to determine the maximum possible sulfate that could be associated with tracer tagged sources of SO_2. In that study the ambient PFT data, scaled by the tracer/SO_2 stack emission ratio, were used to deduce the maximum possible Mohave Power Project (MPP) contribution to particulate sulfur at Meadview and Hopi Point (primary receptor sites) if all SO_2 were to be converted to particulate sulfur and there were no deposition losses (Green and Tombach, 2000). Whenever the maximum possible particulate sulfur that was calculated

in this way exceeded the measured value, then the measured value was set as the maximum possible value (i.e., it was assumed that MPP contributed 100% of the measured particulate sulfate concentration).

Key assumptions of the Tracer Scaling method applied to particulate sulfate attribution includes the following: (1) The tracer and sulfur (emitted as SO_2) are transported and dispersed identically together to the receptor; (2) There is no deposition of tracer or either SO_2 or particulate sulfur enroute (or they all deposit at the same rate); and (3) The tracer/SO_2 emission ratio is constant (i.e., the PFT emissions rate tracked the variations in the SO_2 emissions rate). In actuality, SO_2 and sulfate will undergo some deposition in route, while the tracer is essentially non-depositing; therefore the ratio of sulfur to PFT decreases in time. The assumption of a constant ratio will only be true for extended periods of near constant SO_2 emission rate since the tracer emission rates were held constant (except for the timing tracers).

The fundamental assumption of the Tracer Scaling approach applied to particulate sulfate is that all of the SO_2 is assumed to convert to particulate sulfate or at least enough of it is converted to match the sulfate concentration measured at the receptor. This assumption produces an upper-bound impact of the tracer-tagged source -- it is impossible to have a higher contribution. A lower contribution is certainly possible and is likely, especially in the cloud-free conditions under which sulfate formation proceeds slowly. Application of Tracer Scaling to primary pollutants is expected to produce an upper bound value that is likely to be much closer to the true contribution.
The principal benefit of tracer scaling is to place a firm upper limit on attributed pollutants from tagged sources that can be used to identify periods when other methods must be incorrect. It needs to be re-emphasized, however, that the Tracer Scaling estimates of secondary particulate species do not indicate what a realistic contribution might be.

For BRAVO, the direct use of tracer scaling for the Carbon I/II plants will not be possible due to the use of a surrogate site at Eagle Pass to approximate a Carbon release. For the stack releases of PFT, the tracer scaling approach could be used directly, but is not expected to be particularly useful in this regard because only 2 of many eastern Texas power plants will be tagged directly. The primary use for these releases is to quantify transport and dispersion properties of the airflow that may be expected to similarly affect other elevated pollution sources.

RMAPS

A spatial pattern correlation receptor model, RMAPS (Henry, 1997a) was used in Project MOHAVE to apportion the average concentration of a species, as measured at many sites, among several spatially distinct sources. It can be applied to primary or secondary species; no assumptions concerning transformation or deposition rates are required.

RMAPS was applied to predict the impacts of emissions from several source regions, including one identified as the "Colorado Valley Source" located in the vicinity of MPP and the Las Vegas area (Henry, 1997b). Green and Tombach (2000) describe tests of the RMAPS concentration predictions for the Colorado Valley Source against the maximum particulate sulfur that could be attributed to MPP based on measured PFT concentrations and assuming 100% conversion of SO_2 (Tracer Scaling). This comparison was done at 21 receptor locations, with concentrations averaged over the summer intensive.

The RMAPS-predicted spatial patterns for emissions from the Colorado Valley Source showed significant impact south of MPP, while such impact was not observed in the tracer data. Specifically, for 13 of these receptors, mostly located in the 180-degree sector to the south of MPP, the RMAPS predictions exceeded the maximum amount of particulate sulfur that could be created from MPP emissions. The excess was sometimes more than a factor of two and in all cases was well beyond the uncertainty bounds assigned to the RMAPS and PFT tracer calculations. Based on these observations, Green and Tombach (2000) concluded that the RMAPS predictions of the impacts of the Colorado Valley Source are not a valid representation of the impacts of MPP. The reasons for this discrepancy were never determined.

RMAPS will be applied to the BRAVO Study data in an attempt to identify significant source regions and their contributions to Big Bend aerosol concentrations. As in Project MOHAVE, its results can be checked against other methods including Tracer Scaling.

Tracer Regression.

Another simple method employed in Project MOHAVE involves use of multiple linear regression analysis to explain the variations in light extinction data at the primary receptor site by the variations in the concentrations of several source-specific tracers. In that study the tracer regression method (White *et al.*, 1999) attempted to explain light extinction at Meadview based on contributions from three sources – MPP, Southern California, and southern Arizona/northern Mexico. The light extinction was related to these source contributions through multiple linear regression analysis, in which assumed markers for each of the three sources were the independent variables and b_{ext} at Meadview was the dependent variable. Methylchloroform (an industrial solvent) was taken to represent urbanized Southern California, the mixing ratio of water vapor to air was taken to represent the contribution of air from more humid regions to the south, and the PFT to represented MPP emissions. In each case, the tracer was assumed to be a conservative indicator, as required by the receptor-oriented regression procedure.

The principal assumptions of the tracer regression method have to do with source types or regions represented by each tracer. Except for the use of PFT for tracer-tagged sources, these assumptions involve approximation. Endemic tracers for the BRAVO Study are yet to be identified and as in Project MOHAVE it is unlikely that possible other sources of those materials can be completely ruled out. If the tracers are not unique to the

region or source to which it is assigned, then emissions will be attributed erroneously to that region or source.

It should also be noted that any regression analysis of this kind would underestimate attribution if the "signal" were noisy, as would be the case if the light extinction were to vary because of unaccounted for background effects. (This limitation also applies to other regression based methods such as TMBR below).

TMBR

Tracer Mass Balance Regression (Malm *et al*., 1989; Ames and Malm, 1999) was used in Project MOHAVE to compare the covariance of SO_2 or particulate sulfur measurements with those of the PFT through an ordinary least-squares regression. The regression coefficients were interpreted as indicators of the attribution of the sulfur constituent to MPP.

While TMBR produced a significant regression coefficient (P=.03) in Project MOHAVE which means that there was a highly significant statistical relationship between PFT concentration and ambient sulfate concentration at Meadview, only a small fraction of the ambient SO_4 variability was explained by PFT ($r^2 = 0.06$). This may result from the non-linearity of secondary sulfate production and so these TMBR results alone could not be used to quantify any level of contribution by MPP.

TMBR applications in the BRAVO Study are limited to tracer-tagged sources but can be applied to any emitted pollutant.

DMBR

Differential Mass Balance Regression (Latimer *et al*., 1989, Ames and Malm, 1999) applied to Project MOHAVE expanded on the TMBR approach by explicitly considering the conversion of SO_2 to particulate sulfur. In this hybrid approach, information about transport time from source to receptor and cloud cover was used with linear conversion and deposition rates to estimate the particulate sulfur concentration at the receptor. The rate constants for the conversion of SO_2 and for SO_2 deposition were chosen by statistical optimization of the correlation between the predicted MPP contribution to SO_2 at Meadview and the measured SO_2. This optimization procedure made no *a priori* assumption about the amount of variability explained by the MPP contribution to ambient SO_2.

In addition to the usual constraint on equivalent behavior of tracer and sulfur emissions, the DMBR method estimated the amount of conversion of SO_2 to particulate sulfur based on a linear conversion rate. The time of travel was estimated from a wind field model and an hourly conversion rate was derived empirically based on a Cloud Interaction Potential (CIP) and the measured concentrations of SO_2. The CIP, derived from observations of clouds in photographs, attempted to reflect the presence of cloud water in the conversion process. But, since the height of the clouds could not be readily

deduced from the photographs, the CIP was considered a crude indicator of the effect of cloud water on chemical reactions at the MPP plume height.

