

SPATIAL AND SEASONAL PATTERNS AND TEMPORAL VARIABILITY OF HAZE AND ITS CONSTITUENTS IN THE UNITED STATES

REPORT III

Principal Author: William C. Malm¹

Authors by Chapter

Overview and Summary: William C. Malm¹

Chapter 1: Marc L. Pitchford² and Mark Scruggs¹

Chapter 2: James F. Sisler³

Chapter 3: James F. Sisler³ and William C. Malm¹

Chapter 4: Rodger Ames³

Chapter 5: James F. Sisler³, William C. Malm¹, Scott Copeland³ and Kristi A. Gebhart¹

Chapter 6: William C. Malm¹ and Derek E. Day³

¹National Park Service

²National Oceanic and Atmospheric Administration

³CIRA

Cooperative Institute for Research in the Atmosphere
Colorado State University
Fort Collins, CO 80523

May 2000

ACKNOWLEDGEMENTS

This report is the result of a collaborative effort involving the authors and a number of other individuals. We thank Dr. Lowell Ashbaugh and his staff at the University of California at Davis for their efforts in managing the IMPROVE aerosol monitoring network, managing the aerosol database, and providing input to the report concerning aerosol sampling and analysis. We thank Mr. John Molenaar and Dr. David Dietrich of Air Resource Specialists in Fort Collins, Colorado for management of the IMPROVE visibility monitoring network, supplying the optical and relative humidity data, and for their input to this report. We also wish to thank Ms. Becky Burke for editing and formatting and Mr. Jeff Lemke for graphical presentation. In addition, we thank the reviewers: Dr. Marc Pitchford, Chief of Applied Sciences Branch, National Oceanic and Atmospheric Administration; Dr. Mark Scruggs, Chief Research Branch, National Park Service; Ms. Kristi Heuer, Fish and Wildlife Branch, Air Resources Division, National Park Service; Mr. Dan Ely, Air Pollution Control Division, State of Colorado; and Drs. Lowell Ashbaugh and Robert Eldred, Crocker Nuclear Laboratory, University of California at Davis.

DISCLAIMER

The assumptions, findings, conclusions, judgements, and views presented herein are those of the authors and should not be interpreted as necessarily representing official National Park Service policies.

TABLE OF CONTENTS

<u>Chapter</u>		<u>Page</u>
	OVERVIEW AND SUMMARY	
S.1	OPTICAL AND AEROSOL DATA	S-2
S.2	SPATIAL DISTRIBUTION OF AEROSOL CONCENTRATION AND CHEMICAL COMPOSITION	S-4
S.3	SPATIAL DISTRIBUTION OF RECONSTRUCTED LIGHT EXTINCTION AND SPECIES CONTRIBUTIONS	S-5
S.4	SEASONAL DISTRIBUTION OF FINE MASS AND RECONSTRUCTED LIGHT EXTINCTION	S-11
S.5	CONTRIBUTION OF AEROSOL SPECIES TO PERIODS OF HIGH AND LOW (EXTREMES) FINE MASS CONCENTRATIONS	S-14
S.6	TEMPORAL TRENDS IN VISIBILITY AND AEROSOL CONCENTRATIONS	S-15
S.7	DIURNAL TRENDS IN SCATTERING AND EXTINCTION	S-16
S.8	RECOMMENDED FUTURE RESEARCH	S-17
S.9	REFERENCES	S-18
1	IMPROVE NETWORK - CURRENT AND FUTURE CONFIGURATIONS	
1.1	INTRODUCTION	1-1
1.2	CURRENT NETWORK	1-3
	1.2.1 Particulate Samplers	1-3
	1.2.2 Network Configuration	1-4
1.3	FUTURE NETWORK CONFIGURATION	1-7
	1.3.1 Site Selection Process	1-7
	1.3.1.1 Representative Monitoring for Regional Haze	1-9
	1.3.1.2 Identification of CIA Clusters	1-10
	1.3.1.3 Selecting New Sites	1-13
	1.3.2 Protocol and Equipment Changes	1-14
1.4	CURRENT REPORT OBJECTIVES	1-16
1.5	REFERENCES	1-17
2	AEROSOL MASS BUDGETS AND SPATIAL DISTRIBUTIONS	
2.1	DETERMINATION OF AEROSOL SPECIES MASS	2-1
2.2	ENSEMBLE AVERAGES	2-3
2.3	SPATIAL TRENDS IN AEROSOL CONCENTRATIONS	2-4
2.4	CHARACTERISTICS OF THE REGIONS	2-5
2.5	SPATIAL TRENDS IN AEROSOL CONCENTRATIONS IN THE UNITED STATES	2-15
	2.5.1 PM ₁₀ Aerosol	2-15
	2.5.2 Fine Aerosol	2-16
	2.5.3 Coarse Aerosol	2-17
	2.5.4 Fine Sulfate Aerosol	2-17

