

**Spatial and Seasonal Patterns and Temporal Variability of Haze
and its Constituents in the United States
Report IV**

Principal Author:

Linsey J. DeBell¹

¹Cooperative Institute for Research in the Atmosphere

Colorado State University

Fort Collins, CO 80523-1375

Contributors:

Kristi A. Gebhart²

Jenny L. Hand¹

William C. Malm²

Marc L. Pitchford³

Bret A. Schichtel²

Warren H. White⁴

²National Park Service

CSU/CIRA

Fort Collins, CO 80523-1375

³National Oceanic and Atmospheric Administration

Desert Research Institute

Las Vegas, NV 89119-7363

⁴Crocker Nuclear Laboratory

University of California

Davis, CA 95616-8569

Disclaimer

The assumptions, findings, conclusions, judgments, and views presented herein are those of the authors and should not be interpreted as necessarily representing the National Park Service or National Oceanic and Atmospheric Administration policies.

TABLE OF CONTENTS

Overview and Summary	S-1
S.1 Optical and Aerosol Data	S-2
S.2 Spatial Trends in Aerosol Concentration and Extinction	S-6
S.3 Spatial Variability Of Average Monthly Patterns In Fine Aerosol Species Concentrations And Aerosol Extinction Coefficients.....	S-14
S.4 Temporal Trends in Fine Aerosol Species Concentrations and Aerosol Extinction	S-18
S.5 IMPROVE Data Quality Assurance.....	S-19
S.6 Special Studies Associated with the IMPROVE program	S-19
References.....	S-21
Chapter 1: IMPROVE Network – Purpose, Design, and History.....	1
1.1 Objectives of Visibility Monitoring under the IMPROVE Program.....	2
1.2 Overview of the IMPROVE Monitoring Network.....	4
1.2.1 Current and Historical Sampler Siting	4
1.2.2 Aerosol Sampling and Analysis	14
1.2.3 Optical Sampling and Analysis.....	20
1.3 Protocol and Equipment Changes	24
1.3.1 Analytical Changes	25
1.3.1.1. Transition from PIXE to XRF	25
1.3.1.2. Alternate Nylon Filter Extraction Procedure	25
1.3.2 Sampling Equipment Changes	26
1.3.2.1. Transition from Version I to Version II IMPROVE Sampler	26
1.3.2.2. Denuder Coating Modified	26
1.3.2.3. Changes in Nylon Filter Size	26
1.3.2.4. Changes in Nylon Filter Manufacturer	26
1.3.3 Data Processing Changes	27
1.3.3.1. Change in the Reporting of Gravimetric Measurements	27
1.3.3.2. Change in Batch Size Used in Data Processing Routines at CNL.....	27
1.3.3.3. Change in Flow Rate Validation Flag Definitions.....	27
1.3.3.4. Change in Flow Rate Calculations.....	27
1.3.3.5. Spectral Corrections to S and Al Data from the XRF Cu Anode System	28
1.3.3.6. Change in the Reporting of Organic Pyrolyzed Carbon (OP) Concentrations	28
1.4 The Comparison of Concentrations from Collocated IMPROVE and STN Monitoring Sites	29
References.....	31
Chapter 2: Spatial Distributions of Reconstructed Mass and Mass Budgets and Reconstructed Light Extinction and Light-Extinction Budgets	33
2.1 Estimation of Aerosol Species Mass	33
2.2 Reconstructing Light Extinction from Aerosol Measurements.....	36
2.2.1 Extinction Model.....	37