As with TMBR, application of DMBR in the BRAVO Study will be limited to attribution estimates of tracer-tagged sources.

TAGIT

In Project MOHAVE the Tracer-Aerosol Gradient Interpretive Technique (TAGIT) (Kuhns *et al.*, 1999) used PFT data to identify sites near a receptor site that were not significantly impacted by MPP during specific sampling periods and could be considered to represent the regional background concentration. The MPP-attributable particulate sulfur at a receptor was calculated as the measured excess concentration of sulfur over that at nearby sites with background levels of tracer. Sites with tracer levels below 3 sigma of the background concentration were considered to be representative of regional background sulfur concentrations.

The accuracy of TAGIT depends on the assumption that the only cause for increased sulfur above the regional background at locations where PFT is found was emissions from MPP. If sulfur from another source were transported along the same trajectory as that of MPP, then the assumption would be violated. Under those conditions TAGIT would have erroneously apportioned to MPP the sulfur from the non-MPP source. Because the difference in sulfur particle concentrations in PFT impacted and non-impacted areas was sometimes small, TAGIT occasionally attributed a small negative concentration impact to MPP. The precision of the TAGIT attribution was estimated when there are several nearby sites reporting background tracer concentrations near the impacted receptor. For many instances, the variability of these multiple estimates were larger than the particulate sulfur attributed to MPP by TAGIT. While individual attibutions by TAGIT were noisy, the method was thought to provide credible results of average attribution over the study period.

Application of TAGIT in the BRAVO Study was anticipated in the study design with the location, near Big Bend, and higher time resolution of the 6-hour monitoring sites. These should give a much-improved ability to determine background near Big Bend, which should enhance the performance of TAGIT for sulfate and SO_2. While conceptually TAGIT can be applied to any pollutant, the short time periods and use of only the IMPROVE sampler channel A ($PM_{2.5}$ mass, PIXE and XRF) at the 6-hour sites is expected to restrict the assessment principally to SO_2 and particulate sulfate attribution.

The high time resolution sulfate, SO_2 and tracer data at Big Bend will be used to apply a variant of TAGIT that would operate in a temporal instead of a spatial sense. This temporal TAGIT would use periods before and after a tracer hit at Big Bend as the background concentrations to be subtracted from the concentrations measured during the tracer hit.

As the release of PFT from the Carbon I/II stacks was not possible, use of the Eagle Pass releases for TAGIT may or may not be fruitful. If ambient data show high

correlations between SO_2 and Eagle Pass released PFT at nearby sites, this would argue for the use of Eagle Pass releases as a surrogate for Carbon I/II emissions. The possibility of emissions from the tracer tagged stacks at Big Brown and Parish power plants with other SO_2 sources limits the applicability of TAGIT to these sources.

CMB

The Chemical Mass Balance technique involves apportionment of the composition of the aerosol at receptors among "profiles" of the composition of emissions from various classes of sources. The product of the analysis is an apportionment of the pollutants that are assumed to be conserved including primary particulate species and SO_x (the sum of SO_2 and particulate sulfate) to the selected classes of sources.

CMB assumes that time-invariant source profiles are available for all of the sources or source types to be attributed and that these are conserved during transport from the source to the receptor location. Both of these assumptions are most realistic for sources of primary pollutants that are near the receptor location. For this reason CMB has proven to work well in urban settings to explain local impacts of well-characterized primary pollutant sources. The success of CMB for a remote receptor location where attribution of distant sources is desired is more problematic. In such situations, the number of possible source that may be influential is potentially large so that during any sampling period a large number of sources may be contributing each with a relatively small impact, and sources profiles may change in the atmospheric (deposition & conversion) during long-distance transport.

One CMB type of approach that was tried during Project MOHAVE to account for the potential change in source profiles during transport is to use an effective source profile based upon ambient monitoring data during a period of assumed direct impact from various sources areas. The method (Eatough, *et. al.*, 1999) was employed by investigators to attribute SO_x and particulate sulfate. The Modified CMB (MCMB) method used several elemental and chemical tracers of opportunity as marker species for MPP and major source regions (the Las Vegas area, urban Southern California, the San Joaquin Valley, Baja California, southern Arizona and northern Mexico). The source profile for each source region was determined by measuring the elemental and chemical composition of ambient aerosol approaching the study area from the direction of the source of interest. The chemical conversion of SO_2 to sulfate was addressed using reactivities derived from the Reactive and Optics Model of Emissions (ROME) (a Lagrangian model for particle formation in plumes) and from optimization of assumed linear conversion rates. The transport routes and times of travel were defined by several wind field models and the potential for clouds to affect the chemistry during the transport of MPP emissions was addressed through the Cloud Interaction Potential (CIP) of the DMBR model. It is important to note that the PFT concentration data were used in the evaluation and modification of the model, but are not used as input data.

Fundamental assumptions of the MCMB method were the equal conservation of the tracer and target species and that all significant contributors to SO_2 and sulfate at

Meadview and Hopi Point were identified in the CMB profiles. A further assumption in the MCMB approach was that the ratio of SO_x (sum of SO_2 and sulfate) to the marker species in the source profiles is constant from day to day. Profiles and the profile uncertainty for regional sources, such as Southern California, were developed from ambient measurements at substantial downwind distances during a few days. If the ratios varied outside the determined uncertainty or represent mixes of materials from different source regions the method would apportion SO_2 and sulfate incorrectly among sources. Furthermore, regional profiles tended to be more collinear and less orthogonal than profiles for discrete source types.

A fundamental conceptual problem with use of ambient data as source profiles is the circular reasoning that comes from the use of ambient samples for periods thought to be principally influenced by a specific regional source as the source profiles. These source-specific sample periods were selected by using crude trajectory analysis, making the results subject to all of the uncertainties of the trajectory analysis. MCMB is not scheduled to be used in the BRAVO Study but is described here to illustrate the variations of the CMB that have been used in previous studies and could be developed for use with BRAVO data. Standard CMB analysis will be applied using the source profile information collected for the BRAVO Study. It will also be used to attempt to apportion the particulate organic material using speciated organic source profiles and ambient samples for selected time periods.

Artificial Neural Networks

Neural networks can be used in receptor modeling where source profiles are not known. The self-organizing ANN method of Kohonen (1989) has been presented for local scale problems with a single sampling site (Wienke and Hopke, 1994 a&b) and for multiple sampling sites (Wienke et al., 1994). This method can analyze a three dimensional data bloc as a whole and yield both source profiles and geographical information on the identified emission sources. Application of this type of sophisticated assessment to the BRAVO Study offers a way to compare source profiles as measured at the source with estimates of the effective source profiles at the receptor locations.

Trajectory – Back-trajectory Analysis

Trajectory and back-trajectory analysis methods are based upon calculated transport paths of air parcels. Surface and/or upper level wind measurements are either interpolated or used as input to a meteorological model to create a series of wind field (i.e. two or three dimensional maps of wind speeds and direction) as a function of time. Trajectories are calculated by moving the air parcel from a user selected starting point at a specific time in the direction and at the speed of the wind as determined by the appropriate wind field. With each time step the air parcel is again moved based upon the wind speed and direction at the new point and time to generate the trajectory path. Back-trajectories are calculated in the same way except that the time steps are run back in time and the path generated shows where the air parcel that arrived at a user specified time and location is thought to have taken on its way there. The HYSPLIT trajectory model run

using the Eta Data Assimilation System (EDAS) output will be used in the BRAVO Study as the principal trajectory analysis method. EDAS assimilates observed data into short-term Eta model calculations to obtain meteorological fields. Example HYSPLIT back-trajectories from Big Bend National Park are shown in Figure 5-5.

