

Final Report — September 2004

# Big Bend Regional Aerosol and Visibility Observational Study

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## SPONSORING AND CONTRIBUTING ORGANIZATIONS



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### **Note to Readers**

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## Preface

The following is a report about the results of a study concerning the causes of visibility impairment at Big Bend National Park (NP) in west Texas. The study was prompted by observations in the early 1990s that visibility at the Park was frequently degraded and was apparently getting worse.

A preliminary study was sponsored by the U.S. Environmental Protection Agency (EPA), the National Park Service (NPS), and governmental agencies from Mexico. This preliminary study was conducted in 1996 and a report of its findings released in January 1999. The findings indicated that fine particulate sulfur compounds played a large role in observed impairment and that there was apparent transport of particulate sulfur compounds from sources in Mexico and the U.S. The preliminary report concluded that, in order to get a better understanding of the contributors to impairment at Big Bend NP, an enhanced study would be necessary that expanded the scope of the field measurement activities and expanded the spatial domain of the preliminary study, particularly to the northeast, south, and into the Gulf of Mexico.

The EPA, the NPS, and the Texas Commission on Environmental Quality (TCEQ) comprised the Steering Committee for the enhanced study, the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study. In April 1999, Mexico elected not to participate in the Study, which resulted in the Study being unable to gather ambient monitoring and atmospheric tracer release data in Mexico. Although this was a disappointing development, the monitoring and atmospheric tracer protocols were altered to maximize data collection in the U.S. border area nearest Mexico. The BRAVO Technical Sub-committee designed and directed the field-measurement portion of this study that ran from July through October 1999, and interpretation and analyses of these field data were completed in early 2004.

The BRAVO Study was designed as an investigation of the causes of haze at Big Bend National Park, but not as an assessment of regulatory options. The Study constituted one of the largest and most comprehensive visibility field studies and air quality modeling evaluation efforts conducted in the U.S. It used state-of-the-science monitoring, air quality modeling, and laboratory and statistical analyses and involved over 30 researchers from research and academic institutions throughout the U.S. It used inert atmospheric tracers over a huge geographic scale and made use of the best available air emissions input data. Evaluation of the collected data continued for over three years after the end of the 1999 field study.

While the Steering Committee was responsible for the ultimate publication of the BRAVO final report, the Steering Committee relied upon the BRAVO Technical Sub-committee to conduct or sponsor detailed analyses of the field data and source-region attribution analyses and to prepare the final report. Findings presented in the final report were thoroughly discussed by the Steering Committee, the Technical Sub-committee, and a

Non-governmental Sub-committee consisting of industry and environmental advocacy groups.

The final report provides estimates of the contributions of broad geographic regions to visibility impairment at the Park during the study period. Contributions from the eastern U.S., eastern Texas, and Mexico were noted. Because of the relative proximity of the *Carbón* I and II power plants to the Park, contributions specific to those facilities were estimated in this analysis. Such source-specific calculations were not made for other sources in the study domain. Of particular significance was the indication that sources over a broad geographic region play roles in the observed visibility impairment in the Park, suggesting too that the solution should be based on international and regional, multi-State strategies.

The confidence in these results notwithstanding, it must be emphasized that the endorsement of these findings by the BRAVO Steering Committee is made with the understanding that uncertainties exist and that analysis tools, no matter how sophisticated, only approximate atmospheric transport and chemical reactions. However, the Steering Committee is confident that the results of the study have been fairly presented with the concomitant caveats.

The BRAVO Steering Committee wishes to acknowledge the commitment and contribution of all that participated in this study and the preparation of this report. Our understanding of the science of the effects of atmospheric aerosol on visibility has been greatly expanded, as has our understanding of the causes of visibility impairment at Big Bend NP.

As the Steering Committee for the BRAVO Study:

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## Acknowledgments

The BRAVO Study could not have been accomplished without the enthusiastic support of participant organizations and individuals. From the initial planning in 1997, through the four-month ambient monitoring program in 1999, to the assessment process, and culminating in 2004 with the preparation of the final report, this study has been fortunate to include many talented and dedicated individuals from a number of organizations functioning together as a team. We are indebted to both the individuals for their thoughtful and energetic participation, and to their parent organizations that permitted and encouraged involvement by their staff.

The list of organizations that participated in the BRAVO Study includes

- **Sponsors:** U.S. Environmental Protection Agency, National Park Service, and the Texas Commission on Environmental Quality;
- **Contributors:** EPRI, and the National Oceanic and Atmospheric Administration - Air Resources Laboratory;
- **Research Institutions and Universities:** University of California - Davis, Desert Research Institute and the Cooperative Institute for Atmospheric Science and Terrestrial Applications at the University of Nevada, Cooperative Institute for Research in the Atmosphere at Colorado State University, Pennsylvania State University, Carolina Environmental Program at the University of North Carolina, and Brookhaven National Laboratory;
- **Consulting Firms:** Atmospheric and Environmental Research, Inc, Air Resource Specialists, Inc, and Aerosol Dynamics; and
- **Stakeholders:** the Environmental Defense, the Sierra Club, American Electric Power, TXU, and Reliant Energy.

The list below includes the individual participants that are not already acknowledged on the cover page as authors. It takes a lot of good people to accomplish a program of this magnitude and we were lucky to have a great team.

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## Table of Contents

	<u>Page</u>
Preface.....	i
Acknowledgments.....	iii
Table of Contents.....	v
List of Figures.....	xi
List of Tables.....	xx
List of Abbreviations and Acronyms.....	xxiv
 EXECUTIVE SUMMARY .....	 ES-1
 1. TECHNICAL OVERVIEW .....	 1-1
Which are the major aerosol components contributing to haze at Big Bend NP throughout a year?.....	1-2
How does the composition of haze vary at Big Bend National Park throughout a year during the haziest days? .....	1-4
How does airflow to Big Bend National Park vary throughout the year?.....	1-5
Where are emission sources that may cause particulate sulfate compounds that contribute to Big Bend haze? .....	1-7
How does the composition of haze vary at Big Bend National Park during the four-month BRAVO Study period? .....	1-9
How did different source regions contribute to particulate sulfate compounds affecting haze levels at Big Bend National Park during the BRAVO Study period?.....	1-10
How did different source regions contribute to haze levels at Big Bend National Park during the BRAVO Study period? .....	1-14
How applicable are the particulate sulfate attribution results for the BRAVO Study period to other years or times of year?.....	1-16
 2. INTRODUCTION .....	 2-1
2.1 Setting.....	2-1
2.2 Study Goals.....	2-3
2.3 Management .....	2-3
2.4 Preliminary Study .....	2-3
2.5 Seasonality of the Aerosol Components of Light Extinction .....	2-5
 3. STUDY DESIGN AND IMPLEMENTATION .....	 3-1
3.1 Selection of the Study Period .....	3-1
3.2 Use of Synthetic Tracers.....	3-2
3.2.1 Tracer Release.....	3-2
3.2.2 Tracer Monitoring .....	3-5
3.3 Aerosol and Gaseous Measurements.....	3-6
3.4 Optical Measurements .....	3-11