2.3	Completeness Criteria	41
2.4	Spatial Trends in Aerosol Concentrations in the United States	42
2.4.1	Fine Particle Ammonium Sulfate Mass	42
2.4.2	Fine Particle Carbon Mass	44
2.4.3	Fine Particle Ammonium Nitrate Mass.....	46
2.4.4	Fine Particle Soil Mass.....	47
2.4.5	Reconstructed Fine Mass	48
2.4.6	Coarse Mass	49
2.5	Spatial Trends in Particulate Extinction in the United States.....	63
2.5.1	Fine Particle Ammonium Sulfate Extinction	63
2.5.2	Fine Particle Carbon Extinction	64
2.5.3	Fine Particle Ammonium Nitrate Extinction	65
2.5.4	Fine Particle Soil Extinction	65
2.5.5	Coarse Mass Particle Extinction	66
2.5.6	Total Reconstructed Particulate Extinction (b_{ext}).....	67
2.5.7	Visibility Expressed in Deciviews	67
	References.....	80
Chapter 3: Spatial Variability of Average Monthly Patterns in Fine Aerosol Species Concentrations and Particulate Extinction Coefficients		
		86
3.1	Spatial Variability of Average Monthly Patterns in Fine Aerosol Species Concentrations...	87
3.1.1	Fine Particle Ammonium Sulfate Mass	87
3.1.2	Fine Particle Organic Carbon Mass	88
3.1.3	Fine Particle Light-Absorbing Carbon Mass	89
3.1.4	Fine Particle Ammonium Nitrate Mass.....	90
3.1.5	Fine Particle Soil Concentrations.....	91
3.2	Spatial Variability of Average Monthly Patterns in Particulate Extinction Coefficients	105
3.2.1	Fine Particle Ammonium Sulfate Extinction	105
3.2.2	Fine Particle Organic Carbon Extinction	106
3.3	Fine Particle Light-Absorbing Carbon Extinction	107
3.3.1	Fine Particle Ammonium Nitrate Extinction	107
3.3.2	Fine Particle Soil Extinction	108
3.3.3	Coarse Particle Mass Extinction	108
	References.....	119
Chapter 4: Temporal Trends in Fine Aerosol Species Concentrations and Aerosol Extinction. 120		
4.1	Estimating Measurement Uncertainty in an Ambient Sulfate Trend	120
4.2	A 10-Year Spatial and Temporal Trend of Sulfate across the United States	122
4.2.1	Introduction	122
4.2.2	Yearly Temporal Trends of the 20 th and 80 th Percentile $SO_4^{=}$ Concentrations	123
4.2.3	Yearly Temporal Trends of NET SO_2 Emissions	125
4.2.4	Regional Comparisons of SO_2 Emissions and $SO_4^{=}$ Concentrations	126
4.3	Trends in the Haze Index.....	127

4.4 Organic and Elemental Carbon Long-Term Trends and Spatial Patterns in the Rural United States	129
4.4.1 Introduction	129
4.4.2 EC and OC Long-Term Trends	130
4.5 VIEWS Annual Summary Trends Tools	133
References	135
Chapter 5: IMPROVE Data Quality Assurance	137
5.1 Overview of the IMPROVE Network’s Quality Assurance System and Data Validation Procedures Conducted by CIRA	137
5.1.1 Sampling and Analysis	138
5.1.2 Overview of the IMPROVE QA System	138
5.1.2.1 Roles and Responsibilities	138
5.1.2.2 Data Quality Objectives	139
5.1.2.2.1 Precision, Accuracy, and MQL/MDL	139
5.1.2.2.2 Completeness	139
5.1.2.2.3 Representativeness	139
5.1.2.2.4 Comparability	140
5.1.2.3 Documentation	140
5.1.3 Data Validation	140
5.1.3.1 Data Integrity Tests Performed at CIRA	141
5.1.3.2 Spatial and Temporal Comparability Checks Performed at CIRA	142
5.1.3.2.1 Mass	142
5.1.3.2.2 Sulfate	144
5.1.3.2.3 Soil Elements	149
5.1.3.2.4 Carbon	154
5.1.3.2.5 Nitrate	156
5.1.3.2.6 Cut Point	157
5.1.4 Examples of Data Quality Issues Discovered by CIRA in the 2004 Data	158
5.1.5 Glossary of Terms	164
5.1.6 Data Acquisition, Quality Control, and Data Management	165
5.1.6.1 A.1 Sample Handling	165
5.1.6.2 A.2 Sample Analysis	166
5.1.7 Data Validation Activities at CNL	168
5.1.7.1 Flow Rate Audits and Analysis Performed by CNL	168
5.1.7.2 Accuracy, Uncertainty, and MQL Checks on QC Samples Performed at CNL ..	169
5.1.7.3 Internal Consistency Checks Performed at CNL	170
5.1.7.3.1 Iron	170
5.1.7.3.2 Mass	170
5.1.7.3.3 Sulfate	170
5.1.7.3.4 Carbon	170
5.2 Outcomes from a Historical Review of IMPROVE Data	171