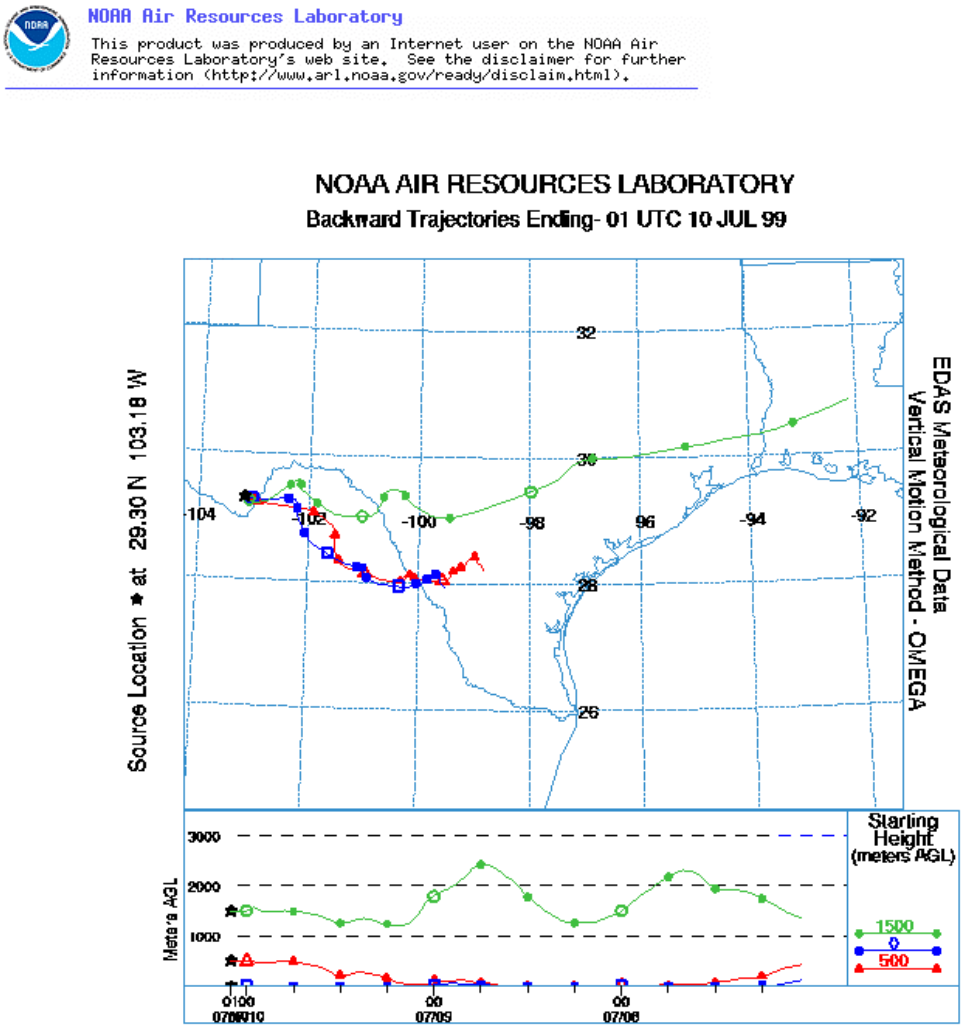


Figure 5-5. Example HYSPLIT back-trajectories from Big Bend National Park for July 10, 1999. The back-trajectories were started from 0, 500 meters, and 1500 meters AGL and were run backward for 72 hours. Differences in trajectories between the near surface and 1500 m level reflect some wind shear with height. The map view shows the horizontal path of the back -trajectory, while the time series plot shows the vertical path as a function of time.

NOAA-ARL will create an archive of EDAS output at 40 Km grid spacing for the BRAVO study period (July 1- October 31, 1999) for use in HYSPLIT. This will provide for archival of data at all grid points, rather than at every other grid point currently archived for HYSPLIT use. BRAVO participants will be provided access to a fully functional version of HYSPLIT that can be used to run forward and backward trajectories for periods of 5 days from any user selected location within the EDAS domain. Output will include graphics showing trajectory pathways, concentration isopleths, etc. and

trajectory endpoint files. Users will be able to run "batch modes"; this would include running trajectories for many time periods and running trajectories/dispersion forward from multiple sources.

After the BRAVO study period concludes (October 31, 1999) a copy of the archived EDAS data sets and HYSPLIT model will be submitted to the BRAVO database manager (DRI-Las Vegas) on CD-ROM. The CD-ROM will include the necessary structure so that HYSPLIT may be easily run from the CD-ROM. The BRAVO database manager will distribute copies of the CD-ROM to BRAVO participants upon request.

Trajectory analysis assumes that the calculated wind fields are good representations of the true wind fields and that a single point can represent the air mass location at any point in time. The first of these involves both measurement uncertainty and the capabilities of the method used to generate the wind field from those measurements. Errors in calculated air parcel position that are associated with imperfect wind fields tend to increase with each time step. Trajectory-calculated air parcel positions more than just a few days (i.e. 3 to 5) from the initial location are generally thought to be uncertain by hundreds of kilometers. Position errors can also be substantial for short-duration trajectories under rapidly changing meteorological conditions such as frontal passage.

The concept of an air parcel used in trajectory analysis is rather vague, but for any practical use it must have some non-zero dimension that can be thought of as containing the emissions of a specific source or sources in a specific area (e.g. a city) for some short period of time (minutes to hours). A point at the center of mass of the air parcel can be used to represent its location at the point of origin. However, the integrity of an air parcel is typically very short-lived because of the effects of turbulence and wind shear. These will cause the air parcel to spread out (e.g., vertically in the mixed layer on a hot summer day) and can cause it to divide into disjointed pieces (e.g., part of the air parcel can be sheared off and separated from the rest). Even if the trajectory path could be perfectly calculated, it may be very misleading to think of its position after several days of transport as of the center of the air parcel distribution.

In spite of the uncertainties, trajectory and back-trajectory analysis have a number of important uses in attribution analysis all of which will be used in the BRAVO Study. Since trajectory methods don't calculate dispersion and deposition they cannot be used directly to determine source contributions at a receptor site. However, they can be used to identify time periods where emissions from specific sources are thought not to contribute at a receptor site because the transport was in a completely different direction. In this way trajectories can be used as an independent check of the reasonableness of receptor modeling attribution results (i.e., check whether the trajectory path connects the receptor site with the primary contributing sources identified for each sample period). Some receptor methods use trajectory analysis-predicted emission age (i.e. transport duration from emission to the receptor locations) to estimate sulfate concentration from a specific source using typical SO_2 to sulfate conversion rates. Comparison of trajectories calculated using wind fields determined by different methods is a simple method to

determine whether the wind fields are significantly different with regard to transport. Trajectories from tracer-tagged sources can be compared to the PFT ambient concentrations at the monitoring sites to evaluate the combined accuracy of the wind field and trajectory algorithm. Statistical associations may be developed between the amount of time air parcels are estimated by trajectory analysis to spend over various source areas and the corresponding receptor site air quality level (e.g. sulfate concentration, light scattering coefficient, etc). Typically this has been done with back-trajectories for sites with multiple years of ambient monitoring data, but it will be tried with some of the sophisticated measurements made during the four months of the BRAVO Study.

CALMET/CALPUFF

CALMET/CALPUFF is a combination of a diagnostic meteorological model (CALMET) and a Lagrangian puff air quality model (CALPUFF) that was used in Project MOHAVE to predict Mohave Power Project (MPP) impacts. Hourly radar profiler wind data was used as input data for CALMET. The choice of input wind data and how to set up the model to use it were made to increase the ability of the model to predict the ambient PFT data. The grid scale of the wind field was 5 km, which was sufficient to represent major topographic features but smoothed over many smaller ridges, peaks, and valleys. The Pasquill-Gifford-Turner (PGT) diffusion algorithm, with transitioning to time-dependent dispersion curves at longer distances, was used to represent the plume diffusion. CALPUFF simulates daytime SO_2 conversion to particulate sulfur using a linear mechanism with a conversion rate that is based on solar radiation, PGT class, ambient ozone concentration, and relative humidity. The algorithm produces a maximum conversion rate of about 4%/hr at 100% RH, which is lower than generally-accepted peak aqueous conversion rates. On the other hand, the algorithm does not attempt to quantify the time spent in clouds, which could produce a lower hourly-average rate than the peak that occurs whenever the plume is in a cloud.

