C.1 OBJECTIVE AND APPROACH

The objective of this task was to use ambient speciated $PM_{2.5}$ data from Class I areas (from the IMPROVE network) in the CENRAP states along with the planned burning emissions estimated in this study to assess whether ambient data can be used to identify planned burning contributions to visibility events in Class I areas, and to perform a preliminary assessment of the impact of planned burns on $PM_{2.5}$ and visibility The following approach was employed:

- Assess the seasonal chemical compositions of $PM_{2.5}$ mass and aerosol light extinction in order to determine what individual species are important to the mass and visibility extinction in the area.
- Determine seasonal concentrations of and ratios between selected species, such as OC, EC and K, to establish a "baseline" average seasonal composition for comparison to days of poor visibility and days potentially influenced by prescribed burning.
- Assess chemical compositions of $PM_{2.5}$ and aerosol light extinction on the 20% best and 20% worst visibility days to determine what species have a large impact on visibility (i.e., are species from burning typically important in visibility reduction?).
- Analyze IMPROVE data, specifically OC, EC, and K concentrations, on dates when extensive burning occurred nearby a monitoring site in order to assess whether wood smoke influences are seen in the ambient measurements and significantly impacts visibility.
- Analyze emissions data on days when elevated OC, EC and K concentrations occurred at IMPROVE sites in order to determine whether days of elevated concentrations corresponded to known burns in the emission inventory data.
- Analyze air mass trajectories on selected days to determine whether meteorology (i.e., transport) explains the observed effects and to determine the extent to which meteorology affects haze

C.2 AMBIENT MONITORING DATA

We analyzed ambient monitoring data from IMPROVE stations in order to assess the potential effect of prescribed burning emissions on visibility in the CENRAP region. We used ambient data from two IMPROVE stations located in Arkansas, Caney Creek (CACR1) and Upper Buffalo Wilderness (UPBU1). At the time of analysis, these sites were located in the area with the highest resolved fire histories, which would allow the best chance of showing direct influence between prescribed burning and ambient Class 1 data. **Figure C-1** shows the locations of IMPROVE stations in the CENRAP region, along with the point locations of prescribed burns that were available from the 2002 emissions inventory.