	2.5.5	Fine Nitrate Aerosol	2-18
	2.5.6	Fine Organic Aerosol	2-21
	2.5.7	Fine Light-Absorbing Carbon Aerosol	2-21
	2.5.8	Fine Soil Aerosol	2-21
2.6		SUMMARY	2-21
2.7		REFERENCES	2-25
3		SPATIAL DISTRIBUTIONS OF RECONSTRUCTED LIGHT EXTINCTION AND LIGHT-EXTINCTION BUDGETS	
	3.1	RECONSTRUCTING LIGHT EXTINCTION FROM AEROSOL MEASUREMENTS	3-1
	3.2	RECONSTRUCTED LIGHT EXTINCTION AND LIGHT- EXTINCTION BUDGETS	3-8
	3.2.1	Characteristics of the Regions	3-8
	3.2.2	Spatial Trends in Reconstructed Light Extinction in the United States	3-22
	3.2.3	Spatial Trends in Visibility in the United States	3-30
	3.3	SUMMARY	3-34
	3.4	REFERENCES	3-35
4		FINE PARTICLE MASS CONCENTRATION FREQUENCY DISTRIBUTIONS	
	4.1	DATA	4-1
	4.2	RESULTS AND DISCUSSION	4-2
	4.2.1	Fine Mass Frequency Distributions	4-2
	4.2.2	Maps of Chemical Species Contributions to Fine Mass (1994-1998)	4-8
	4.3	SUMMARY	4-14
	4.4	REFERENCES	4-15
5		TRENDS ANALYSIS	
	5.1	SELECTED EXAMPLES OF TRENDS IN FINE MASS PM _{2.5} AND DECIVIEW	5-12
	5.2	TRENDS IN PM _{2.5} AND DECIVIEW ACROSS THE UNITED STATES	5-14
	5.3	SEASONAL TRENDS IN FINE MASS AND EXTINCTION	5-24
	5.4	DIURNAL TRENDS IN RELATIVE HUMIDITY AND SCATTERING AND EXTINCTION	5-27
	5.4.1	Most Common Patterns	5-27
	5.4.1.1	Gila Cliff Dwelling National Monument/Gila Wilderness Area, New Mexico	5-30
	5.4.1.2	Lone Peak Wilderness Area, Utah	5-31
	5.4.1.3	San Geronio Wilderness Area, California	5-31
	5.4.1.4	Yosemite National Park, California	5-33
	5.4.1.5	Alpine Lake Wilderness Area at Snoqualmie Pass, Washington	5-34