In Project MOHAVE the CALPUFF/CALMET system was used to simulate two types of conditions, both of which may be considered as bounds to the range in which actual impacts of MPP might lie. One type of conditions was based on the assumption that all sulfate formation took place in cloud-free air. This can be considered to produce a lower bound with respect to actual sulfate formation. The other type of conditions that was simulated was based on the assumption that the MPP plume interacted with clouds for a specified period of time each day. Because clouds were not present every day and the assumed period of interaction was long compared to conversion rates in clouds, this condition was taken to approximate an upper bound to potential source impacts.

For the first type of conditions, the internal chemistry algorithm of the model was used to calculate the conversion of SO_2 to sulfate. This algorithm is based on homogeneous, “dry” chemistry. For the second type of conditions, where the MPP plume was assumed to interact with clouds, aqueous phase chemistry was likely to occur, which would result in much higher conversion rates than the internal algorithm of the model would predict. Therefore, as a bounding exercise, for the second analysis it was assumed that all the plume material interacted with clouds for three hours every day and the SO_2 was converted to particulate sulfate at a rate of 20% per hour during those three hours.

These two analyses, labeled "CALPUFF Dry" and "CALPUFF Wet," respectively, can be considered as estimates of lower and upper bounds to the impacts of MPP emissions The initial settings and choices of input meteorological data were selected to improve comparisons between predicted and measured PFT concentrations (Vimont, 1997).

All air quality simulation models are subject to uncertainties associated with the limitations of spatial and temporal resolution resulting from practical computational restrictions, input data uncertainty and/or lack of representativeness (e.g. meteorology, air quality, & emission data), and assumptions and parameterizations to required to provide the myriad input information not available from measurements. Even in models that incorporate terrain, it is typically done so by accounting for the average terrain elevation of a rectangular grid at the surface which is often much larger than critical terrain dimensions. Canyons, narrow mountain passes and ridges that may be influential to flow and dispersion are not well characterized by the model-generated virtual terrain of uneven height cell-sized blocks. Uncertain or non-representative measurements used as input to air quality models result in some level of prediction uncertainty depending on the model's use of the data. Model sensitivity analysis is a standard approach to evaluate this source of uncertainty. Sensitivity analysis can also be used to evaluate assumptions and parameterizations but it is rarely done on more than a small fraction of the many assumptions because of the effort involved.

In the BRAVO Study CALPUFF will be used as a tool to evaluate the utility of various input data, wind-fields, etc. by identifying those that yield the best comparison between predicted and measured PFT concentrations. Presuming it produces credible results; CALPUFF will also be available as a sort of general-purpose regional air quality model that can be used to perform reality checks on results of receptor source apportionment methods. As in MOHAVE, it will also be used to estimate sulfate impact bounds for some of the major SO_2 point sources to provide a possible range of impacts that corresponds to whether or not cloud chemistry occurs.

Lagrangian models like CALPUFF are most appropriate to simulate one or a few isolated emission sources that are relatively near to the receptor location (e.g. Carbon I & II with respect to Big Bend). However, they are limited in that they treat each source's emissions separately and combine the results, so that chemical interactions of pollutants from different sources cannot be simulated. They also tend to be awkward to use if emissions from many sources are to be combined. With this in mind CALPUFF will not be depended upon to simulate all major sources in the study region that contribute to Big Bend haze.

REMSAD

The Regulatory Modeling System for Aerosols and Deposition (REMSAD) modeling system was designed to estimate particulate concentrations averaged over horizontal grid scales of roughly 20 km and with a vertical resolution of 50 to a few hundred meters. It is capable of treating sub-domains at higher resolution, which allows savings of computer time in outlying areas of lesser interest while still resolving the areas

of greatest importance (e.g. receptor locations). The particulate concentrations can be broken down into size categories (and mass distributions) and the predictions can include the effects of photochemistry.

The REMSAD core model for aerosol and toxic deposition (ATDM) is a three-dimensional grid (Eulerian) model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations. The pseudo-first order PM oxidation chemistry package from RTM-II has been incorporated, and the dry and wet deposition routines have been updated to include additional species.

The model framework extends vertically to treat the entire troposphere with a sigma (terrain following) vertical coordinate. It can provide two-way interactive nesting of fine grids within coarser mesh grids in both the horizontal and vertical. The model uses a precomputed hydroxyl chemistry package based on a multidimensional lookup table. This table takes into account variations in pressure, temperature, moisture, solar intensity, clouds, ozone, NO_x and a representative VOC species. The model includes a cumulus convective parameterization scheme and a stratiform parameterization scheme for the distribution and removal of pollutant species.

In addition to the fundamental assumption that are required for any air quality simulation model (indicated above for CALPUFF), Eulerian air quality model such as REMSAD are subject to numerical dispersion. Input and predicted conditions are assumed to be uniform in any grid cell. If a receptor location is within one or two cell dimensions of a source being monitored, a Eulerian model will indicate a greater than true frequency of impacts that are of lower than true concentrations. This happens because the true plume is much narrower than the cell it is in causing it to miss the site more than in the simulation, and it is more concentrated than the cell-averaged concentration in the simulation.

The primary purpose of REMSAD for the BRAVO Study is to estimate haze impacts at Big Bend of all the major emission sources in the region. It is the only method proposed for use in the BRAVO Study that has the capabilities to estimate impact for all sources in the region for which there are emission rate data. Other methods are limited to certain pollutants, to artificial tracer-tagged sources, sources for which there is a prominent endemic tracer or to large sources near Big Bend. This is not to say that REMSAD results will be accepted without critical evaluation. In fact the very purpose of employing multiple attribution methods is to permit comparisons and evaluations (further discussed below in the section on Reconciliation of Results). REMSAD use in BRAVO may be modified to mitigate problems identified during the reconciliation process and improve performance. Also the level of uncertainty ascribed to its results may be modified to reflect its performance compared to other methods.

Table 5- 3 shows the responsible organization, the sources that can be examined and the particulate species and/or optical parameters that will be addressed for each of the attribution methods discussed above.

Attribution Method	Responsible Organization	Attributable Sources	Attributed Components
Tracer Scaling	DRI	PFT-tagged	Sulfate, SO_2, primary particles
RMAPS	NPS	All source by areas	All major PM species
Tracer Regression	DRI, NPS, & TNRCC	PFT & endemic-tagged	Light extinction, all major PM species
DMBR	NPS	PFT-tagged	Sulfate
TAGIT	DRI	PFT-tagged	Sulfate, SO_2, primary particles
CMB	NPS, DRI, & CSU	All sources with profiles	Primary PM species, SO_x, organic species
Neural Networks	NPS (Phil Hopke)	All major sources	Primary PM species, SO_x
Trajectory	NPS, DRI, & TNRCC	All major sources	Light extinction, all major PM species
CALPUFF/CALMET	NPS	Selected major sources	All major PM species
REMSAD	NPS	All large sources	All major PM species

Case Studies and Episode Analysis

Analysts preparing case studies and conducting episode analysis draw on diverse measurement data and model results to construct a story (or conceptual model) that explains how sources produce impacts and why the pollution levels at monitoring site change over time. Case studies usually focus on what is happening with emissions from a source (or sources) and in that way are analogous to air quality simulation models, while episode analysis tends to focus on why the pollutant concentrations or haze level is changing at a receptor location which is analogous to receptor modeling. Both are documented by the preparation of descriptive narratives that illustrates our understanding of the phenomenon of importance. Case study and episode analysis is performed because none of the attribution methods provides this type of a direct and clear answer to questions such as these: How does that source's emissions cause haze? How do atmospheric processes contribute or reduce the impacts of responsible sources? What is the sequence of events that leads to the changing impacts at the receptor location?