**Table of Contents (continued)**

	<u>Page</u>
3.5 Meteorological Measurements.....	3-11
3.6 Source Characterization.....	3-13
3.7 Aircraft Measurements .....	3-14
4. EMISSIONS INFORMATION .....	4-1
4.1 Emission Inventory .....	4-1
4.2 Emissions Modeling .....	4-5
4.3 Emissions Inventory Assessment .....	4-7
5. THE ATMOSPHERIC ENVIRONMENT OBSERVED AT BIG BEND NATIONAL PARK DURING THE BRAVO STUDY .....	5-1
5.1 Particulate Matter Characterization by the Routine Measurement Network.....	5-1
5.1.1 Particulate Matter Temporal and Spatial Characteristics .....	5-1
5.1.2 Properties of Particulate Matter at Big Bend National Park .....	5-4
5.2 Detailed Characterization of the Particulate Matter at Big Bend National Park.....	5-6
5.2.1 Ionic Composition of Big Bend Particulate Matter.....	5-7
5.2.2 Short Time Resolution Sulfate Concentrations at Big Bend.....	5-8
5.2.3 Organic Source Markers in Big Bend Aerosol.....	5-10
5.2.4 Particle Size Distribution .....	5-12
5.2.5 Very Fine PM as a Source Tracer .....	5-13
5.3 Characterization of Optical Conditions at Big Bend National Park .....	5-15
5.3.1 Light Absorption Measurements.....	5-15
5.3.2 Optical Measurements of the Big Bend Atmosphere.....	5-19
5.4 Meteorology During the BRAVO Study .....	5-21
5.5 Perfluorocarbon Tracer Experiment Findings .....	5-26
5.5.1 Continuous Tracer Results .....	5-26
5.5.2 Analysis of Timing Tracer Data.....	5-30
6. ANALYSIS OF BRAVO MEASUREMENTS.....	6-1
6.1 Collocated Measurements.....	6-1
6.2 Fine PM Mass Closure.....	6-3
6.3 Extinction Budget.....	6-4
6.3.1 Light Scattering by Dry Particles .....	6-4
6.3.2 Species Contributions to Light Extinction .....	6-5
6.4 Evaluation of the IMPROVE Equation for Estimating Light Extinction at Big Bend National Park.....	6-8
7. STUDY PERIOD REPRESENTATIVENESS .....	7-1
7.1 Meteorology.....	7-1
7.2 Transport Climatology.....	7-4
7.3 Aerosol and Light Extinction.....	7-9
7.4 Assessment of BRAVO Study Representativeness .....	7-19

**Table of Contents (continued)**

	<u>Page</u>
8. ATTRIBUTION ANALYSIS AND MODELING METHODS .....	8-1
8.1 Data Analysis Methods.....	8-1
8.1.1 Tracer Methods – TAGIT .....	8-1
8.1.2 Empirical Orthogonal Function Analysis.....	8-3
8.1.3 Factor Analysis.....	8-4
8.2 Meteorological Fields .....	8-4
8.2.1 EDAS .....	8-5
8.2.2 FNL .....	8-5
8.2.3 MM5.....	8-6
8.3 Trajectory-Based Analyses.....	8-7
8.3.1 ATAD Trajectories.....	8-7
8.3.2 HYSPLIT Trajectories .....	8-8
8.3.3 CAPITA Monte Carlo Trajectories.....	8-8
8.3.4 Ensemble Air-Mass History Analyses .....	8-9
8.3.5 Trajectory Mass Balance (TrMB).....	8-9
8.3.6 Forward Mass Balance Regression (FMBR) .....	8-12
8.4 Air Quality Simulation Modeling.....	8-14
8.4.1 CAPITA Monte Carlo .....	8-14
8.4.2 REMSAD .....	8-15
8.4.3 CMAQ.....	8-16
8.4.4 Synthesized REMSAD and CMAQ .....	8-18
8.5 Attribution Source Regions .....	8-18
8.6 Visualization of Spatial Patterns.....	8-21
9. EVALUATION OF SOURCE ATTRIBUTION METHODS .....	9-1
9.1 Evaluation of Simulations of Meteorological Fields.....	9-1
9.1.1 Evaluation of MM5 Surface Meteorology Simulations .....	9-2
9.1.2 Comparison of MM5, EDAS, and FNL Wind Fields to Radar Wind Profiler Measurements .....	9-5
9.1.3 Evaluation of REMSAD/MM5 Simulations of Precipitation and Clouds.....	9-9
9.2 Sensitivity of Trajectories to Wind Fields.....	9-13
9.2.1 Effect of Wind Field Choice .....	9-14
9.2.2 Effect of Trajectory Model Choice .....	9-15
9.2.3 Effect of Back Trajectory Start Height .....	9-16
9.2.4 Effect of Using FNL Winds in October .....	9-17
9.3 Evaluation of the Trajectory Mass Balance (TrMB) Method using Perfluorocarbon Tracer Measurements .....	9-17
9.4 Evaluation of the CAPITA Monte Carlo Model Using Perfluorocarbon Tracer Measurements .....	9-20

**Table of Contents (continued)**

	<u>Page</u>
9.5 Evaluation of the Forward Mass Balance Regression (FMBR) Method Using Perfluorocarbon Tracer Measurements.....	9-25
9.5.1 Retrieval of Tracer Release Locations and Rates.....	9-25
9.5.2 Source Apportionment of Tracer Concentrations .....	9-27
9.5.3 Discussion of FMBR Tracer Evaluation .....	9-28
9.6 Evaluation of the Tracer Mass Balance (TrMB) Method Using REMSAD-Modeled Sulfate Concentrations .....	9-28
9.7 Evaluation of the Forward Mass Balance Regression (FMBR) Method Using REMSAD-Modeled Sulfate Concentrations.....	9-32
9.8 Evaluation of REMSAD Simulations of Perfluorocarbon Tracers.....	9-34
9.9 Evaluation of REMSAD Simulations of SO <sub>2</sub> , and Sulfate Measurements.....	9-39
9.10 Evaluation of CMAQ Simulations of Perfluorocarbon Tracers .....	9-45
9.11 Evaluation of CMAQ Simulations of SO <sub>2</sub> , Sulfate, and Other Aerosol Components.....	9-51
9.11.1 Development of Base Case .....	9-51
9.11.2 Base Case Performance .....	9-53
9.11.3 Discussion of CMAQ-MADRID Performance .....	9-63
9.12 Synthesis Inversion – Merging Modeled Source Apportionment Results and Receptor Data .....	9-64
9.13 Conclusions Concerning Performance of the Source Attribution Methods .....	9-66
10. SOURCE ATTRIBUTIONS BY AMBIENT DATA ANALYSIS.....	10-1
10.1 Sulfur Attributions via TAGIT .....	10-1
10.2 Attribution of PM <sub>2.5</sub> Components via Exploratory Factor Analysis.....	10-3
10.3 Attribution of Big Bend Particulate Sulfur and Soil via EOF Analysis .....	10-7
10.4 Transport Patterns to Big Bend during Periods of High and Low Sulfur Concentrations.....	10-11
10.5 Attribution of Big Bend Particulate Sulfur via Trajectory Mass Balance (TrMB) .....	10-15
10.6 Attribution of Big Bend Sulfate via Forward Mass Balance Regression (FMBR).....	10-18
11. SOURCE ATTRIBUTIONS BY AIR QUALITY MODELING.....	11-1
11.1 Sulfate Attribution via REMSAD.....	11-1
11.2 Sulfate Attribution via CMAQ-MADRID.....	11-11
11.3 Refined Sulfate Attribution using Synthesized Modeling Approaches.....	11-17
12. ATTRIBUTION RECONCILIATION, CONCEPTUAL MODEL, AND LESSONS LEARNED .....	12-1
12.1 Introduction.....	12-1
12.2 Phase I: Tracer Screening and Evaluation .....	12-3
12.3 Phase II: Initial Application.....	12-5
12.4 Refined Attribution Approaches.....	12-8