	5.4.1.6 Great Smoky Mountains National Park, Tennessee	5-36
	5.4.1.7 Boundary Waters Canoe Area, Minnesota	5-37
5.5	REFERENCES	5-38
6	SPECIAL STUDIES	
6.1	GREAT SMOKY MOUNTAINS STUDY	6-2
6.1.1	Experimental Methods	6-3
6.1.1.1	Humidograph	6-3
6.1.1.2	Integrating Nephelometers	6-3
6.1.1.3	Relative Humidity Sensors	6-4
6.1.1.4	Particulate Samplers	6-4
6.1.2	Estimating Particle Scattering	6-5
6.1.2.1	Aerosol Growth as a Function of Relative Humidity	6-5
6.1.2.2	Estimation of Size Dependent Specific Scattering	6-6
6.1.2.3	The Externally Mixed - Constant Dry Specific Scattering Model	6-7
6.1.2.4	The Externally Mixed-Sulfate Ammoniated-Variable Specific Scattering Model	6-8
6.1.2.5	The Internally Mixed Variable Mass and Size Scattering Model	6-8
6.1.3	Results	6-8
6.1.3.1	Summary of Aerosol Measurements	6-8
6.1.3.2	Comparison of Measured and Theoretical Predictions of Ambient Scattering	6-12
6.1.3.3	Comparison of Measured and Theoretical Estimations of $b_{scat}(RH)/b_{scat,dry}$	6-16
6.1.4	Summary of the Great Smoky Mountains Study	6-20
6.2	GRAND CANYON STUDIES	6-22
6.2.1	Experimental Methods	6-24
6.2.1.1	Transmissometer	6-24
6.2.1.2	Aethalometer	6-24
6.2.2	Summary of Measurements	6-24
6.2.3	Summary of Particulate Measurements	6-28
6.2.4	Estimates of Coarse Mass Scattering Efficiencies	6-32
6.2.5	Absorption Estimates	6-34
6.2.6	Reconciliation Between Measured and Scattering Reconstructed from Aerosol Measurements	6-37
6.3	HYGROSCOPIC CHARACTERISTICS OF AEROSOLS AT GRAND CANYON AND GREAT SMOKY MOUNTAINS NATIONAL PARKS	6-40
6.3.1	General Features of the $f(RH) = b_{scat}(RH)/b_{scat,dry}$ Curves	6-42
6.3.3	Comparison of Measured $f(RH)$ with Theoretical Predictions	6-47
6.3.3.1	Statistical Estimates of $b_{scat}(RH)/b_{scat,dry}$	6-48
6.3.4	Summary of Hygroscopic Characteristics of Aerosols	6-50
6.4	REFERENCES	6-52