In addition to addressing these types of questions, data analysts performing case study and episode analysis typically draw on a variety of information, some of which may not have been explicitly used in any of the attribution methods. This provides valuable opportunities to further challenge conceptual models and the results of attribution methods by comparisons with independent information. If these challenges result in consistency, the conceptual model gains credibility; if the result is inconsistency, either the model or the independent information it is being compared with must be incorrect.

One of the most important uses of case studies and episode analysis is to communicate with non-technical interested people (e.g. the public, policy makers, etc.)

concerning our understanding of the important processes responsible for haze at Big Bend. Generally it is not enough to summarize the results of an attribution study in tables and graphs, interested non-experts want an explanation of how emissions from various sources and the atmosphere work to generate these results. Without such explanations, the results may not be fully believed and/or inappropriate public policy may be promoted to deal with a misconceived understanding of the situation (e.g. control of a source that is a substantial contributor thinking that it will improve summer haze episodes, but the source rarely contributes in summer).

Air quality modelers and receptor modeling data analysts usually do some level of case study and episode analysis as a means to communicate and sell their methods' results. These will be compared and expanded on by DRI scientists to compile a set of descriptions of case studies and episodes that are self-consistent and in accord with independent information.

Computer Simulation of Visual Air Quality

In order to assist in interpreting the quantitative data of impacts on the light extinction coefficient, b_{ext}, various levels of visibility degradation in typical Big Bend National Park views will be displayed in images that can be viewed on a computer screen. Mathematical models of radiative transfer will be used to calculate the changes in the appearances of these views due to various levels of light extinction. The approach used to generate these simulated views is described here.

Radiant energy, as it passes through the atmosphere, is altered by the scattering and absorption by gases and particles. Image-forming information is lost by scattering of radiant energy out of the sight path and absorption within the sight path. Further, ambient light from direct, diffuse, and reflected radiance is scattered into the sight path. This adds radiant energy called "path radiance" to the observed radiation field.

The transmittance of the sight path is calculated from measured extinction or the distribution of particles and gases along the sight path. The path radiance is more difficult to estimate. A reasonable assumption under uniform illumination (cloud free sky or uniform overcast) is to estimate the path radiance with an equilibrium radiance model.

Equations for path radiance and observed image radiance are applied to each pixel of a photographic image, to represent the effect of the atmosphere on that image. The bulk atmospheric optical properties such as extinction, scattering, and absorption coefficients, single scattering albedo, and the scattering phase matrix are required to apply the equations to each element of a scenic view. They are calculated by an aerosol model. The Mie theory model assumes spherical particles for externally-mixed, homogeneous or internally-mixed, coated aerosols.

A backward photon trajectory, multiple scattering, Monte Carlo, radiation-transfer model will be used to calculate sky radiances. The inherent radiance of each terrain pixel

will be estimated with the equilibrium radiance model, sky radiance model, and distance to the target for each pixel.

The modeled image radiance field for a selected level of extinction will then be calculated by first using the new extinction value and distance to each terrain pixel to calculate a new path transmittance. Second, the new path radiance will be calculated using this transmittance and modeled sky radiance. Third, the new apparent image radiance field will be calculated. These new image radiance files will then be used in the image processing modules to generate the final images, as described below.

The original images that start the process described above will be 35 mm color slides taken at Big Bend National Park. The slides necessarily will represent cloudless skies under the cleanest visual air quality conditions possible. Aerosol and optical data associated with the day the picture was taken will also be used. The slide images will be digitized through three wide band filters at different colors.

To produce the new image, which displays the scene appearance at a chosen level of extinction, the new radiance field is calculated as previously described. That modeled radiance field describes the appearance of every pixel on the photograph, each of which has been altered by the scattering and absorption that were artificially added to the initial image. The results, when viewed as a photograph or on a color computer monitor, then portray the original digitized photograph under the different atmospheric conditions.

The simulation of human perception of actual scenes by using photographs or computer images is not perfect. Based on color matching experiments performed at the Grand Canyon, Henry (1999) points out that such images are less colorful and more blue than the true scenic view that is observed on site. These conditions appear to derive from the limitations of the photographic film that is the basis for the initial images that were digitized. A consequence of these limitations is that the artificial images overstate the visual effects of increasing haziness.

Consequently, one should not rely on the computer images to provide quantification of thresholds of human perception of visibility change in terms of extinction changes. Rather, these images should be considered approximations that portray the essential effects of extinction change, albeit only semi-quantitatively.

5.6 Reconciliation of Results

Reconciliation of results is a process that begins in an informal way midway through the data analysis phase of the study, but can only be completed near the end of that phase. Each of the attribution assessment approaches produces results that address the contributions by emission sources to visibility impairment measured at Big Bend. Preliminary results of these methods will be shared internally among the study participants (other analysts, sponsors, etc.) at data analysis meetings as results become available. This process of technical communications is expected to spawn critical review,

comparisons with other methods, and method refinements. There may be several rounds of review, refinement and reapplication for some methods. Initially only about half of the PFT measurement data will be distributed to the data analysts to use in any way they choose in their models (i.e. input data or to refine the methods), but towards the end of the data analysis phase of the study the rest of the PFT data will be released and used to evaluate the methods. This may provide valuable insight concerning which models are credible and may convince some data analysts to withdraw their method as unsatisfactory for BRAVO. Shortly after the release of the last of the PFT data, final results from the surviving methods will be compiled. There is no expectation that the results of the various methods will be consistent with each other at that point in the process.

At this point in the process, it is necessary to reconcile what may be disparate final results in order to produce the BRAVO Study findings. Reconciliation involves judgments of the credibility of technical information. These are based principally on a process of inter-comparing information from independent sources. Some technical information is inherently more credible than other information. An information credibility hierarchy can be constructed which divides sources of information in to three groups based upon its source. The most credible source of information is generated directly from well-established physical principles and involves few if any assumptions. Examples include: pollutant concentrations must be positive, and pollutants are transported in the direction of airflow. The next category of information sources contains well-characterized measurements and simple parameters derived from them. These are assumed to be credible within their uncertainty bounds. The category of information with the least credible information includes results from physical and statistical models, which contain the combined uncertainty of input measurements and model assumptions.

The most productive comparisons are between model results and measurements or physical principles. An inconsistency with information from these more credible sources is a strong indication that the model result is not correct. However a consistent comparison does not ensure that the result is correct, and there may be situations where the comparison is indeterminate or no comparison can be made. It is also likely that models may work satisfactorily for some situations but be unsatisfactory for other situations. So a poor comparison for some of the periods does not necessarily mean the model results should all be ruled unreliable.

In spite of the relatively poor power to resolve credibility issues between information sources in the same category, a systematic intercomparison of results from all of the attribution models will be conducted. This is made more difficult because many of the attribution models address sources in quite different ways (e.g. specific sources, source areas, source types). The predictions of each of the attribution model for every sample period at the primary receptor site will be compared. The next steps depend on the results of these comparisons. If there is substantial agreement among many of the methods most of the time, then the outlier methods and time periods will be examined to attempt to understand why they seemed to disagree. It is also important to determine whether the methods that agreed do so because they are not very independent (i.e. use the same input data in much the same way) in which case their agreement does not greatly

increase the credibility of their results. Alternatively, if very independent methods produce results that substantially agree, their results do gain in credibility.

If the model results do not group or if the methods that do seem to group are all interdependent then there may be no basis for deciding which is more credible for any particular sample period. This was the situation in Project MOHAVE, where the results that agreed best on a daily basis all depended on measured PFT concentrations. An irresolvable inconsistency on a sample period by sample period basis represents a serious degradation of study finding credibility, but it does not necessarily mean that the study is without useful results. In the Project MOHAVE case, the primary question was the impacts of MPP at the primary receptor site. While the methods did not agree on which days had the biggest impacts, they did define a rather narrow range of impacts for the worst days that each identified. Cumulative frequency distribution plots that showed the range and frequency of impacts by each method for the period of the study illustrated this, which was a useful finding of the study. Figure 5-6 shows the cumulative frequency distribution of 12-hour sulfate attributed to MPP by various models and bounding calculations.