## Table of Contents (continued)

	<u>Page</u>
12.5 Haze Source Attribution .....	12-12
12.6 Big Bend Haze Conceptual Model .....	12-15
12.7 Lessons Learned and Recommendations .....	12-19
12.7.1 Overall Design and Management .....	12-20
12.7.2 Field Measurements .....	12-21
12.7.3 Source Attribution Approaches .....	12-22
12.7.4 Results .....	12-24
 13. REFERENCES .....	 13-1
 APPENDIX.....	 CD-ROM disc on the last page of this report
A.1 Baylor University (2000). 1999 Executive Summary: Airborne Pollution Monitoring Services. ....	filename: A1_Baylor2000AircraftMeasurements.pdf
A.2 Cahill, T.A., et al. (2003). UC Davis DELTA Group Final report to BRAVO on the project – Very fine (0.26 > Dp > 0.09 µm) Silicon plus Sulfur as a Tracer of Coal Fired Power Plants during BRAVO. .....	filename: A2_Cahill2003UCDavisSiliconSulfur.pdf
A.3 Georgoulas, B. (2003). Was BRAVO Meteorology “Typical”? .....	filename: A3_Georgoulas2003Meteorology.pdf
A.4 Georgoulas, B., et al. (2003). Evaluation of the Reconstruction Equation at Big Bend during BRAVO & Using Factor Analysis to Relate Aerosol Concentrations to Light Extinction. .....	filename: A4_Georgoulas2003ReconEqFA.pdf
A.5 Kuhns, H., et al. (2003). Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study Emissions Inventory. .....	filename: A5_Kuhns2003EmissInv.pdf
A.6 Mercado, F., et al. (2004). Application of Factor Analysis to the BRAVO Dataset. ....	filename: A6_Mercado2004FactorAnalysis.pdf
A.7 Pun et al. (2004). Modeling Analysis of the Big Bend Regional Aerosol Visibility Observational (Bravo) Study. .....	filename: A7_Pun2004Modeling.pdf
A.8 Schichtel et al. (2004). Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study Results: Air Quality Data and Source Attribution Analyses Results from the National Park Service / Cooperative Institute for Research in the Atmosphere. .....	filename: A8_Schichtel2004CIRARReport.pdf
A.8.1 REMSAD Animations	
.....	filenames: A8_so2_oct1999.avi
.....	A8_so4_oct1999.avi
.....	A8_so4_clouds_oct1999.avi
.....	A8_winds_clouds_oct1999.avi

**Table of Contents (continued)**

	<u>Page</u>
A.8.2 Backward Trajectories	
..... <i>filename:</i> A8_Appendix4b_CAPITAMC_Trajectories.ppt	
..... A8_Appendix4c_HYSPLIT_Trajectories.ppt	
..... A8_Appendix4d_ATAD_Trajectories.ppt	
A.8.3 Daily Maps of Fine Particulate Sulfur Concentrations	
..... <i>filename:</i> A8_Appendix8b_DailySulfurPatterns.ppt	
A.9 Seaman, N.L.; and Stauffer, D.R. (2003). Final Report to Electric Power Research Institute Contract EP-P3883/C1886 for MM5 Modeling in support of the Big Bend Regional Aerosol and Visibility Observation Study (BRAVO). .... <i>filename:</i> A9_Seaman2003MM5Modeling.pdf	
A.10 Vukovich, J. (2002). Technical Report: Emissions Processing for the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study. ..... <i>filename:</i> A10_Vukovich2002EmissProcess.pdf	
A.11 Watson, T.B., et al. (2000). The Perfluorocarbon Tracer Releases during the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study. .... <i>filename:</i> A11_Watson2000Tracer.pdf	
Pitchford, M.L., et al. (2004). Big Bend Regional Aerosol and Visibility Observational Study Final Report. .... <i>filename:</i> BRAVOFinalReport9-04.pdf	

## List of Figures

		<u>Page</u>
Figure 1-1	Big Bend National Park five-year composite contributions to haze by components. ....	1-3
Figure 1-2	Quarterly aerosol contributions to light extinction averaged over five years (1998 – 2002). ....	1-4
Figure 1-3	Examples of geographic distribution of the fraction of time that air parcels spend during the five days prior to arriving at Big Bend National Park for the months of January, May, July and September based upon a five-year analysis period (1998 to 2002). ....	1-6
Figure 1-4	Monthly fractions of time that air parcels spend in a region prior to arrival at Big Bend, based on five-day back trajectory calculations for the five-year period from 1998 to 2002. ....	1-6
Figure 1-5	(Left) SO <sub>2</sub> emissions based on the 1999 BRAVO emissions inventory used in the REMSAD and CMAQ-MADRID modeling. ....	1-8
Figure 1-6	Contributions to haze by components during the BRAVO Study period. (LAC is light absorbing carbon.).....	1-9
Figure 1-7	Estimates by several data analysis and modeling methods of the study-period averaged percent contributions to particulate sulfate at Big Bend by U.S. and Mexico sources. ....	1-12
Figure 1-8	Smoothed daily estimates by source regions to particulate sulfate concentration (top plot) and fraction of total predicted particulate sulfate (bottom plot) at Big Bend during the study period. ....	1-13
Figure 1-9	Estimated contributions to light extinction by various particulate sulfate source regions. ....	1-15
Figure 1-10	Estimated contributions by particulate sulfate source regions to Big Bend light extinction levels for the 1/5 haziest days and the 1/5 least hazy days of the BRAVO Study period. ....	15
Figure 1-11	Fraction of time that air parcels spent during five-day trajectories for periods with the 20% highest concentrations of particulate sulfate compounds and for the periods with the 20% lowest concentrations of particulate sulfate compounds during the BRAVO Study period July through October 1999. ....	1-17
Figure 2-1	Location map of Big Bend National Park in southwestern Texas. ....	2-1
Figure 2-2	Texas and Mexico (above) and the terrain surrounding Big Bend National Park in western Texas and northern Mexico (below). ....	2-2
Figure 2-3	Map showing monitoring sites for preliminary visibility study. ....	2-4
Figure 2-4	Big Bend National Park five-year composite contributions to haze by components. ....	2-5
Figure 2-5	Big Bend extinction budget time plots of individual years. ....	2-6