5.2.1	Introduction	171
5.2.2	Measured Fine Mass versus Reconstructed Fine Mass Review	171
5.2.3	Sulfate Review	171
5.2.4	Soil	172
5.2.5	Carbon	173
5.2.6	Nitrate	173
5.2.7	Cut Point	174
5.3	Nitrate Sampling Methods Investigation	175
5.3.1	Introduction	175
5.3.2	Methods	175
5.3.2.1.	Field Sites	175
5.3.2.2.	Sampling and Analysis Protocol for Filter Comparisons	175
5.3.2.3.	Sampling and Analysis Protocol for Denuder Comparisons	176
5.3.3	Conclusions	176
5.3.3.1.	Particulate Nitrate Measurement Using Nylon Filters	176
5.3.3.2.	Loss of Fine Particle Ammonium from Denuded Nylon Filters	177
5.3.3.3.	Efficiency of IMPROVE Network Denuders for Removing Nitric Acid	177
	References	178
Chapter 6: Special Monitoring Studies & Data Analyses Associated with the IMPROVE Program		179
6.1	Executive Summary: 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	180
6.1.1	Characterization of Big Bend's Haze	181
6.1.2	Apportionment of Big Bend's Sulfate Haze	183
6.1.2.1.	Spatial Patterns of Aerosol Components	185
6.1.2.2.	Airmass Transport to Big Bend during BRAVO Days with High and Low Particulate Sulfate Concentrations	185
6.1.2.3.	Quantitative Source Apportionment of Big Bend's Sulfate Haze	187
6.1.2.4.	The Contribution of Sulfur Source Regions to Particulate Haze Levels at Big Bend National Park during the BRAVO Study Period	190
6.1.3	Application of the Source Attribution Results to Other Months and Years	193
6.1.4	Implications	194
6.2	Executive Summary: The Yosemite Aerosol Characterization Study	196
6.2.1	Study Objectives	197
6.2.2	Study Findings	197
6.3	Executive Summary: Review of the IMPROVE Equation for Estimating Ambient Light Extinction Coefficients	203
6.3.1	Introduction	203
6.3.2	Particulate Organic Matter and the R_{oc} Multiplier	204
6.3.3	Scattering Enhancement Curve ($f(RH)$)	206

6.3.4	Sea Salt.....	207
6.3.5	Mass Scattering Efficiencies.....	208
6.3.6	Site-Specific Rayleigh Scattering.....	210
6.3.7	Light Absorption by NO ₂	210
6.3.8	New IMPROVE Equation.....	210
	References.....	212
6.4	Coarse Particle Speciation at Selected Locations in the Rural Continental United States ..	215
	Abstract.....	215
6.4.1	Introduction.....	215
6.4.2	Particulate Samplers.....	216
6.4.3	Estimation of Aerosol Mass.....	217
6.4.4	The Data Set.....	219
6.4.5	Spatial Variability of Coarse and Fine Monthly Patterns in Species Mass Concentrations	220
6.4.6	Summary	227
	References.....	229
6.5	The Comparability of IMPROVE and STN Measurements—A Summary of the Results and Conclusions from an Analysis of Collocated Measurements Detailed in Appendix E	238
	Chapter 7: Bibliography of Journal Articles using IMPROVE Data.....	241

Appendices A–E available on cd or at

http://vista.cira.colostate.edu/improve/Publications/improve_reports.htm

Appendix A: Annual Average Reconstructed Fine Mass and Aerosol Extinction Budgets for Each Site

Appendix B: Seasonal and Annual Regional Reconstructed Fine Mass and Reconstructed Extinction Budgets

Appendix C: Monthly and Annual Reconstructed Fine Mass and Reconstructed Extinction and their Associated Budgets from the IMPROVE Network for 2000 through 2004

Appendix D: Articles Reporting the Results from IMPROVE Special Monitoring Studies Conducted since 2000

Appendix E: An Assessment of Measurement Errors in the IMPROVE and STN Networks from In-Network and Cross-Network Collocated Data and the Estimated Comparability of Data Collected from the Two Networks

LIST OF FIGURES

Figure S.1. The locations current and discontinued IMPROVE and IMPROVE protocol monitoring sites as of December 2004. The IMPROVE regions used for grouping the sites in some analyses in this report are indicated by green shading and bold text. Urban sites included in the IMPROVE network for quality assurance purposes are identified by stars.	S-5
Figure S.2. Five-year average (2000–2004) deciview (DV) using only IMPROVE data.	S-8
Figure S.3. Five-year average (2000–2004) reconstructed particulate light extinction using only IMPROVE data.	S-9
Figure S.4. Five-year average (2000–2004) sulfate light scattering using only IMPROVE data.	S-9
Figure S.5. Five-year average (2000–2004) sulfate light scattering using IMPROVE and STN data.	S-10
Figure S.6. Five-year average (2000–2004) organic carbon light scattering using only IMPROVE data.	S-10
Figure S.7. Five-year average (2000–2004) organic carbon light scattering using IMPROVE and STN data.	S-11
Figure S.8. Five-year average (2000–2004) ammonium nitrate light scattering using only IMPROVE data.	S-11
Figure S.9. Five-year average (2000–2004) ammonium nitrate light scattering using IMPROVE and STN data.	S-12
Figure S.10. Five-year average (2000–2004) fine soil light scattering using only IMPROVE data.	S-12
Figure S.11. Five-year average (2000–2004) fine soil light scattering using IMPROVE and STN data. Note comparisons of collocated data indicate the STN fine soil concentrations and light scattering were typically 30% smaller than from the IMPROVE monitors.	S-13
Figure S.12. Five-year average (2000–2004) coarse mass light scattering using only IMPROVE data.	S-13
Figure S.13. Monthly particulate contributions to reconstructed b_{ext} (Mm^{-1}) for regions in the eastern United States using IMPROVE data (top) and STN data (bottom). Note, STN does not measure coarse mass.	S-15
Figure S.14. Monthly particulate contributions to reconstructed b_{ext} (Mm^{-1}) for regions in the southwestern United States using IMPROVE data (top) and STN data (bottom). Note, STN does not measure coarse mass.	S-16
Figure S.15. Monthly particulate contributions to reconstructed b_{ext} (Mm^{-1}) for regions in the northwestern United States using IMPROVE data (top) and STN data (bottom). Note, STN does not measure coarse mass.	S-17
Figure 1.1. All Class I areas of the contiguous United States are identified on the map. The color coding identifies the managing agency of each Class I area.	3
Figure 1.2. The locations of IMPROVE and IMPROVE protocol sites are shown for all discontinued and current sites as of December 2004. The IMPROVE regions used for grouping	