In addition to determining credible attribution results, the reconciliation process will determine suitable uncertainty limits to associate with those finding. In Project MOHAVE it was the range of results at any frequency (e.g. 50th percentile or 90th percentile) from the various attribution methods.

The BRAVO Study Technical Manager working with DRI and in close consultation with the technical steering committee will be responsible for the overall reconciliation of the study attribution results.

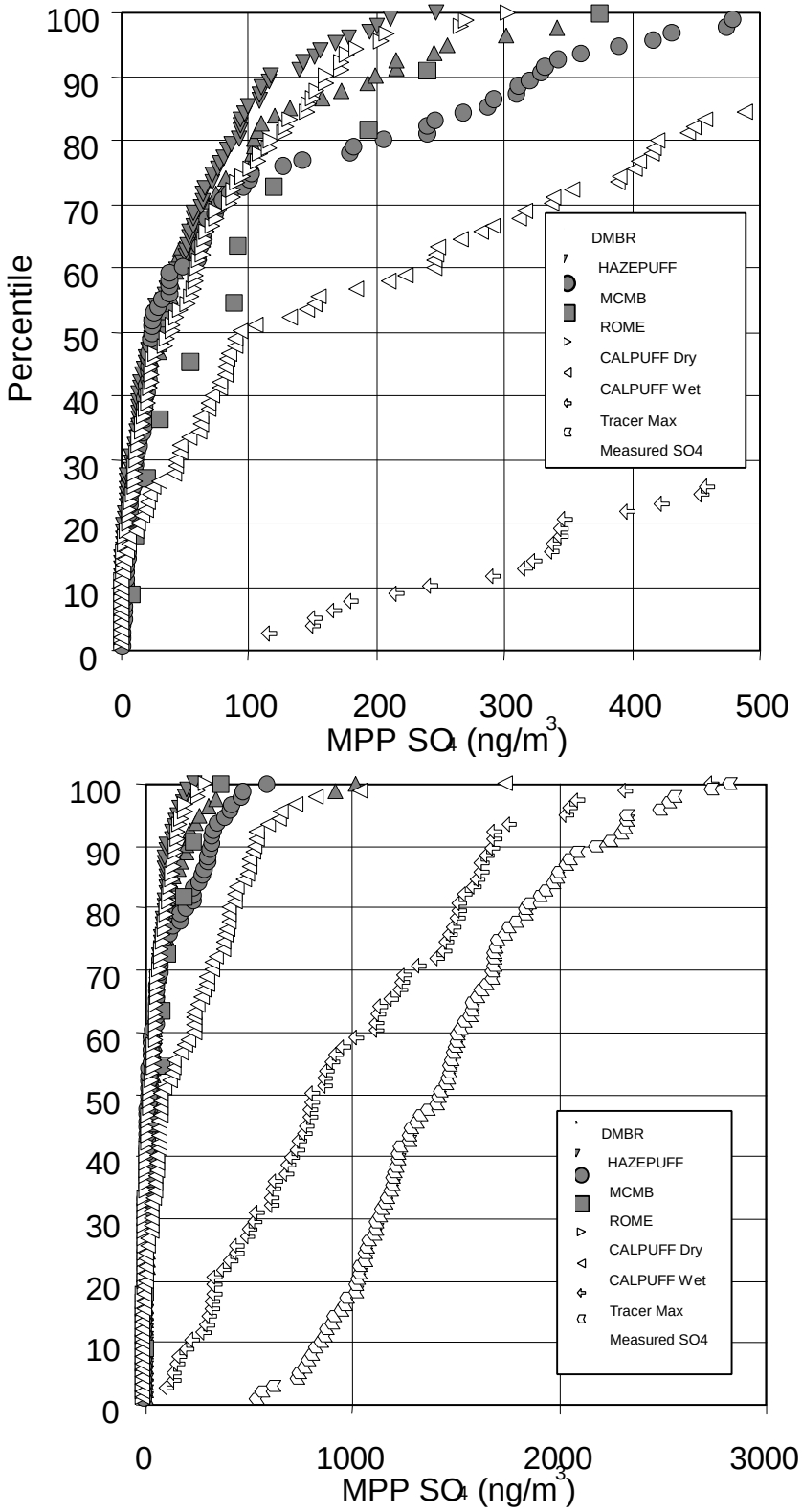


Figure 5-6. Cumulative frequency plots of 12 hour sulfate attribution to MPP at Meadview during the summer intensive. Note: filled symbols represent estimates of MPP attribution; open symbols indicate bounding calculations and physical upper bounds.

6 Data Management

6.1 Introduction

The number and variety of measurements in large collaborative efforts such as BRAVO generate volumes of data that must be stored in an organized, easily accessible format. DRI is responsible for assembling and maintaining the BRAVO database. This section outlines the protocol for management of BRAVO data.

6.2 BRAVO Data

There are several different types of data that are expected to result from BRAVO. They can be grouped roughly into one of four categories.

I. Automated pseudo-continuous samples (Analysis occurs at the time of sample procurement): This category encompasses data from instruments that are self-contained sample procurement and measurement devices. Typically, measurements are made at regular intervals that range from several minutes to one or two hours. Examples include surface meteorology, continuous measurement of airborne species (SO_2, SO_4^{2-}), nephelometers, and transmissometers.

II. Time-averaged samples (analysis occurs post-sample procurement): This category contains samplers that utilize a substrate such as a filter that requires chemical analysis in the lab. Generally the durations of the measurements are between one hour and one day. Examples include measurement of PM_{10} and $PM_{2.5}$ on filters, and speciated chemical analysis of aerosols.

III. Upper Air data: This category is different from the previous two because measurements can be at irregular intervals and because the same parameter(s) is measured at multiple altitudes at the same site.

IV. Size and Chemically Speciated Aerosol Data: This category includes analysis methods that break down particle measurements both by particle size and by chemical composition. SEM analysis of polycarbonate filters is an example of this type of measurement.

Table 6.1 lists the measurements obtained as part of BRAVO as well as the type of data they represent.

Table 6-1. Measurements obtained as part of BRAVO, the duration of the averaging times, and the type of data generated.

Measurement Type	Duration(s)	DataType
$PM_{2.5}$ elements (H, Na-Pb, mass, b_{abs}) (Teflon filter)	6, 12, 24 hr	II
$PM_{2.5}$ carbon (quartz filter)	12, 24 hr	II
$PM_{2.5}$ ions (nylon filter)	12, 24 hr	II
PM_{10} elements, ions, carbon	24 hr	II
SO2	6, 24 hr	II
Tracer	1, 6, 24 hr	II
$PM_{2.5}$ carbonaceous aerosol	24 hr	II
Carbon speciation by GC/MS for selected periods	24 hr	II
Gaseous nitric acid	24 hr	II
Gaseous ammonia	24 hr	II
MOUDI size resolved aerosol	24 hr	II
Scanning electron microscopy (SEM) analysis	24 hr	II
Gaseous hydro-peroxides	1 hr	I
High time resolution, high sensitivity SO_2	10 min	I
High time resolution particulate sulfate	10 min	I
High time resolution organic carbon	?	I
High time resolution particulate nitrate	?	I
Rawinsonde	Twice daily	III
SODAR Wind Profiler	1 hr	III
RADAR Wind Profiler	1 hr	III
Size resolved chemically speciated $PM_{2.5}$	12 hr	IV

6.3 Importing Data into the BRAVO Database

Data received by the data manager from the various groups that are collaborating in BRAVO has to be imported into a master database. The primary objective of the data management portion of the BRAVO study is to provide an efficient and simple way to extract desired data from a well-documented, accurate, and uncomplicated database. This requires that a thorough account be kept of all data that end up in the BRAVO database. The first step in this process is ensuring that data providers and the data manager are in agreement on a consistent, well-documented format for the raw data files. Important factors include measurement units, time reporting conventions, site mnemonics/codes, mnemonics and codes for the parameters that are measured, and data flagging conventions.