**List of Figures (continued)**

	<u>Page</u>
Figure 3-1	Data recovery of 24-hr tracer sample data during the two periods when 24-hr tracer sampling took place. ....3-7
Figure 3-2	Network of 24-hour gas and aerosol sampling locations. ....3-9
Figure 3-3	Network of 6-hour gas and aerosol sampling locations. ....3-9
Figure 3-4	Upper-air meteorological sites. ....3-12
Figure 4-1	The BRAVO Study emission inventory was compiled for the shaded areas of the U.S. and Mexico shown here. ....4-2
Figure 4-2	Locations of offshore platforms included in the BRAVO Study emissions inventory. ....4-4
Figure 4-3	SO <sub>2</sub> emissions rates from the BRAVO Study emissions inventory are shown as proportional to the bar heights on the map. ....4-4
Figure 4-4	(Left) SO <sub>2</sub> emissions based on the 1999 BRAVO emissions inventory used in the REMSAD and CMAQ-MADRID modeling. ....4-9
Figure 5-1	Groups of BRAVO sampling sites that showed similar particulate matter behavior. ....5-2
Figure 5-2	Sulfate and SO <sub>2</sub> time series at K-Bar. ....5-2
Figure 5-3	Composition of PM <sub>2.5</sub> aerosol throughout Texas during the August 29-September 4, 1999, sulfate episode at Big Bend. ....5-3
Figure 5-4	Timelines of the PM <sub>2.5</sub> molar ratio of NH <sub>4</sub> <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup> and aerosol acidity at Big Bend National Park. ....5-8
Figure 5-5	Example of hourly fine sulfate and sulfur dioxide concentration measurements at Big Bend National Park. ....5-9
Figure 5-6	Example of light scattering coefficient measured at ambient humidity for particles below 2.5 μm, compared with measured hourly-averaged sulfate concentration, accumulation mode volume and light scattering coefficient, and coarse mode particle scattering, all derived from physical size distribution measurements. ....5-10
Figure 5-7	The n-alkane carbon preference index (CPI) for the BRAVO organic aerosol sample composites. ....5-11
Figure 5-8	Timelines of dry particulate matter volume concentrations (in μm <sup>3</sup> /cm <sup>3</sup> ) at Big Bend National Park for the accumulation and coarse modes, as computed from measured size distributions. ....5-13
Figure 5-9	Timeline of very fine (0.26 μm > D <sub>p</sub> > 0.09 μm) silicon (x 25) and sulfur concentrations at Big Bend National Park during August 1999. ....5-14

**List of Figures (continued)**

	<u>Page</u>
Figure 5-10	Comparisons of 12-hour averages of the photoacoustic light absorption measurements and the aethalometer black carbon measurements (top) and IMPROVE EC measurements (bottom) during the BRAVO Study. ....5-17
Figure 5-11	Comparison of hourly averaged black carbon and light absorption measurements during the BRAVO study time period of Figure 5-10. ....5-18
Figure 5-12	Average distribution of the measured components of extinction at Big Bend during the BRAVO Study period .....5-21
Figure 5-13	Frequencies of wind directions at three height ranges during July-October 1999, as measured by the BRAVO radar wind profilers. ....5-22
Figure 5-14	July 1999 monthly resultant winds at 850 mb (approximately 1500 m MSL), showing flow from the south in the Big Bend area. ....5-23
Figure 5-15	Surface weather map for 6 am CST on August 20, 1999. ....5-24
Figure 5-16	Surface weather map for 6 am CST on August 29, 1999. ....5-24
Figure 5-17	Surface weather map for 6 pm CST on September 11, 1999. ....5-25
Figure 5-18	Surface weather map for 6 pm CST on September 13, 1999. ....5-26
Figure 5-19	Time series of influence functions at 6-hr sampling sites for the Eagle Pass continuous tracer, ocPDCH. ....5-28
Figure 5-20	Time series of influence functions at 6-hr sampling sites for the Northeast Texas tracer, i-PPCH. ....5-28
Figure 5-21	Time series of influence functions at 6-hr sampling sites for the San Antonio tracer, PDCB. ....5-29
Figure 5-22	Time series of influence functions at 6-hr sampling sites for the Houston tracer, PTCH. ....5-29
Figure 5-23	Alternate day tracer PDCB versus continuous tracer ocPDCH influence functions at 6 hour sites for periods of timing tracer release (7/5/99- 9/13/99). ....5-30
Figure 5-24	Daytime only (8 am to 8 pm CDT) tracer PTCH versus continuous tracer ocPDCH influence functions at 6 hour sites for periods of timing tracer release (7/5/99- 9/13/99). ....5-31
Figure 5-25	Normalized ratio of PDCB to ocPDCH released from Eagle Pass at four monitoring sites. ....5-32
Figure 5-26	Distribution of estimated transport times of Eagle Pass tracers to 6-hour monitoring sites in each 6-hour period during the timing tracer study (7/5/99- 9/13/99). ....5-33

**List of Figures (continued)**

	<u>Page</u>
Figure 6-1	Comparison of sulfate and ammonium measurements by UC Davis and Colorado State University. ....6-1
Figure 6-2	Molar ratio of ammonium to sulfate as measured by UC Davis and Colorado State University during the BRAVO Study period. ....6-2
Figure 6-3	Nitrate concentrations at K-Bar as measured by UC Davis and Colorado State University during the BRAVO Study Period. ....6-3
Figure 6-4	Calculated contributions to haze by components of the aerosol during the BRAVO Study period. ....6-8
Figure 6-5	Comparison of extinction measured by the BIBE1 transmissometer and calculated from PM species concentrations. ....6-10
Figure 6-6	Comparison of extinction measured by the BBEP transmissometer (with additional lamp brightening adjustments) with that calculated from PM species concentrations. ....6-13
Figure 7-1	Comparison of wind roses for July 1995-1998 (left) and 1999 (right). ....7-2
Figure 7-2	Comparison of wind roses for August 1995-1998 (left) and 1999 (right). ....7-3
Figure 7-3	Comparison of wind roses for September 1995-1998 (left) and 1999 (right). ....7-3
Figure 7-4	Comparison of wind roses for October 1995-1998 (left) and 1999 (right). ....7-4
Figure 7-5	Residence times for July-October 1999 (left) and the five-year July-October average (right), for 10 and 1,500 meter back-trajectory starting heights at Big Bend. ....7-6
Figure 7-6	Differences in residence times between July-October 1999 and the five-year (1998-2002) July-October average for all three back trajectory starting elevations. ....7-7
Figure 7-7	Differences in residence times between July-October 1998, 2000, 2001, and 2002 and the five-year (1998-2002) July-October average for the 500m starting elevation. ....7-8
Figure 7-8	Big Bend extinction budget time plots of individual years. ....7-10
Figure 7-9	Big Bend National Park five-year composite contributions to haze by components. ....7-11
Figure 7-10	Means and standard deviations of concentrations of components of PM <sub>10</sub> at Big Bend National Park during four different averaging periods. ....7-12
Figure 7-11	Means and standard deviations of particle-caused light extinction estimated from concentrations of components of PM <sub>10</sub> at Big Bend National Park during four different averaging periods. ....7-14