APPENDIX A VISIBILITY MAPS DERIVED FROM MEASURED
AND SPATIALLY INTERPOLATED IMPROVE AND
CDN DATA

APPENDIX B

APPENDIX C

APPENDIX D

APPENDIX E MONTHLY RECONSTRUCTED FINE MASS AND
BUDGETS FROM THE IMPROVE NETWORK—MARCH
1996 THROUGH FEBRUARY 1999

APPENDIX F

APPENDIX G A COMPARISON OF SULFATE AND NITRATE
PARTICLE MASS CONCENTRATIONS FROM IMPROVE
AND THE CDN

LIST OF FIGURES

<u>Chapter</u>		<u>Page</u>
	OVERVIEW AND SUMMARY	
	S.1 A Map of the IMPROVE sites included in this report.	S-2
	S.2 Three-year averages of deciview values using only data collected in the IMPROVE Network.	S-7
	S.3 Three-year averages of deciview values using data collected in the IMPROVE Network and CASTNet.	S-7
	S.4 Three-year averages of total reconstructed aerosol light-extinction coefficient (1/Mm) using only data collected in the IMPROVE Network.	S-8
	S.5 Three-year averages of total reconstructed aerosol light-extinction coefficient (1/Mm) using data collected in the IMPROVE Network and CASTNet.	S-8
	S.6a Fractional contribution of sulfates to total aerosol reconstructed light extinction (%).	S-9
	S.6b Fractional contribution of nitrates to total aerosol reconstructed light extinction (%).	S-9
	S.6c Fractional contribution of organics to total aerosol reconstructed light extinction (%).	S-10
	S.6d Fractional contribution of light-absorbing carbon to total aerosol reconstructed light extinction (%).	S-10
	S.6e Fractional contribution of soil/dust to total aerosol reconstructed light extinction (%).	S-11
	S.7 Summary plot of reconstructed fine mass and the fractional contribution of each species for the 20 monitoring regions in the IMPROVE Network, excluding Washington, D.C.	S-12
	S.8 Summary plot of reconstructed light extinction and the fractional contribution of each species for the 20 monitoring regions in the IMPROVE Network, excluding Washington, D.C.	S-13
	S.9 This map summarizes the trends in deciview (dv/yr) for group 90 (top 20% of fine mass) days.	S-16
1	IMPROVE NETWORK-CURRENT AND FUTURE CONFIGURATIONS	
	1.1 Map showing all of the Federal Class I areas where visibility is deemed an important value and the locations of the original IMPROVE, IMPROVE Protocol and new IMPROVE sites.	1-2
	1.2 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.	1-4
	1.3 A map of the IMPROVE sites used for the spatial, trend and extreme values analyses.	1-8
	1.4 Schematic of a new version of the IMPROVE sampler PM _{2.5} module.	1-16

2	AEROSOL MASS BUDGETS AND SPATIAL DISTRIBUTIONS	
2.1	Average PM ₁₀ mass concentrations (in $\mu\text{g}/\text{m}^3$) for each site in the IMPROVE Network, excluding Washington, D.C.	2-16
2.2	Average fine mass aerosol concentrations (in $\mu\text{g}/\text{m}^3$) for each site in the IMPROVE Network, excluding Washington, D.C.	2-17
2.3	Average coarse particle mass concentrations (in $\mu\text{g}/\text{m}^3$) for each site in the IMPROVE Network, excluding Washington, D.C.	2-18
2.4	Average fine sulfate aerosol concentrations (in $\mu\text{g}/\text{m}^3$) (top map) and sulfate fine mass (in %) (bottom map) for each site in the IMPROVE Network, excluding Washington, D.C.	2-19
2.5	Average fine nitrate aerosol concentrations (in $\mu\text{g}/\text{m}^3$) (top map) and nitrate fine mass (in %) (bottom map) for each site in the IMPROVE Network, excluding Washington, D.C.	2-20
2.6	Average fine organic aerosol concentrations (in $\mu\text{g}/\text{m}^3$) (top map) and organic fine mass (in %) (bottom map) for each site in the IMPROVE Network, excluding Washington, D.C.	2-22
2.7	Average light-absorbing carbon concentrations (in $\mu\text{g}/\text{m}^3$) (top map) and light-absorbing carbon fine mass (in %) (bottom map) for each site in the IMPROVE Network, excluding Washington, D.C.	2-23
2.8	Average fine soil aerosol concentrations (in $\mu\text{g}/\text{m}^3$) (top map) and soil fine mass (in %) (bottom map) for each site in the IMPROVE Network, excluding Washington, D.C.	2-24
3	SPATIAL DISTRIBUTIONS OF RECONSTRUCTED LIGHT EXTINCTION AND LIGHT-EXTINCTION BUDGETS	
3.1	Best-fit relation between a site's annual average RH and its annual average RH correction factor.	3-5
3.2	The process by which IMPROVE data is used to develop site specific seasonal and annual RH correction factors.	3-6
3.3	RH factors ($f_T(RH)$) derived from Tang's ammonium sulfate growth curves smoothed between the crystallization and deliquescence points.	3-8
3.4	Three-year averages of total reconstructed aerosol (Rayleigh is not included) light-extinction coefficient (1/Mm) for each site in the IMPROVE Network, excluding Washington, D.C.	3-24
3.5	Three-year averages of total reconstructed aerosol light-extinction coefficient (1/Mm) (Rayleigh is not included) for sites in the IMPROVE Network and CASTNet, excluding Washington, D.C.	3-24
3.6	Three-year averages of ammonium sulfate light-extinction coefficient in 1/Mm (top) and sulfate fraction in percent of aerosol light extinction (bottom), for each of the sites in the IMPROVE Network, excluding Washington, D.C.	3-25
3.7	Three-year averages of nitrate light-extinction coefficient in 1/Mm (top) and nitrate fraction in percent of aerosol light extinction (bottom), for each of the sites in the IMPROVE Network, excluding Washington, D.C.	3-26
3.8	Three-year averages of light extinction due to organic material in 1/Mm (top) and percent of aerosol extinction (bottom), for each of the sites in	3-27