Once the conventions for reporting data are firmly in place, computer codes, written primarily in Microsoft Visual Basic and Visual C++ are used to import data into the database and convert measurement units, sampling times, measurement locations and so forth into the standard formats of the BRAVO database. In addition, during the data import process Level 1b validation is applied to each data set; it is expected that Level 1a validation is performed by the data provider (See section 6.4 for an explanation of data validation levels).

6.4 Data Validation

Mueller (1980), Mueller et al., (1983) and Watson et al. (1983, 1989, 1995) define a three-level data validation process that should be mandatory in any environmental measurement study. Data records are designated as having passed these levels by entries in the VAL column of each data file. Data providers are asked to report data only after Level 1A validation has been performed. These levels, and the validation codes that designate them, are defined as follows:

?? **Level 0 (0)**: These data are obtained directly from the data loggers that acquire data in the field. Averaging times represent the minimum intervals recorded by the data logger, which do not necessarily correspond to the averaging periods specified for the data base files. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline and span changes been applied. Level 0 data are not contained in the BRAVO data base, although they are consulted on a regular basis to ascertain instrument functionality and to identify potential episodes prior to receipt of Level 1A data.

?? **Level 1A (1A)**: These data have passed several validation tests applied by the network operator that are specific to the network. These tests are applied prior to submission of data to the BRAVO data manager. The general features of Level 1A are: 1) removal of data values and replacement with -99 when monitoring instruments did not function within procedural tolerances; 2) flagging measurements when significant deviations from measurement assumptions have occurred; 3) verifying computer file entries against data sheets; 4) replacement of data from a backup data acquisition system in the event of failure of the primary system; 5) adjustment of measurement values for quantifiable baseline and span or interference biases; and 6) identification, investigation, and flagging of data that are beyond reasonable bounds or that are unrepresentative of the variable being measured (e.g. high light scattering associated with adverse weather).

?? **Level 1B (1B)**: After data are received by the data manager, converted, and incorporated into the database, validation at level 1B is performed. This is accomplished by software which flags the following: 1) data which are less than a specified lower bound; 2) data which are greater than a specified upper bound; 3) data which change by greater than a specified amount from one measurement period to the next; and 4) data values which do not change over a specified period, i.e., flat data. The intent is that these tests will catch data which are obviously nonphysical, and such data will be invalidated and flagged. Data supplied by project participants which fail these tests may result in a request for data re-submittal.

?? **Level 2 (2)**: Level 2 data validation takes place after data from various measurement methods have been assembled in the master database. Level 2 validation is the first step in data analysis. Level 2 tests involve the testing of measurement assumptions (e.g. internal nephelometer temperatures do not

significantly exceed ambient temperatures), comparisons of collocated measurements (e.g. filter and continuous sulfate and absorption), and internal consistency tests (e.g. the sum of measured aerosol species does not exceed measured mass concentrations).

?? **Level 3 (3)**: Level 3 is applied during the reconciliation process, when the results from different modeling and data analysis approaches are compared with each other and with measurements. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. The Level 3 designation is applied only to those variables that have undergone this re-examination after the completion of data analysis and modeling. Level 3 validation continues for as long as the data base is maintained.

A higher validation level assigned to a data record indicates that those data have gone through, and passed, a greater level of scrutiny than data at a lower level. The validation tests passed by Level 1B data are stringent by the standards of most air quality and meteorological networks, and few changes are made in elevating the status of a data record from Level 1B to Level 2. Since some analyses are applied to episodes rather than to all samples, some data records in a file will achieve Level 2 designation while the remaining records will remain at Level 1B. Only a few data records will be designated as Level 3 to identify that they have undergone additional investigation. Data designated as Levels 2 or 3 validations are not necessarily "better" than data designated at Level 1B. The level only signifies that they have undergone additional scrutiny as a result of the tests described above.

6.5 Database Architecture

There are two different designs for the BRAVO database, a master database, and a user database. The master database includes information that is superfluous for the day-to-day user, but important for the data manager. Examples of such information are: the line numbers in the original data files that are associated with each data point, the units used by the data provider before conversion to standard units, and the dates that data were imported into the database. While much of the information related to the data points that appear in the BRAVO database does not appear in the user version of the database, some fields such as data validity flags and sample analysis method descriptions are included for completeness.

Within the BRAVO master database, all data are stored in tables with consistent structures. Within the data tables there exists one record for every measurement that results in a datum. This record contains links to the information stored in the following fields (Actual field names are mnemonics of the field names shown below):

1. **Site_Parameter_ID:** This is a number that is unique for each combination of site, parameter measured, sample duration, particle size (if applicable), and source file (The name of the data file as provided by the data supplier). The Site_Parameter_ID number is linked to the "Site Information Table", The "Parameter List Table", the "Particle Size Definitions Table", and the "Source Data Files Table".
2. **Start_Date_Time:** Date and Time stamp indicating the beginning of the sample period.
3. **Duration:** Duration of sampling/averaging period in minutes
4. **Value:** Value of measurement.
5. **Uncertainty:** Uncertainty associated with the value.
6. **Value_Suspect:** A Flag field that contains either a "V" for valid data or an "S" for suspect data.
7. **Flag_Comment:** text field containing flags and comments as reported by the data provider.
8. **Source_File_Line_No:** The line number in the source file (data file from provider).
9. **Alt:** The altitude of the measurement (For Upper Air Data Only).
10. **Size_Bin_ID:** This field is linked to a table that contains lists of different particle size bins. This is different from the "Particle Size Definitions Table" which only contains standard particle size cuts e.g. D_p<10 ?m, D_p <2.5 ?m, etc. The Size_Bin_ID Field is only used when non-standard size cuts are reported from instruments like impactors, DMA, etc.

Note that traceability of data is built into the architecture of the master database. In other words, it is possible to take any record in a data table and trace the record entries back to the original source file. Likewise, using database queries, it is possible to modify/isolate a set of records by data provider, sample times, sample durations, source file, etc.

Note that the measurements obtained as part of BRAVO range in duration between 10 minutes and 24 hours (Table 5.1). Frequently, this can lead to difficulties in comparing data of different types. For example, comparing 10 minute-averaged SO_2 concentrations at one site with 24 hour-averaged SO_2 concentrations at another site requires averaging the 10 minute samples over the appropriate 24 hour period. In order to avoid cumbersome spreadsheet calculations, the BRAVO database (both master and user) contains time-averaged data tables. For example, in addition to a table that has all 10 minute-averaged SO_2 data, there are three more tables that contain those same data averaged over 1 hour, 6 hours, and 24 hours. While this design increases the amount of computer storage space required for the database, the presence of these additional tables considerably increases the speed with which different types of data can be extracted from the database and compared to one another.

6.6 End Product

In addition to being a means to safely and efficiently store data, the purpose of the BRAVO database is to provide quick and easy access to data that have been gathered as part of the study. The database will be made accessible to the different participants in BRAVO via internet. Figure 5.1 gives an example of a data request form that can be made available on the internet and can be used to retrieve BRAVO data. The user is asked to select the dates and times that are of interest, one or more sites where measurements were performed, one or more parameters that were measured, the averaging time of the measurement(s), and additional information regarding the desired format for the output file. A map of the BRAVO network on the form aids in the selection of sites that may be of interest to the user. Once the information is entered into the form, a program written in Microsoft Visual Basic for Applications will retrieve the relevant data and write a file (filename specified by user) to the DRI ftp server. The user may then download the file directly from the ftp server. The benefit of having a central database that is queried remotely is that updates to the database are available to the user as soon as they are implemented. Some users may require more complex data analysis tools or more flexible data retrieval options; in such cases, users can be provided with a copy of the BRAVO database either on CD-ROM or by specially arranged ftp.