**List of Figures (continued)**

	<u>Page</u>
Figure 7-12	Estimated relative contributions of various particulate matter components to particle-caused light extinction during four different averaging periods. ....7-15
Figure 7-13	Box plots of measured fine mass concentration frequency distributions during four different averaging periods. ....7-15
Figure 7-14	Box plots of measured coarse mass concentration frequency distributions during four different averaging periods. ....7-16
Figure 7-15	Box plots of ammonium sulfate concentration frequency distributions during four different averaging periods. ....7-17
Figure 7-16	Box plots of particle chemical extinction frequency distributions during four different averaging periods. ....7-18
Figure 8-1	Locations of the triply-nested MM5 domains, with grid resolutions of 36, 12, and 4 km. ....8-7
Figure 8-2	Source areas with map identification numbers used for Trajectory Mass Balance Modeling. ....8-11
Figure 8-3	Locations of 17 source areas composed of 100-km grid virtual sources used to track transport and dispersion in the Forward Mass Balance Regression method. ....8-13
Figure 8-4	Map of the REMSAD attribution source regions. ....8-19
Figure 8-5	The CMAQ-MADRID attribution source regions. ....8-20
Figure 8-6	Plumes of a conservative tracer, released from four sites within Texas, as simulated by the REMSAD air quality model (4 October 1999). ....8-21
Figure 8-7	Comparison of spatial patterns of observed sulfate (left) and simulated sulfate (right) (19 August 1999). ....8-22
Figure 8-8	Precipitating clouds (yellow), non-precipitating clouds (blue), wind vectors, and streamlines predicted by the MM5 weather model (1 October 1999). ....8-22
Figure 9-1	Comparisons of MM5 and EDAS wind direction frequencies versus radar wind profiler measurements, by level above ground, for July-September 1999 at Big Bend National Park. ....9-8
Figure 9-2	Comparisons of MM5 and EDAS wind direction frequencies versus radar wind profiler measurements, by level above ground, for July-September 1999 at Llano, Texas. ....9-10
Figure 9-3	Examples of REMSAD precipitation prediction and observed precipitation maps (for July 2, 1999). ....9-11
Figure 9-4	Examples of REMSAD predicted cloud cover and corresponding GOES satellite picture (for July 3, 1999). ....9-12

**List of Figures (continued)**

	<u>Page</u>
Figure 9-5	Examples of the effects of EDAS and MM5 wind fields on back trajectories produced by the CAPITA Monte Carlo model. ....9-15
Figure 9-6	Examples of the effect of start height on the trajectories produced by the HYSPLIT model with the EDAS wind field. ....9-16
Figure 9-7	The tracer release regions (shaded boxes) defined for the TrMB evaluation. ....9-18
Figure 9-8	Comparison of observed and modeled tracer concentrations, for the Eagle Pass, San Antonio, and Houston tracers, at Big Bend National Park over the duration of the study. ....9-22
Figure 9-9	Comparison of spatially-averaged observed and modeled tracer concentrations in southwest Texas (in the same format as Figure 9-8). ....9-23
Figure 9-10	FMBR reconstructions of the Eagle Pass and northeast Texas tracer release locations and rates. ....9-26
Figure 9-11	Average percentage source contributions to measured tracer at Big Bend, as estimated by FMBR (red) and as measured (blue). ....9-28
Figure 9-12	Scatter plots of REMSAD sulfate concentration attributions vs. number of endpoints for each of four large source areas using 5-day back trajectories from the CAPITA MC Model and MM5 winds. ....9-31
Figure 9-13	Example of the REMSAD-simulated dispersion of the four tracer plumes on 28 September 1999. ....9-35
Figure 9-14	Comparison of 24-hr three-site average REMSAD predictions (red) of the spatially-averaged concentrations in Big Bend National Park versus three-site average measurements (blue) for the continuous Eagle Pass tracer. ....9-36
Figure 9-15	Comparison of 24-hr three-site average REMSAD predictions (red) of the spatially-averaged concentrations in Big Bend National Park versus three-site average measurements (blue) for the northeast Texas tracer. ....9-37
Figure 9-16	Comparison of 24-hr three-site average REMSAD predictions (red) of the spatially-averaged concentrations in Big Bend National Park versus three-site average measurements (blue) for the San Antonio tracer. ....9-37
Figure 9-17	Comparison of 24-hr three-site average REMSAD predictions (red) of the spatially-averaged concentrations in Big Bend National Park versus three-site average measurements (blue) for the Houston tracer. ....9-38
Figure 9-18	Comparisons of observed (blue) and modeled (red) time series of 24-hr averaged concentrations of SO <sub>2</sub> , sulfate, and total sulfur at the K-Bar sampling site in Big Bend National Park. ....9-39
Figure 9-19	Smoothed REMSAD simulation of ground-level sulfate concentrations at 1700 CDT on 28 September 1999. ....9-43

**List of Figures (continued)**

	<u>Page</u>
Figure 9-20	Scatter plots of REMSAD 24-hr sulfur concentration predictions versus measured values at 37 BRAVO network locations over the full BRAVO Study period. ....9-45
Figure 9-21	Measured (top) and CMAQ-simulated (bottom) time series of NE Texas tracer concentrations (in ppq) at K-Bar. ....9-46
Figure 9-22	Measured (top) and CMAQ-simulated (bottom) time series of Eagle Pass PDCH tracer concentrations (in ppq) at K-Bar. ....9-47
Figure 9-23	Measured (top) and CMAQ-simulated (bottom) time series of Houston tracer concentrations (in ppq) at K-Bar. ....9-47
Figure 9-24	Measured (top) and CMAQ-simulated (bottom) time series of San Antonio tracer concentrations (in ppq) at K-Bar. ....9-48
Figure 9-25	Spatial distributions of mean normalized bias and mean normalized error in CMAQ-MADRID predictions of fine sulfate over the BRAVO network. ....9-55
Figure 9-26	Measured and simulated 24-hr SO <sub>2</sub> (top) and sulfate (bottom) concentrations at K-Bar. ....9-58
Figure 9-27	Measured and simulated daily SO <sub>2</sub> concentrations (top) and fine sulfate concentrations (bottom) at Big Thicket. ....9-59
Figure 9-28	Compositions of observed and simulated PM <sub>2.5</sub> at K-Bar, averaged over the duration of the BRAVO Study. ....9-62
Figure 10-1	Contour plot of locations of top 50 loadings scores for Factor 1 (Soils). ....10-4
Figure 10-2	Contour plot of locations of top 50 loadings scores for Factor 2 (Coal Burning). ....10-4
Figure 10-3	Contour plot of locations of top 50 loadings for Factor 3 (Undetermined source type). ....10-5
Figure 10-4	Contour plot of locations of top 50 loadings for Factor 4 (Smelting). ....10-5
Figure 10-5	Distribution of mean particulate sulfur concentrations over the portion of the study period when all sites had sufficiently complete data for EOF analysis. ....10-8
Figure 10-6	Composite of mean sulfur concentrations (ng/m <sup>3</sup> ) measured during September and October in 1996 (the preliminary study) and 1999 (the BRAVO Study). ....10-9
Figure 10-7	The four EOF analysis-derived spatial factors for particulate sulfur and their temporal weights during most of the BRAVO Study period. ....10-10
Figure 10-8	Air mass transport patterns to Big Bend during three particulate sulfur episodes. ....10-12