	the IMPROVE Network, excluding Washington, D.C.	
3.9	Three-year averages of absorption in 1/Mm (top map) and absorption fraction in percent of aerosol light extinction (bottom map), for each of the sites in the IMPROVE network, excluding Washington, D.C.	3-28
3.10	Three-year averages of light extinction due to coarse material in 1/Mm (top map) and percent of aerosol extinction (bottom map), for each of the sites in the IMPROVE network, excluding Washington, D.C.	3-29
3.11	Average visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the three-year period, March 1996 through February 1999, of IMPROVE, excluding Washington, D.C.	3-31
3.12	Average visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the three-year period, December 1995 through November 1998, of IMPROVE and CASTNet, excluding Washington, D.C.	3-31
3.13	Average winter visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the three-year period, March 1996 through February 1999, excluding Washington, D.C.	3-32
3.14	Average summer visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the three-year period, March 1996 through February 1999, excluding Washington, D.C.	3-32
3.15	Average spring visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the three-year period, March 1996 through February 1999, excluding Washington, D.C.	3-33
3.16	Average autumn visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the three-year period, March 1996 through February 1999, excluding Washington, D.C.	3-33
4	FINE PARTICLE MASS CONCENTRATION FREQUENCY DISTRIBUTIONS	
4.1	(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Shenandoah National Park.	4-3
4.2	(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Big Bend National Park.	4-4
4.3	(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Yellowstone National Park.	4-5
4.4	(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Yosemite National Park. Data shown are for winter only.	4-6
4.5	(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Rocky Mountain National Park.	4-7

4.6	(a) Map of mean sulfate contribution (%) to RCFM at IMPROVE monitoring sites across the United States. (b) Map of sulfate contribution to the upper two percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution).	4-9
4.7	(a) Map of mean particle carbon contribution to RCFM (%) at IMPROVE monitoring sites across the United States. (b) Map of particle carbon contribution to the upper two percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution).	4-11
4.8	(a) Map of mean soil contribution to RCFM (%) at IMPROVE monitoring sites across the United States. (b) Map of soil contribution to the upper two percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution).	4-12
4.9	(a) Map of mean particle nitrate contribution to RCFM (%) at IMPROVE monitoring sites across the United States. (b) Map of particle nitrate contribution to the upper five percentiles of RCFM (shown as mean contribution subtracted from the extreme contribution). Data are shown for winter only.	4-13
5	TREND ANALYSIS	
5.1	Trends in annual and five-year rolling averages for PM _{2.5} and deciview for Pinnacles National Monument.	5-13
5.2	Trends in annual and five-year rolling averages for PM _{2.5} and deciview for Badlands National Park.	5-13
5.3	Trends in annual and five-year rolling averages for PM _{2.5} and deciview for Big Bend National Park.	5-14
5.4	Map summarizing the trends in deciview (dv/yr) for group 90 (top 20% of fine mass) days.	5-15
5.5	Map summarizing the trends in aerosol extinction (1/Mm/yr) for group 90 (top 20% of fine mass) days.	5-15
5.6	Map summarizing the trends in sulfate mass concentration (ng/m ³ /yr) for group 90 (top 20% of fine mass) days.	5-16
5.7	Map summarizing the trends in nitrate mass concentration (ng/m ³ /yr) for group 90 (top 20% of fine mass) days.	5-16
5.8	Map summarizing the trends in organic mass concentration (ng/m ³ /yr) for group 90 (top 20% of fine mass) days.	5-17
5.9	Map summarizing the trends in fine soil mass concentration (ng/m ³ /yr) for group 90 (top 20% of fine mass) days.	5-17
5.10	Map summarizing the trends in coarse mass concentration (ng/m ³ /yr) for group 90 (top 20% of fine mass) days.	5-18
5.11	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Badlands National Park.	5-18
5.12	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Jarbidge Wilderness Area.	5-19