the sites in some analyses in this report are indicated by green shading and italicized text. Urban sites included in the IMPROVE network for quality assurance purposes are identified by stars. . 5

Figure 1.3. Schematic view of the IMPROVE sampler showing the four modules with separate inlets and pumps. The substrates with analyses performed for each module are also shown. 15

Figure 1.4. Schematic of a new version of the IMPROVE sampler PM_{2.5} module. 17

Figure 2.1. RH factors (f_T (RH)) derived from Tang’s ammonium sulfate growth curves smoothed between the crystallization and deliquescence points. 39

Figure 2.2. Isopleth maps of annual ammonium sulfate concentrations in panels a and b and percent contributions to reconstructed fine mass in panels c and d. Panels a–d include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites from 2000–2004. Panels b and d also include all sites from the STN network that met the prescribed completeness criteria. 52

Figure 2.3. Isopleth maps of annual total carbon concentrations. Panels a and b include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met the prescribed completeness criteria. 53

Figure 2.4. Isopleth maps of annual organic carbon concentrations in panels a and b and percent contributions to reconstructed fine mass in panels c and d. Panels a–d include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panels b and d also include all sites from the STN network that met the prescribed completeness criteria. 55

Figure 2.5. Isopleth maps of annual light-absorbing carbon concentrations in panels a and b and percent contributions to reconstructed fine mass in panels c and d. Panels a–d include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panels b and d also include all sites from the STN network that met the prescribed completeness criteria. 57

Figure 2.6. Isopleth maps of annual ammonium nitrate concentrations in panels a and b and percent contributions to reconstructed fine mass in panels c and d. Panels a–d include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panels b and d also include all sites from the STN network that met the prescribed completeness criteria. 59

Figure 2.7. Isopleth maps of annual soil concentrations in panels a and b and percent contributions to reconstructed fine mass in panels c and d. Panels a–d include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panels b and d also include all sites from the STN network that met the prescribed completeness criteria. 61

Figure 2.8. Isopleth maps of annual reconstructed fine mass concentrations. Panels a and b include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met the prescribed completeness criteria. 62

Figure 2.9. Isopleth map of annual coarse mass concentrations; includes all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004.....	63
Figure 2.10. Isopleth maps of annual ammonium sulfate extinction coefficients in panels a and b and percent contribution to reconstructed particulate extinction in panel c. Panels a, b, and c include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met prescribed completeness criteria.	69
Figure 2.11. Isopleth maps of annual organic mass by carbon extinction coefficients in panels a and b and percent contribution to reconstructed particulate extinction in panel c. Panels a, b, and c include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met prescribed completeness criteria.	71
Figure 2.12. Isopleth maps of annual light-absorbing carbon extinction coefficients in panels a and b and percent contribution to reconstructed particulate extinction in panel c. Panels a, b, and c include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met prescribed completeness criteria.	73
Figure 2.13. Isopleth maps of annual ammonium nitrate extinction coefficients in panels a and b and percent contribution to reconstructed particulate extinction in panel c. Panels a, b, and c include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met prescribed completeness criteria.	75
Figure 2.14. Isopleth maps of annual fine soil extinction coefficients in panels a and b and percent contribution to reconstructed particulate extinction in panel c. Panels a, b, and c include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Panel b also includes all sites from the STN network that met prescribed completeness criteria.	77
Figure 2.15. Isopleth maps of annual coarse mass extinction coefficients in panel a and percent contribution to reconstructed particulate extinction in panel b. Panels a and b include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004.....	78
Figure 2.16. Isopleth map of annual total reconstructed particulate extinction in panel a. Includes all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004. Rayleigh scattering was not included.....	79
Figure 2.17. Isopleth map of annual visibility in deciviews in panel a. Includes all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites for 2000–2004.....	79
Figure 3.1. Map of stacked bar charts of monthly mean concentrations ($\mu\text{g}/\text{m}^3$) of fine aerosol species in the northwestern U.S. regions of the IMPROVE network.....	93
Figure 3.2. Map of stacked bar charts of monthly mean concentrations ($\mu\text{g}/\text{m}^3$) of fine aerosol species in the northwestern U.S. regions of the STN network.	94