**List of Figures (continued)**

	<u>Page</u>
Figure 10-9	Residence time probability distributions showing transport pathways during high particulate sulfur days, based on the EDAS/FNL wind fields. ....10-13
Figure 10-10	Residence time probability distributions showing transport pathways during high particulate sulfur days, based on the BRAVO 36km MM5 wind fields. ....10-14
Figure 10-11	Residence time probability distributions showing transport pathways during low particulate sulfur days, based on the EDAS/FNL wind fields. ....10-15
Figure 11-1	Map of the REMSAD modeling domain and the four principal geographic regions to which sulfate at Big Bend National Park (red diamond) was attributed. ....11-2
Figure 11-2	REMSAD simulation of sulfate concentrations on 17 August 1999 at 1500 UTC using the full BRAVO emissions inventory. ....11-3
Figure 11-3	REMSAD simulation of sulfate concentrations from emissions in the Eastern U.S. source region on 17 August 1999 at 1500 UTC. ....11-4
Figure 11-4	REMSAD simulation of sulfate concentrations from emissions in the Mexican source region on 17 August 1999 at 1500 UTC. ....11-4
Figure 11-5	REMSAD simulation of sulfate concentrations from emissions in Texas on 17 August 1999 at 1500 UTC. ....11-5
Figure 11-6	REMSAD simulation of sulfate concentrations from emissions in the Western U.S. source region on 17 August 1999 at 1500 UTC. ....11-5
Figure 11-7	REMSAD simulation of sulfate concentrations attributable to sulfur concentrations defined along the modeling domain boundaries by the GOCART global model on 17 August 1999 at 1500 UTC. ....11-6
Figure 11-8	Observed and REMSAD-estimated sulfate concentrations at Big Bend and REMSAD-estimated contributions by source region (using the “emissions out” approach) for (a) the 4-month BRAVO Study period and (b-e) July through October, respectively. ....11-7
Figure 11-9	REMSAD-estimated relative attributions, of average sulfate concentrations at Big Bend for each source region (using the “emissions out” approach) for (a) the 4-month BRAVO Study period and (b-e) the months of July through October, respectively. ....11-8
Figure 11-10	Daily REMSAD attributions of sulfate concentrations at Big Bend to the four source regions and the GOCART boundary concentrations, based on the “emissions out” approach. ....11-9
Figure 11-11	Source regions used for CMAQ-MADRID sulfate attributions. No source attribution simulations were conducted for the open water Gulf of Mexico (red) region. ....11-12

**List of Figures (continued)**

	<u>Page</u>
Figure 11-12	CMAQ-MADRID average attribution of fine sulfate at K-Bar over the 4-month BRAVO Study period, expressed as ratios of estimated average regionally-attributed concentrations of sulfate to average total estimated sulfate. ....11-13
Figure 11-13	Daily CMAQ-MADRID attributions of sulfate concentrations (in $\mu\text{g}/\text{m}^3$ ) at Big Bend to the four source regions and the boundary concentrations. ....11-15
Figure 11-14	Study-period source attributions of fine sulfate (in $\mu\text{g}/\text{m}^3$ ) at K-Bar by the synthesized and original models. ....11-19
Figure 11-15	Synthesized REMSAD estimates of K-Bar sulfate source attributions for seven selected episodes. ....11-20
Figure 11-16	Synthesized CMAQ-MADRID estimates of K-Bar sulfate source attributions for seven selected episodes. ....11-21
Figure 11-17	Smoothed daily Synthesized CMAQ-MADRID attributions of sulfate at K-Bar. ....11-22
Figure 12-1	Simulated surface layer PTCH tracer concentrations (released from Houston TX) for October 12 <sup>th</sup> 1999 generated by REMSAD at 36km and 12km and by CMAQ at 12km. ....12-4
Figure 12-2	Smoothed daily BRAVO Estimates of contributions to Big Bend particulate sulfate by source region. ....12-12
Figure 12-3	Estimated contributions to light extinction by various particulate sulfate source regions. ....12-13
Figure 12-4	BRAVO Estimates of contributions by particulate sulfate source regions to Big Bend light extinction levels for the 1/5 haziest days and the 1/5 least hazy days of the BRAVO Study period. ....12-14
Figure 12-5	Big Bend National Park five-year composite contributions to haze by components. ....12-15
Figure 12-6	Big Bend extinction budget time plots for individual years. ....12-16
Figure 12-7	Monthly fractions of time that air parcels spend in a region prior to arrival at Big Bend in 1998 to 2002 are shown as solid bars, based on five-day back trajectory calculations. ....12-17
Figure 12-8	Percent of time that air parcels en route to Big Bend spent over various locations during five-day trajectories for periods with the 20% highest concentrations of particulate sulfate compounds at Big Bend (left) and for the periods with the 20% lowest concentrations of particulate sulfate compounds at Big Bend (right) during the BRAVO Study period of July through October 1999. ....12-19

## List of Tables

		<u>Page</u>
Table 3-1	Tracer release schedule first phase of study. ....	3-4
Table 3-2	Tracer release schedule for the second half of the study. ....	3-4
Table 3-3	PFT data uncertainty (RMS error) in parts per quadrillion and correlation coefficients for collocated measurements. ....	3-6
Table 3-4	Number of measurement sites by measurement type. ....	3-8
Table 3-5	Aerosol and tracer monitoring site abbreviations, names, latitude, longitude, elevation, and purpose. ....	3-10
Table 3-6	Specialized aerosol and gaseous measurements at Big Bend. ....	3-11
Table 3-7	Upper-air meteorological monitoring site locations and types. ....	3-13
Table 4-1	BRAVO Study emissions inventory data sources. ....	4-2
Table 4-2	Point source emissions data for Mexico. ....	4-3
Table 4-3	Surrogate types for the BRAVO modeling domains. ....	4-5
Table 5-1	Summary of fine mass component concentrations (in $\mu\text{g}/\text{m}^3$ ) at Big Bend National Park. ....	5-5
Table 5-2	Summary of coarse mass concentrations (in $\mu\text{g}/\text{m}^3$ ) at Big Bend National Park. ....	5-6
Table 5-3	Summary of measurements of particle absorption and scattering (in $\text{Mm}^{-1}$ ) at Big Bend National Park. ....	5-20
Table 5-4	Summary of tracer data at the 6-hour sampling sites. Shown are the percentage of observations with concentrations greater than 2 times analytical uncertainty, the 90th percentile influence function ( $\chi/Q$ ) in $10^{-11} \text{ s}/\text{m}^3$ , and the distance of the monitoring site from the tracer release location. ....	5-27
Table 6-1	Mass extinction efficiencies derived by Mie theory for PM measured at Big Bend National Park. ....	6-6
Table 6-2	Summary of extinction measurements and calculations. ....	6-7
Table 6-3	Summary of factor analysis results (Varimax rotation) for Big Bend $\text{PM}_{2.5}$ data. ....	6-11
Table 6-4	Multiple regression fits of factor scores and CM to BIBE1 transmissometer daily average $b_{\text{ext}}$ . ....	6-12
Table 6-5	Summary of results from regressing measured extinction ( $\text{Mm}^{-1}$ ) against extinction calculated using the IMPROVE equation. ....	6-13
Table 6-6	Multiple regression fits of factor scores and CM to BBEP daily average $b_{\text{ext}}$ . ....	6-14