5.13	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Great Sand Dunes National Monument.	5-20
5.14	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Yellowstone National Park.	5-20
5.15	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Bandelier National Monument.	5-21
5.16	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Bryce Canyon National Park.	5-22
5.17	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Mesa Verde National Park.	5-22
5.18	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Chiricahua National Monument.	5-23
5.19	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Big Bend National Park.	5-23
5.20	Temporal plot of reconstructed extinction and extinction of constituent species for the group 90, 50, and 10 categories for Great Smoky Mountains National Park.	5-24
5.21	Summary plot of reconstructed fine mass and the fractional contribution of each species for the 20 monitoring regions in the IMPROVE Network (Washington, D.C. is not shown).	5-25
5.22	Summary plot of reconstructed light extinction and the fractional contribution of each species for the 20 monitoring regions in the IMPROVE Network (Washington, D.C. is not shown).	5-26
5.23	Diurnal patterns by season for RH and b_{ext} measured at Pinnacles National Monument from 1988 to August 1993.	5-28
5.24	Diurnal patterns by season for RH and b_{ext} measured at Grand Canyon National Park from 1986 to August 1997.	5-29
5.25	Diurnal patterns by season for RH and b_{scat} measured at Gila Wilderness Area from 1994 to August 1997.	5-30
5.26	Diurnal patterns by season for RH and b_{scat} measured at Lone Peak Wilderness Area from 1993 to August 1997.	5-32
5.27	Diurnal patterns by season for RH and b_{ext} measured at San Geronio Wilderness Area from 1989 to August 1997.	5-33
5.28	Diurnal patterns by season for RH and b_{ext} measured at Yosemite National Park from 1988 to August 1997.	5-34
5.29	Diurnal patterns by season for RH and b_{scat} measured at Snoqualmie Pass from 1993 to August 1997.	5-35
5.30	Diurnal patterns by season for RH and b_{scat} measured at Great Smoky Mountains National Park from 1993 to August 1997.	5-36