Figure 3.3. Map of stacked bar charts of monthly mean concentrations ($\mu\text{g}/\text{m}^3$) of fine aerosol species in the southwestern U.S. regions of the IMPROVE network.....	95
Figure 3.4. Map of stacked bar charts of monthly mean concentrations ($\mu\text{g}/\text{m}^3$) of fine aerosol species in the southwestern U.S. regions of the STN network.	96
Figure 3.5. Map of stacked bar charts of monthly mean concentrations ($\mu\text{g}/\text{m}^3$) of fine aerosol species in the eastern U.S. regions of the IMPROVE network.	97
Figure 3.6. Map of stacked bar charts of monthly mean concentrations ($\mu\text{g}/\text{m}^3$) of fine aerosol species in the eastern U.S. regions of the STN network.	98
Figure 3.7. Map of stacked bar charts of monthly percent contribution to reconstructed fine mass (%) of fine aerosol species in the northwestern U.S. regions of the IMPROVE network.....	99
Figure 3.8. Map of stacked bar charts of monthly percent contribution to reconstructed fine mass (%) of fine aerosol species in the northwestern U.S. regions of the STN network.	100
Figure 3.9. Map of stacked bar charts of monthly percent contribution to reconstructed fine mass (%) of fine aerosol species in the southwestern U.S. regions of the IMPROVE network.....	101
Figure 3.10. Map of stacked bar charts of monthly percent contribution to reconstructed fine mass (%) of fine aerosol species in the southwestern U.S. regions of the STN network.	102
Figure 3.11. Map of stacked bar charts of monthly percent contribution to reconstructed fine mass (%) of fine aerosol species in the eastern U.S. regions of the IMPROVE network.	103
Figure 3.12. Map of stacked bar charts of monthly percent contribution to reconstructed fine mass (%) of fine aerosol species in the eastern U.S. regions of the STN network.....	104
Figure 3.13. Map showing stacked bar charts of monthly distributions of particulate extinction coefficients for the northwestern U.S. regions of the IMPROVE network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, soil, and coarse mass are the order of presentation.	110
Figure 3.14. Map showing stacked bar charts of monthly distributions of fine particulate extinction coefficients (Mm^{-1}) for the northwestern U.S. regions of the STN network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, and soil are the order of presentation. Coarse mass measurements were not available for STN and so are not included.	111
Figure 3.15. Map showing stacked bar charts of monthly distributions of particulate extinction coefficients (Mm^{-1}) for the southwestern U.S. regions of the IMPROVE network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, soil, and coarse mass are the order of presentation.....	112
Figure 3.16. Map showing stacked bar charts of monthly distributions of fine particulate extinction coefficients (Mm^{-1}) for the southwestern U.S. regions of the STN network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, and soil are the order of presentation. Coarse mass measurements were not available for STN and so are not included.	113
Figure 3.17. Map showing stacked bar charts of monthly distributions of particulate extinction coefficients (Mm^{-1}) for the eastern U.S. regions of the IMPROVE network. Starting from the	