**List of Tables (continued)**

	<u>Page</u>
Table 7-1	Monthly average temperature, RH, and $f(\text{RH})$ at Big Bend for hours with RH < 90%. ..... 7-1
Table 8-1	Summary of ensemble air mass history analysis methods. .... 8-9
Table 8-2	Names and map identification numbers for individual source areas composite source regions. .... 8-12
Table 8-3	Annual SO <sub>2</sub> emissions (units of million metric tons per year) from the BRAVO emissions inventory for area and point sources within the four attribution source regions of the REMSAD model domain (see Figure 8-4). ..... 8-19
Table 9-1	Ad hoc benchmarks of surface-layer meteorological model accuracy for air-quality applications (from Emery et al., 2001). .... 9-3
Table 9-2	Performance metrics for the 12-km and 36-km grid MM5 simulations over the area of the 12-km modeling domain. .... 9-4
Table 9-3	Comparison of modeled winds to radar wind profiler measurements for July-September 1999. .... 9-6
Table 9-4	Comparison of modeled winds to radar wind profiler measurements in October 1999. .... 9-7
Table 9-5	Example of the qualitative ratings of predicted and observed precipitation for the five regions, for the maps shown in Figure 9-3. .... 9-12
Table 9-6	Results of TrMB attribution of the tracer material that arrived at K-Bar from 9/17 to 10/28/99. .... 9-19
Table 9-7	Model performance statistics for the Monte Carlo simulation of tracer concentrations averaged over the Big Bend sites (San Vicente, K-bar and Persimmon Gap) and over all six-hour tracer sites (San Vicente, K-bar, Persimmon Gap, Marathon, Fort Stockton and Monahans Sandhills) for the entire 4-month study period. .... 9-24
Table 9-8	Performance of the FMBR method in estimating tracer release rates. .... 9-27
Table 9-9	Percent attributions of REMSAD-simulated sulfate by TrMB using MM5 winds and various trajectory models, compared to the corresponding REMSAD attributions in the two bottom rows show. .... 9-29
Table 9-10	Source attribution estimates from application of the FMBR method using a set of REMSAD-predicted sulfate concentrations, and comparison with a sample set of REMSAD source attributions. .... 9-33
Table 9-11	REMSAD model performance statistics for the four tracers. .... 9-38
Table 9-12	Performance statistics over the full BRAVO Study period for REMSAD simulations of SO <sub>2</sub> , sulfate, and total sulfur at the three sampling locations within Big Bend National Park. .... 9-40

**List of Tables (continued)**

	<u>Page</u>
Table 9-14	Intersite correlations of 24-hr average concentrations of SO <sub>2</sub> , sulfate, and total sulfur measured at the three Big Bend National Park monitoring sites. ....9-42
Table 9-15	Consolidated performance statistics over the full BRAVO Study period for REMSAD simulations of SO <sub>2</sub> , sulfate, and total sulfur at 37 BRAVO network measurement locations. ....9-44
Table 9-16	Performance of CMAQ at simulating tracer concentrations at K-Bar for all tracers released during the study. ....9-49
Table 9-17	Network-average CMAQ-MADRID SO <sub>2</sub> and fine SO <sub>4</sub> <sup>2-</sup> performance statistics for preliminary and final base case simulations. ....9-52
Table 9-18	CMAQ-MADRID performance for 24-hr averages of particulate matter components at K-Bar over the duration of the BRAVO study. ....9-53
Table 9-19	CMAQ-MADRID performance for 24-hr averages of particulate matter components over all BRAVO sites over the duration of the BRAVO study. ....9-54
Table 9-20	CMAQ-MADRID performance for sulfur species at the K-Bar site, BBNP, over the duration of the BRAVO study. ....9-57
Table 9-21	CMAQ-MADRID performance for sulfur species at the Big Thicket site over the duration of the BRAVO study. ....9-57
Table 9-22	CMAQ-MADRID performance for 24-hr concentrations at the K-Bar site over the duration of the BRAVO study. ....9-61
Table 9-23	Comparison of sulfate simulation performance of the synthesized REMSAD and CMAQ models at Big Bend over the period 9 July through 28 October 1999. ....9-65
Table 10-1	Average study-period TAGIT attributions of particulate sulfur, SO <sub>2</sub> , and total sulfur (± the standard errors of the means) to local source emissions. ....10-2
Table 10-2	Components with the most significant factor loadings for each factor of the regional data set. ....10-3
Table 10-3	Components with the most significant factor loadings for each factor of the Big Bend data set. ....10-6
Table 10-4	Relative attributions of median 24-hour particulate sulfur at Big Bend to each major source region by TrMB using various trajectory model/wind field combinations. ....10-16
Table 10-5	FMBR attribution results and performance statistics using MM5 and EDAS/FNL 10-day transport trajectories. ....10-19
Table 11-1	REMSAD source attributions of fine sulfate at the K-Bar site during seven selected episodes. ....11-11

**List of Tables (continued)**

	<u>Page</u>
Table 11-2	CMAQ-MADRID estimates of average source region contributions to sulfate concentrations (in $\mu\text{g}/\text{m}^3$ ) at K-Bar during each of the BRAVO Study period months and during the entire study. ....11-13
Table 11-3	Source region attributions of fine sulfate at K-Bar as estimated by CMAQ-MADRID for each month of the study period. ....11-14
Table 11-4	CMAQ source attributions of fine sulfate at the K-Bar site during seven selected episodes. ....11-16
Table 11-5	Source region attributions of fine sulfate at K-Bar as estimated by CMAQ-MADRID for the 20 days with the greatest relative underestimates and the 20 days with the greatest relative overestimates. ....11-17
Table 11-6	Relative study-period source attributions (in %) of fine sulfate at K-Bar by the synthesized and original models. ....11-18
Table 12-1	Estimates of Big Bend's relative sulfate source attributions (in percent) by the various air quality and receptor modeling techniques. ....12-6
Table 12-2	Estimates of Big Bend's relative sulfate source attributions (in percent) by the refined approaches. ....12-10

## List of Abbreviations and Acronyms

ACARS .....	Aircraft Communications Addressing and Reporting System
AGL .....	above ground level
AIM.....	Aerosol Inorganics Model
AP .....	accumulation potential
ARL.....	NOAA Air Resource Laboratory
ATAD .....	NOAA ARL's Atmospheric Transport and Dispersion model
$b_{\text{abs}}$ .....	coefficient of optical absorption (a measure of light absorption)
BBNP .....	Big Bend National Park
BC .....	black carbon
BEIS.....	Biogenic Emissions Inventory System
BELD .....	Biogenic Emissions Landcover Database
$b_{\text{ext}}$ .....	coefficient of optical extinction (a measure of light extinction)
BNL.....	Brookhaven National Laboratory
$b_{\text{sp}}$ .....	coefficient of optical scattering (a measure of light scattering by particles)
CAPITA .....	Center for Air Pollution Impact and Trend Analysis (Washington University, St. Louis, MO)
CASTNET.....	USEPA Clean Air Status and Trends Network
CEM.....	continuous emissions monitors
CENEPRED .....	Centro Nacional de Prevención de Desastres (Mexico's National Center for Disaster Prevention)
CJ .....	Ciudad Juarez
CM .....	coarse-particle mass
CMAQ.....	Models-3/Community Multiscale Air Quality model (simulates various chemical and physical processes that are thought to be important for understanding atmospheric trace gas transformations and distributions over urban and regional scales)
CMB.....	Chemical Mass Balance (a receptor model)
CMC.....	CAPITA Monte Carlo
COSPEC .....	correlation spectrometer
CPI .....	carbon preference index