5.31	Diurnal patterns by season for RH and b_{scat} measured at Boundary Waters Canoe Area from 1993 to August 1997.	5-37
6	SPECIAL STUDIES	
6.1	Time lines of fine mass (FM), sulfate species mass, ammonium nitrate, organic mass (OCM), elemental carbon (EC), and soil.	6-9
6.2	An elemental sulfur mass size distribution at ambient RH for JD 229, which corresponds to a σ_g of 1.5 and a D_g equal to 0.60 μm . The smooth curve is the mass size distribution calculated using the Twomey [1975] inversion technique.	6-10
6.3	A sulfur mass size distribution at ambient RH for JD 237, which corresponds to a σ_g of 1.8 and a D_g equal to 0.47 μm . The smooth curve is the mass size distribution calculated using the Twomey [1975] inversion technique.	6-11
6.4	An example of a measured $f(RH)$ curve on sampling period corresponding to JD 205.29. The curve through the data points is a best fit using an equation with a functional form containing $RH/(1-RH)$.	6-13
6.5	A scatter plot of reconstructed and measured $\text{PM}_{2.5}$ scattering assuming external mixing but with measured sulfur size distributions.	6-14
6.6	Time lines showing measured $\langle b_{scat} \rangle$, sulfate species scattering, ammonium nitrate scattering, organic specific scattering, and soil scattering. The best estimate D/D_0 growth curve and measured sulfur mass size distributions were used.	6-15
6.7	Scatter plot of reconstructed and measured scattering along with the 1:1 line. The upper and lower bound of reconstructed scattering correspond to assuming an internally and externally mixed aerosol.	6-16
6.8	$f(RH)$, $b_{scat}(RH)/b_{scat,dry}$, is plotted as a function of relative humidity for Julian Day 204.29.	6-17
6.9	$f(RH)$, $b_{scat}(RH)/b_{scat,dry}$, is plotted as a function of relative humidity for Julian Day 202.79.	6-18
6.10	$f(RH)$, $b_{scat}(RH)/b_{scat,dry}$, is plotted as a function of relative humidity for Julian Day 206.79.	6-18
6.11	Scatter plot of measured vs. modeled $b_{scat}(RH)/b_{scat,dry}$ for the external mixture-variable sulfate size ($b_{scat_E_e_s_a_B}$) calculation.	6-19
6.12	Scatter plot of b_{scat} measured by the Radiance Research and Optec nephelometers for relative humidities less than 45%.	6-25
6.13	Temporal plot of measured extinction and scattering by particles less than 2.5 μm .	6-27
6.14	Temporal plot of measured extinction, scattering, and absorption by particles less than 2.5 μm for 16-hour time intervals.	6-27
6.15	Scatter plot, along with the 1:1 line, of measured and reconstructed extinction.	6-29
6.16	Temporal plot of coarse particle (PM_{10} - $\text{PM}_{2.5}$ μm) concentrations.	6-30
6.17	Temporal plot of fine particle concentrations.	6-30
6.18	Scatter plot, along with the 1:1 line, of measured and reconstructed fine mass.	6-32

6.19	Scatter plot of coarse mass scattering efficiency as a function of coarse mass concentration.	6-33
6.20	Multiple scatter plots, along with 1:1 lines, of absorption measured in a number of different ways.	6-36
6.21	Scatter plot of measured and reconstructed fine particle scattering along with the 1:1 line when nominal values of mass scattering efficiencies were used.	6-38
6.22	Scatter plot of measured and reconstructed fine particle scattering along with the 1:1 line when the nominal value of the organic dry mass scattering efficiency was lowered from 4.0 m ² /g to 1.2 m ² /g.	6-39
6.23	Scatter plot of all measured $f(RH)$ data points collected during the Great Smoky study.	6-42
6.24	Scatter plot of measured $f(RH)$ data points that have been averaged into 5% relative humidity "bins" for the Grand Canyon data set.	6-43
6.25	Plot of measured $f(RH)$ on Julian day 212.	6-45
6.26	Plot of measured $f(RH)$ on Julian day 204.	6-45
6.27	Plot of measured $f(RH)$ on Julian day 217.	6-46
6.28	Plot of measured $f(RH)$ on Julian days 207, 211, and 224 for the Great Smoky data set.	6-46
6.29	$f(RH)$ is plotted as the solid and broken line for ammonium bisulfate and sulfuric acid, respectively, while the single data points with error bars show the OLS regression with an intercept derived $f(RH)$ for sulfates and organics.	6-49
6.30	$f(RH)$ is plotted as the solid line for ammonium sulfate, while the single data points with error bars show the OLS regression with an intercept derived $f(RH)$ for sulfates and organics.	6-51