base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, soil, and coarse mass are the order of presentation.	114
Figure 3.18. Map showing stacked bar charts of monthly distributions of fine particulate extinction coefficients (Mm^{-1}) for the eastern U.S. regions of the STN network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, and soil are the order of presentation. Coarse mass measurements were not available for STN and so are not included.....	115
Figure 3.19. Map showing stacked bar charts of monthly percent contribution to reconstructed particulate extinction (%) for particulate extinction coefficients for the northwest U.S. regions of the IMPROVE network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, soil, and coarse mass are the order of presentation.....	116
Figure 3.20. Map showing stacked bar charts of monthly percent contribution to reconstructed particulate extinction (%) for particulate extinction coefficients for the southwest U.S. regions of the IMPROVE network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, soil, and coarse mass are the order of presentation.....	117
Figure 3.21. Map showing stacked bar charts of monthly percent contribution to reconstructed particulate extinction (%) for particulate extinction coefficients for the eastern U.S. regions of the IMPROVE network. Starting from the base of the chart, ammonium sulfate, organics, light-absorbing carbon, ammonium nitrate, soil, and coarse mass are the order of presentation.....	118
Figure 4.1. Ratio of 24-hour sulfate concentrations measured by collocated and routine IMPROVE B modules at Big Bend NP.	121
Figure 4.2. Summary of the results of Theil regressions for the 80 th percentile SO_4^{2-} (3*S for IMPROVE program) concentrations from 1989 to 1999. Solid up or down arrows show which sites have trends with a significance level of at least 10%. Arrows with enclosed hatch lines show whether the trend was up or down but not statistically significant. Arrows with a bar across the tail represent CASTNet sites, while arrows without the bar show IMPROVE monitoring sites. The numbers are the percent changes from the overall median of the 80th percentile.....	124
Figure 4.3. Summary of the results of Theil regressions for the 20 th percentile SO_4^{2-} (3*S for IMPROVE program) concentrations from 1989 to 1999. Solid up or down arrows show which sites have a trend with a significance level of at least 10%. Arrows with enclosed hatch lines show whether the trend was up or down but not statistically significant. Arrows with a bar across the tail represent CASTNet sites, while arrows without the bar show IMPROVE monitoring sites. The numbers are the percent changes from the overall median of the 20th percentile.....	125
Figure 4.4. The percent change in the NET SO_2 emissions for each state in the conterminous United States from 1990 through 1999. The light gray states have decreasing trends, while the dark gray states have increasing trends. States without hatch marks have trends that are significant with two-sided P values below 0.1. The percent changes were calculated by dividing the change in emissions over the 10-year period by the 1990 emissions estimated from the trend line. The 1999 SO_2 emission rates for each state are in parentheses.	126

Figure 4.5. Comparison of the 80th percentile SO_4^{2-} concentrations (3*S for IMPROVE program) and NET SO_2 emissions aggregated over northeastern, southeastern, south-middle, and western United States regions. In each plot the SO_4^{2-} and SO_2 emission scales have a factor of 3 change between the low and high values. 127

Figure 4.6. Their trends in the haze index of the annual average 20% best visibility days. 128

Figure 4.7. Their trends in the haze index of the annual average 20% worst visibility days. 129

Figure 4.8. The wintertime elemental carbon trend using IMPROVE data from monitoring sites with a minimum of 7 years of data. The triangles indicate a increasing (up) or decreasing (down) trend, and black arrows have a significant trend at the 0.05 level. The isopleths are the slope of the trend line as the % change from the median EC concentration per 10 years. 130

Figure 4.9. The wintertime organic carbon trend using IMPROVE data from monitoring sites with a minimum of 7 years of data. 131

Figure 4.10. The summertime elemental carbon trend using IMPROVE data from monitoring sites with a minimum of 7 years of data. 132

Figure 4.11. The summertime organic carbon trend using IMPROVE data from monitoring sites with a minimum of 7 years of data. 133

Figure 5.1. An example of the data validation charts from the fall 2004 report. Reconstructed fine mass concentrations, measured fine mass, and the reconstructed fine mass to measured fine mass concentration ratios are shown for the 2001–2004 time period at BIBE1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 144

Figure 5.2. An example of the data validation charts from the fall 2004 report. Sulfate concentrations, sulfur concentrations, and the sulfate to sulfur concentration ratios are shown for the 2001–2004 time period at OLYM1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 147

Figure 5.3. An example of the data validation charts from the fall 2004 report. Z scores calculated from the sulfate and sulfur concentrations and reported uncertainties are shown for the 2001–2004 time period at OLYM1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 148

Figure 5.4. The percentage of valid sample pairs with significant disagreement between SO_4^{2-} and 3*S are calculated for each month. This provides a way of tracking 1) the overall magnitude of the number of sample pairs with poor agreement relative to the number of samples collected, as well as 2) the direction of bias at the network level. 149

Figure 5.5. An example of the data validation charts from the fall 2004 report. Aluminum concentrations, iron concentrations, and the aluminum to iron enrichment factors are shown for the 2001–2004 time period at DENA1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 150

Figure 5.6. An example of the data validation charts from the fall 2004 report. Calcium concentrations, iron concentrations, and the calcium to iron enrichment factors are shown for the 2001–2004 time period at DENA1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 151

Figure 5.7. An example of the data validation charts from the fall 2004 report. Silicon concentrations, iron concentrations, and the silicon to iron enrichment factors are shown for the 2001–2004 time period at DENA1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 152

Figure 5.8. An example of the data validation charts from the fall 2004 report. Titanium concentrations, iron concentrations, and the titanium to iron enrichment factors are shown for the 2001–2004 time period at DENA1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 153