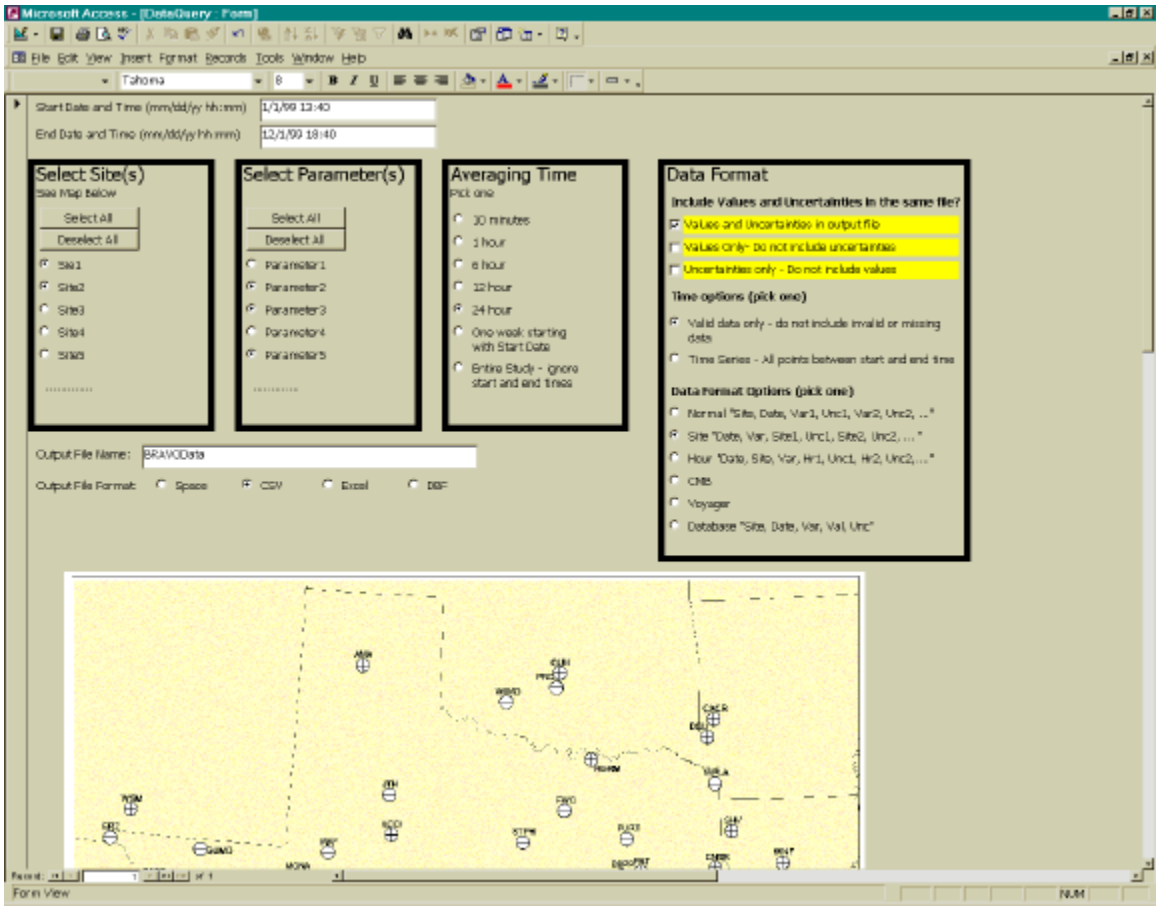


Figure 6-1. Example of form available on the internet used to retrieve BRAVO data.

A "BRAVO Database Information" web page will also be placed on the internet for user access. This latter page contains information about the BRAVO database, specifically, the date and time of the last database update, the nature of the update (i.e. what was changed from the previous version), the current status of the database, and a general description of the database.

7. Quality Assurance

A well-defined program to assure the quality of data collected in a monitoring program is essential to the credibility of its results. Each of the monitoring components (e.g. aerosol sampling, laboratory analysis, & upper air meteorology) has written protocols that describe how the method is done. These protocols also identify the quality control procedures used to avoid problems with the data and to document their quality. An independent quality assurance audit program is used to check how well the protocols, especially the quality control procedures, are being followed.

The major emphasis of independent quality assurance in BRAVO is upon verifying the adequacy of the participants' measurement procedures and quality control procedures, and upon identifying problems and making them known to project management. Although routine audits play a major role, emphasis is also placed upon the efforts of senior scientists in examining methods and procedures in depth. This approach has been adopted because fatal flaws in experiments often emerge not from incorrect application of procedures by operators at individual sites or laboratories, but rather from incomplete procedures, inadequately tested methods, deficient quality control tests, or insufficient follow-up of problems.

At the beginning of the study, senior auditors will review study design documents to ensure that all measurements are being planned to produce data with known precision and accuracy. The auditors will focus on verifying that adequate communications exist between measurement and data analysis groups to ensure that measurements will meet data analysis requirements for precision, accuracy, detection limits, and temporal resolution. Quality control components of the measurements include: determination of baseline or background concentrations and their variability; tests for sampler contamination; adequate measurements of aerosol and tracer sampler volume and time; blank, replicate, and collocated samples; assessment of lower quantifiable limits (LQL), and determination of measurement uncertainty at or near the LQL; regular calibrations traceable to standard reference materials; procedures for collecting QC test data and for calculating and reporting precision and accuracy; periodic QC summary reports by each participant; documented data validation procedures; and verification of comparability among groups performing similar measurements.

Field performance and system audits will be conducted at each of the BRAVO monitoring sites in Texas and adjoining states. Measurement systems to be audited at the majority of sites included aerosol sampling using the IMPROVE sampler and tracer sampling using the Brookhaven BATS sampler. Performance audits will include flow rate

checks of the IMPROVE sampler and checks of the various settings on the BATS sampler. System audits will evaluate the adequacy of project components such as Standard Operating Procedures, measurement documentation, operator training, quality control checks, and sample chain of custody.

In addition to the IMPROVE and BATS sampler audits, system and performance audits of additional special measurements will be conducted at the Big Bend K-Bar site. Nephelometers will be challenged with SUVA gas, and transmissometer sight paths were evaluated. A high-sensitivity sulfur dioxide monitor and a continuous particulate sulfate monitor will both be challenged with an independent SO2 audit standard gas. Flow rates will be audited on a variety of aerosol instruments designed to measure aerosol composition and particle size distribution. System audits will be conducted on the radar profiler/RASS system at K-Bar and at several other sites in Texas. The profiler/RASS audits will focus on the orientation of the profiler modules and on the operational status of the instrument.

Field system audits will be conducted at each of the BRAVO tracer release sites in Texas. The audits will focus on the ability of the tracer release system to control the tracer emission rates and to quantify the rates accurately and precisely. The audits will also evaluate the adequacy of project components such as Standard Operating Procedures, measurement documentation, operator training, and quality control checks.

A laboratory system audit will be conducted at Brookhaven National Laboratory (tracer analysis), and additional system audits will be conducted at UC Davis (elemental analysis), Desert Research Institute (carbon), and. These system audits evaluate the adequacy of project components such as Standard Operating Procedures, measurement documentation, quality control checks, operator training, and sample chain of custody. Performance audits specific to Project BRAVO will not be conducted. Instead, senior auditors will evaluate the results of prior audits or performance tests in which these laboratories have participated.

A system audit will be conducted on-site at the BRAVO central data management center (DRI- Las Vegas). The audit will evaluate the adequacy of project components such as communications between the study participants and the data manager, calculation procedures, handling of quality control test data, data archiving procedures, data base security, and data validation procedures. It will also include a spot check of data flow, in which a few selected data points will be subjected to manual calculation at all steps from field generation to final form in the validated data base.

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