LIST OF TABLES

<u>Chapter</u>		<u>Page</u>
	OVERVIEW AND SUMMARY	
	S.1 IMPROVE monitoring sites listed according to region.	S-3
1	IMPROVE NETWORK-CURRENT AND FUTURE CONFIGURATIONS	
	1.1 Tabular summary of the sites used for spatial, trend, and extreme values analyses presented in this report.	1-5
	1.2 Final list of Class I areas organized by clusters with numbers corresponding to the map in Figure 1.1.	1-11
2	AEROSOL MASS BUDGETS AND SPATIAL DISTRIBUTIONS	
	2.1 Five hypothetical observations that correspond to the 20% highest fine mass concentrations for one season as sorted by gravimetric fine mass (FM).	2-4
	2.2 Measured fine and coarse aerosol concentrations (in $\mu\text{g}/\text{m}^3$) for the 21 regions in the IMPROVE Network. Fine mass is reconstructed from the sum of individual species.	2-6
	2.3 Measured fine aerosol mass budgets (in %) for the 21 regions in the IMPROVE Network.	2-8
3	SPATIAL DISTRIBUTIONS OF RECONSTRUCTED LIGHT EXTINCTION AND LIGHT-EXTINCTION BUDGETS	
	3.1 Parameters of the best-fit equation relating the relative humidity light extinction correction factors (F_T) to seasonal and annual average site relative humidity ($F = b_o + b_1/(1-RH) + b_2/(1-RH)^2$).	3-5
	3.2 Seasonal and annual averages of reconstructed total light-extinction coefficient (including Rayleigh) for the 21 regions in the IMPROVE Network. Also shown are light scatterings resulting from fine and coarse aerosols, light absorption for carbonaceous aerosol, percentage of total extinction resulting from aerosol extinction, and the average regional relative humidity.	3-10
	3.3 Seasonal and annual averages of reconstructed aerosol light-extinction coefficient for the 21 regions in the IMPROVE Network. Also shown are light extinctions resulting from sulfate, nitrate, organic carbon, light-absorbing carbon, and soil and coarse particles.	3-13
	3.4 Seasonal and annual averages of percentage contributions to the reconstructed aerosol light-extinction coefficient (light-extinction budget) for the 21 regions in the IMPROVE Network for sulfate, nitrate, organic carbon, light-absorbing carbon, and soil and coarse particles.	3-16

5	TRENDS ANALYSIS	
5.1	The Theil slope estimates for a five-year rolling average of fine mass and deciview for the 90, 50, and 10 percentile groups. Each slope is paired with the probability for rejection.	5-2
6	SPECIAL STUDIES	
6.1	Statistical summary of aerosol species concentrations and the fraction of reconstructed fine mass attributed to certain species.	6-9
6.2	Statistical summary of DRUM data.	6-11
6.3	Statistical summary of measured scattering $\langle b_{scat} \rangle$, reconstructions of b_{scat} assuming different mixing rules and specific scattering and the scattering associated with each aerosol species.	6-12
6.4	Summary of ordinary least square regressions of measured and estimated $b_{scat}(RH)/b_{scat,dry}$ as the dependent and independent variables, respectively.	6-19
6.5	A summary of the percent differences between model estimations of $b_{scat}(RH)/b_{scat,dry}$ for three ranges of relative humidities.	6-20
6.6	Statistical summary of ten-minute optical and relative humidity measurements. The scattering and extinction values include Rayleigh scattering.	6-25
6.7	Summary of OLS regression with $b_{ext}-b_{scat,2.5\mu m}$ as the dependent variable and $b_{scat,open}-b_{scat,2.5\mu m}$, and $b_{abs,2.5\mu m}$ as independent variables.	6-28
6.8	Statistical summary of aerosol measurements.	6-29
6.9	Summary of results of an ordinary least square (OLS) regression with coarse mass as the dependent variable and soil and organics as the independent variables.	6-31
6.10	Statistical summary of absorption measurements.	6-35
6.11	Statistical summary of measured $b_{scat,2.5\mu m}$, reconstructed scattering, as well as the scattering associated with each aerosol species assuming an external mixture.	6-37
6.12	Summary of an ordinary least square regression with $b_{scat,2.5\mu m}$, as the dependent variable and sulfate + nitrate, organic, and soil estimated scattering as the independent variables.	6-39
6.13	Statistical summary of mean $f(RH)$ values in selected relative humidity ranges for the Great Smoky data set.	6-43
6.14	Statistical summary of mean $f(RH)$ values in selected relative humidity ranges for the Grand Canyon data set.	6-44