Figure 5.9. An example of the data validation charts from the fall 2004 report. Soil concentrations, the A module cut point and the soil to reconstructed mass concentration ratios are shown for the 2001–2004 time period at DENA1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 154

Figure 5.10. An example of the data validation charts from the fall 2004 report. Organic carbon concentrations, elemental carbon concentrations, and the organic carbon to elemental carbon concentration ratios are shown for the 2001–2004 time period at YOSE1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 155

Figure 5.11. An example of the data validation charts from the fall 2004 report. OMC concentrations, OMH concentrations, and the OMH to OMC concentration ratios are shown for the 2001–2004 time period at ACAD1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 156

Figure 5.12. An example of the data validation charts from the fall 2004 report. Nitrate concentrations, reconstructed fine mass concentrations, and the ammonium nitrate to reconstructed fine mass concentration ratios are shown for the 2001–2004 time period at ACAD1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 157

Figure 5.13. An example of the data validation charts from the fall 2004 report. Equation 3 in section 5.1.7 is used to calculate the A, B, and C module cut points from the reported flow rates. The cut points for the A, B, and C modules are shown for the fall–December 2004 data delivery batch at VOYA2. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 158

Figure 5.14. An example of the flow rate problem discovered in the data validation charts from the fall 2004 report. Equation 3 in section 5.1.7 is used to calculate the A, B, and C module cut points from the reported flow rates. The cut points for the A, B, and C modules are shown for the fall–December 2004 data delivery batch at HOOV1. Definitions of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 160

Figure 5.15. An example of the data validation charts from CNL (a) and from CIRA’s summer 2004 report (b). Panel a shows sulfate and three times sulfur concentrations for summer 2004 at CHAS1. Panel b shows sulfate concentrations, sulfur concentrations, and the sulfate to sulfur concentration ratios for 2001–2004 at CHAS1. While the incomplete sampling on the A module is obvious in panel b, the sulfate to sulfur discrepancies in panel a do not look similarly alarming. The sampling problem, which is obvious starting in early 2003, was not caught until the 2004 data were examined at CIRA and was not fully acted upon until the summer of 2004. Definitions

of all terms used in the axis titles can be found in the glossary in section 5.1.5 of this document. 163

Figure 5.16. The plot shows the 50% cut point as a function of flow rate as determined by two separate collection efficiency tests. The collection efficiency of the IMPROVE cyclone was characterized at the Health Sciences Instrumentation Facility at the University of California at Davis. The efficiency was measured as a function of particle size and flow rate using two separate methods: PSL and SPART. The PSL method uses microspheres of fluorescent polystyrene latex particles (PSL) produced by a Lovelace nebulizer and a vibrating stream generator and analyzed by electron micrographs. The SPART method uses a mixture of PSL particles produced by a Lovelace nebulizer and analyzed by a single particle aerodynamic relaxation time (SPART) analyzer. The aerodynamic diameter for 50% collection, d_{50} , was determined for each flow rate. 168

Figure 6.1. A terrain map of Texas and Mexico as well as some major cities and points of interest from the BRAVO study. 181

Figure 6.2. Big Bend’s particulate light extinction budget during BRAVO. 182

Figure 6.3. Big Bend National Park five-year light extinction budget. All days with that fall on the same day of the year were averaged together, then the data were smoothed using a 15-day moving average. 183

Figure 6.4. (Left) SO_2 emissions based on the 1999 BRAVO emissions inventory used in the REMSAD and CMAQ-MADRID modeling. No emissions were included beyond the black outline shown in the figure. Mexico City and Popocatepetl volcano emissions are located in the three most southern emission grid cells. 184

Figure 6.5. Fraction of time that air parcels spent during ten-day trajectories for periods with the a) 20% highest concentrations of particulate sulfate compounds and b) for the periods with the 20% lowest concentrations of particulate sulfate during the BRAVO study period July through October 1999. 186

Figure 6.6. Airmass transport patterns to Big Bend, TX, during three sulfate episodes. Each isopleth shows the most likely pathway the airmass traversed prior to impacting Big Bend. 187

Figure 6.7. 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. TAGIT only attributed the Carbón power plants, while CMAQ and Synthesized CMAQ attribution did not distinguish Carbón from Mexico. 189

Figure 6.8. 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. 190

Figure 6.9. Estimated contributions to particulate haze by various particulate sulfate source regions. The top plot shows the absolute haze contributions by the various particulate sulfate sources as well as the total particulate haze level (black line). The bottom plot shows the fractional contribution to haze by the various sources. 191

Figure 6.10. Estimated contributions by particulate sulfate source regions to Big Bend particulate haze levels for the 20% haziest days and the 20% least hazy days of the BRAVO study period. 192