**List of Abbreviations and Acronyms (continued)**

CSU.....	Colorado State University
D.....	normalized directional frequency
EC .....	elemental carbon
EDAS .....	Eta Data Assimilation System (collects data for input to the Eta weather forecast model)
EDGAR.....	Emission Database for Global Atmospheric Research
EI.....	emissions inventory
EOF .....	Empirical Orthogonal Function
EPS.....	Emissions Preprocessor System
ERG.....	Eastern Research Group
$f(RH)$ .....	relative humidity adjustment factor (adjusts the light scattering effect of sulfates and nitrates to account for particle growth caused by water vapor in the atmosphere)
FA .....	factor analysis
fL.....	femtoliter
FMBR .....	Forward Mass Balance Regression
GC/MS .....	gas chromatography with mass spectrometry
GDAS.....	Global Data Assimilation System
GEIA.....	Global Emissions Inventory Activity
GOCART .....	Global Ozone Chemistry Aerosol Radiation Transport global climate model
GOES .....	NOAA Geostationary Operational Environmental Satellites system
HCP.....	high conditional probability
HIP .....	high incremental probability
HRT.....	high condition residence time (residence time for transport during high concentration or haze level conditions, typically the top 10% to 20% of conditions)
HSC.....	high condition source contribution
HYSPLIT .....	Hybrid Single-Particle Lagrangian Integrated Trajectory model
IF .....	influence function
IMPROVE.....	Interagency Monitoring of Protected Visual Environments

**List of Abbreviations and Acronyms (continued)**

INE.....	Instituto Nacional de Ecología (Mexico's National Institute of Ecology)
INEGI.....	Instituto Nacional de Estadística Geografía e Informática
IPCC.....	Intergovernmental Panel on Climate Change
i-PPCH.....	perfluoro-iso-propylcyclo-hexane (a perfluorocarbon used as an artificial tracer)
LAC.....	light-absorbing carbon
LCP.....	low conditional probability
LIP.....	low incremental probability
LRT.....	low condition residence time (residence time for transport during low concentration or haze level conditions, typically the lowest 10% to 20% of conditions)
LSC.....	low condition source contribution
MADRID.....	Model for Aerosol Dynamics, Reaction, Ionization, and Dissolution (simulates atmospheric particulate matter)
MAE.....	mean absolute error
MCIP.....	Meteorology Chemistry Interface Processor, Meteorology- Chemistry Interface Processor
MDL.....	minimum detection limit
Mm <sup>-1</sup> .....	inverse megameter (1/1,000,000 meter; a light extinction measurement unit)
MM5.....	Pennsylvania State University/National Center for Atmospheric Research mesoscale model (a limited-area, nonhydrostatic, terrain- following sigma-coordinate model designed to simulate or predict mesoscale atmospheric circulation)
MMS.....	Minerals Management Service
MOAD.....	Outer Continental Activity Database
MOHAVE.....	Measurement of Haze and Visibility Effects
MOUDI.....	Micro-Orifice Uniform Deposit Impactor (a cascade impactor that collects size-fractionated aerosol particle samples for gravimetric and chemical analysis)
MRF.....	Medium Range Forecast model
N MX NEI.....	Mexico's national emissions inventory
NCEP.....	National Centers for Environmental Prediction

**List of Abbreviations and Acronyms (continued)**

NEI.....	National Emissions Inventory
ng.....	nanogram
NGO.....	non-governmental organization
NO.....	nitrogen oxide
NOAA.....	National Oceanic and Atmospheric Administration
NO <sub>x</sub> .....	oxides of nitrogen
NO <sub>y</sub> .....	sum of NO <sub>x</sub> + HNO <sub>3</sub> + HONO + PAN
NPS.....	National Park Service (part of the U.S. Department of the Interior)
OC.....	organic carbon
OCM.....	organic carbon mass concentration
OLS.....	ordinary least squares
OMC.....	organic carbon compounds
oPDCH.....	perfluoro-1,2-dimethylcyclohexane (a perfluorocarbon used as an artificial tracer)
ocPDCH.....	an isomer of oPDCH accounting for 45% (a perfluorocarbon used as an artificial tracer)
ORT.....	overall residence time
OSC.....	overall source contribution
PAVE.....	Package for Analysis and Visualization for Environmental data (a software application to visualize multivariate gridded environmental datasets)
PDCB.....	1,1,2,2,3,4-hexafluoro-3,4-bis(trifluoro-methyl) cyclobutane (a perfluorocarbon used as an artificial tracer)
PDF.....	probability density function
pg.....	picogram (10 <sup>-12</sup> g)
PM <sub>10</sub> .....	particulate matter with aerodynamic diameters smaller than 10 μm
PM <sub>2.5</sub> .....	particulate matter with aerodynamic diameters smaller than 2.5 μm
ppq.....	parts per quadrillion
PROFEPA.....	La Procuraduría Federal de Protección al Ambiente (Mexico's Program of Environmental Justice Procuration)
PTCH.....	perfluoro-1,3,5-trimethylcyclohexane (a perfluorocarbon used as an artificial tracer)

**List of Abbreviations and Acronyms (continued)**

r or R	correlation coefficient
$r^2$ or $R^2$	correlation coefficient squared, also coefficient of determination
RADM	Regional Acid Deposition Model
RASS	radio acoustic sounding system
READY	NOAA ARL's Real-Time Environmental Applications and Display System
REMSAD	Regional Modeling System for Aerosols and Deposition
RH	relative humidity
RMSE	root mean square error
RT	residence time
RWP	radar wind profiler
SC	source contribution
SEM	scanning electron microscopy
SEMARNAT	Secretaría de Medio Ambiente y Recursos Naturales (Mexico's Ministry of the Environment)
SMOKE	Sparse Matrix Operator Kernel Emissions model
SO <sub>2</sub>	sulfur dioxide
SO <sub>4</sub> or SO <sub>4</sub> <sup>-</sup> or SO <sub>4</sub> <sup>2-</sup>	sulfate
SSI	Spectral Statistical Interpolation
TAGIT	Tracer-Aerosol Gradient Interpretive Technique (uses tracer data from a monitoring network to distinguish sites impacted by a source tagged with artificial tracer from nonimpacted sites)
TCEQ	Texas Commission on Environmental Quality (formerly Texas Natural Resource Conservation Commission)
TJ	Tijuana
TOR	thermal/optical reflectance
TrMB	Tracer Mass Balance
TS	total sulfur (contributed by both SO <sub>2</sub> and SO <sub>4</sub> <sup>-</sup> )
UCD	University of California at Davis
URG	University Research Glassware
USEPA	U.S. Environmental Protection Agency

**List of Abbreviations and Acronyms (continued)**

UTC.....	Coordinated Universal Time (the international time standard; UTC is the current term for what was commonly referred to as Greenwich Meridian Time [GMT]; zero [0] hours UTC is midnight in Greenwich, England)
VIF .....	variance inflation factor (indicates the collinearity of a source area with all other source areas in TrMB analysis)
Vis5d.....	an OpenGL-based volumetric visualization program for scientific datasets in 3+ dimensions
WRAP.....	Western Regional Air Partnership
$\sigma_z$ .....	standard deviation of the vertical dispersion of a Gaussian plume for stable conditions