Figure 6.11. 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).....	194
Figure 6.12. Annual variation of organic carbon mass concentrations in the fine mode of the aerosol (PM _{2.5}), from data obtained from the IMPROVE database (http://vista.cira.colostate.edu/views/). A measure of interannual variability is indicated by the yellow shaded area, which envelops one standard deviation in the data. Blue lines indicate the fraction of fine particulate mass concentration apportioned to organic carbon over the long-term average and for 2002.....	196
Figure 6.13. Fine mass concentrations reconstructed from individual species concentration measurements, plotted against fine mass concentrations determined by gravimetry (weighing of filters). Reconstructions are shown for two assumptions regarding the elemental-to-molecular mass conversion for organic carbon.	198
Figure 6.14. PM ₁₀ aerosol mass concentrations reconstructed from individual species concentration measurements, for the Turtleback Dome and Valley Floor sites.	199
Figure 6.15. Reconstructed, study-averaged extinction budget at Turtleback Dome. All species except coarse mass are in the fine aerosol mode.	200
Figure 6.16. MODIS image (August 18) of smoke from fires (red areas) in Oregon and in Sequoia National Park transported into California's Central Valley.....	201
Figure 6.17. Study-averaged source contributions of fine aerosol organic carbon (expressed as % of OC) at Turtleback Dome.	202
Figure 6.18. Annual mean value of R_{oc} multiplier derived from an ordinary least square multi-linear regression analysis.	206
Figure 6.19. Map of the mean ammonium sulfate mass scattering efficiency ($m^2 g^{-1}$). The size of the circle reflects the magnitude of the efficiency, which is printed near the circle.....	209
Figure 6.20. Map of the mean POM mass scattering efficiency ($m^2 g^{-1}$). The size of the circle reflects the magnitude of the efficiency, which is printed near the circle.	209
Figure 6.21. Scatter plot of gravimetric and reconstructed fine mass. An ordinary least square slope with the intercept set equal to 0 is 1.03 ± 0.004 with an $R^2 = 96$	232
Figure 6.22. Scatter plot of gravimetric and reconstructed coarse mass. An ordinary least square slope with the intercept set equal to 0 is 0.95 ± 0.01 with an $R^2 = 81$	233
Figure 6.23. A map of stacked bar charts showing the fine mass concentration of each species at each of the nine locations at which measurements were made. The continuous lines are running averages of the data collected historically at each monitoring site.....	234
Figure 6.24. A map of stacked bar charts showing the coarse mass concentration of each species at each of the nine locations at which measurements were made. The continuous lines are running averages of the data collected historically at each monitoring site.	235
Figure 6.25. A map of stacked bar charts showing the fractional contribution of each fine mass species to gravimetric mass at each of the nine locations at which measurements were made..	236

Figure 6.26. A map of stacked bar charts showing the fractional contribution of each coarse mass species to gravimetric mass at each of the nine locations at which measurements were made. The stacked bar chart for the month of January is not shown for Sequoia National Park because of a large uncertainty in PM_{10} gravimetric mass. 237

LIST OF TABLES

Table S.1. IMPROVE monitoring sites listed according to region. The monitoring site codes are in parentheses.....	S-2
Table 1.1. Discontinued and current IMPROVE particulate monitoring sites. The site groupings are displayed in Figure 1.2.....	6
Table 1.2. Class I areas and the representative monitoring site.....	11
Table 1.3. Sites with a fifth collocated module.	17
Table 1.4. Transmissometer receiver and transmitter locations.	21
Table 1.5. IMPROVE nephelometer network site locations.....	23
Table 1.6. Major network-wide changes in sampling, analysis and data reporting.....	28
Table 1.7. Comparison of annual average concentrations between collocated IMPROVE and STN monitoring sites.	30
Table 2.1. IMPROVE equations.	35
Table 4.1. Five-year trends in measurement differences at Shenandoah NP.....	121
Table 4.2. Important differences between samplers deployed in the CASTNet and IMPROVE networks.....	123
Table 5.1. Data validation levels as defined by IMPROVE.	140
Table 5.2. Flow rate-related validation flag definitions and application criteria.....	169
Table 6.1. Site description.	216
Table 6.2. Assumed molecular forms of each particulate species and method of estimation used.	217
Table 6.3. Statistical summary of all fine mass and fine mass species concentrations.	219
Table 6.4. Statistical summary of all coarse mass and coarse mass species concentrations.	219
Table 6.5. Statistical summary of annual fine mass and fine mass species concentrations by site.	220
Table 6.6. Statistical summary of annual coarse mass and coarse mass species concentrations by site.	222