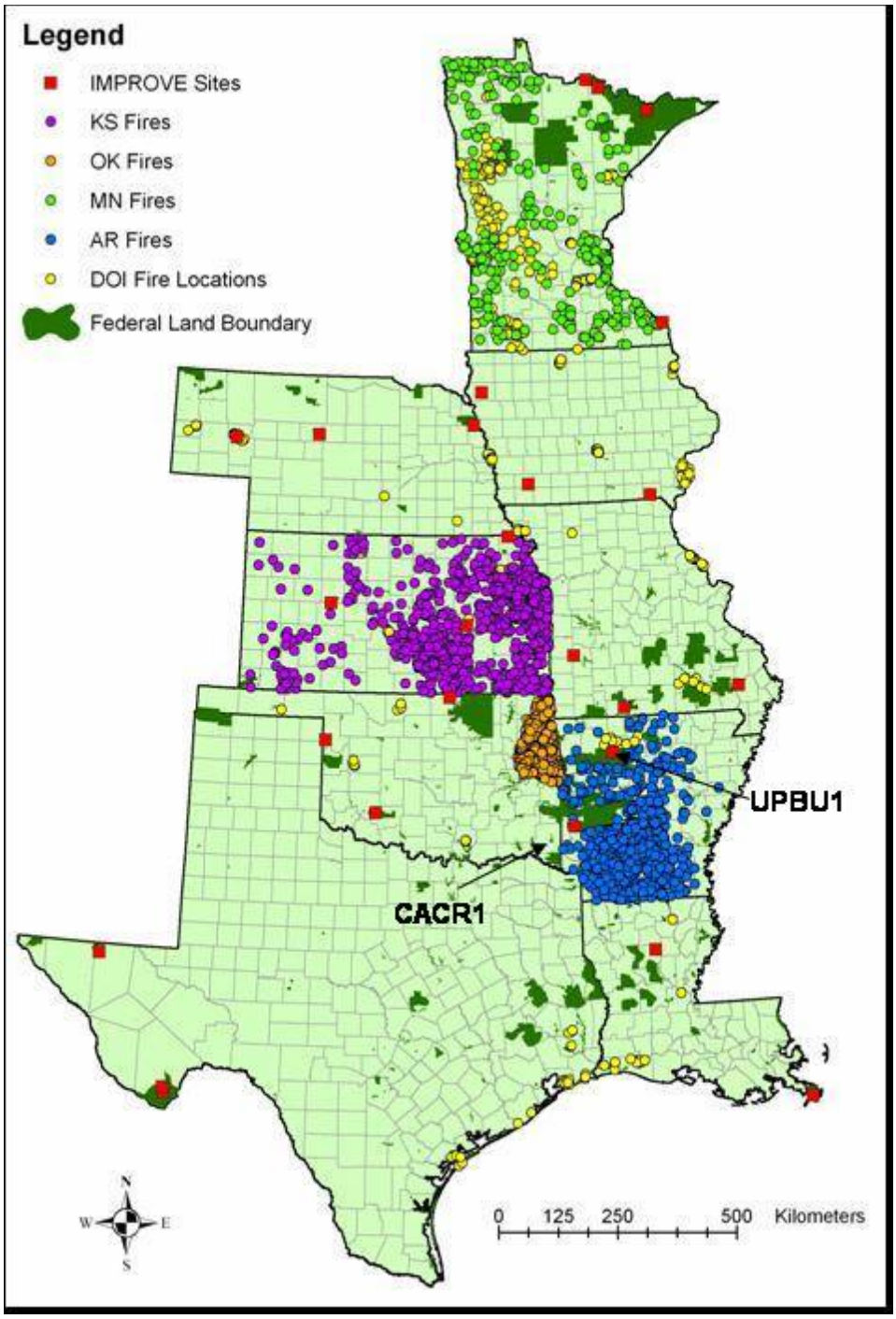


Figure C-1. IMPROVE station and fire locations.

We acquired data from the two ambient monitoring stations from the online IMPROVE database (http://vista.cira.colostate.edu/improve/). Specifically, we obtained values of all available parameters for the years 2000, 2001, and 2002, during which years the IMPROVE network collected 24-hr samples once every three days. Although the emissions inventory included fires only from 2002, IMPROVE data from all three years were used to ensure a robust

statistical analysis of seasonal and annual aerosol compositions and species ratios. **Table C-1** summarizes the number of complete samples that we obtained from the IMPROVE database for 2000 through 2002 and for 2002 alone. The complete samples were cases in which all key species in our analysis were available: elemental carbon (EC), organic carbon (OC), potassium (K), ammonium nitrate (NH_4NO_3), and ammonium sulfate ($(NH_4)_2SO_4$).

Table C-1. Number of complete samples available from 2000–2002 and from 2002 at Caney Creek and Upper Buffalo Wilderness.

Site	N samples (2000 – 2002)	N samples (2002)
Caney Creek	254	110
Upper Buffalo Wilderness	318	117

In analyzing the ambient monitoring data with respect to fire activity data, we focused on species that generally characterize fine particulate aerosols and species that derive from wood smoke: elemental carbon (EC), organic carbon mass (OCM), ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$), potassium (K), non-soil potassium (KNS), and a composite of species that derive from soils (GEO). Several of the parameters were calculated from measured values according to IMPROVE protocol, as summarized in **Table C-2**.

Table C-2. IMPROVE algorithms for mass concentrations of fine aerosol species.

Species	Abbreviation	IMPROVE Calculation
Organic Carbon Mass	OCM	1.4*[organic carbon]
Ammonium Nitrate	NH_4NO_3	1.29*[nitrate]
Ammonium Sulfate	$(NH_4)_2SO_4$	4.125*[sulfur]
Non-soil Potassium	KNS	[potassium]-0.6*[iron]
Soil Elements	Soil	2.20*[aluminum]+2.49*[silicon]+1.63*[calcium] +2.42*[iron]+1.94*[titanium]

The IMPROVE algorithm for OCM adjusts the measured OC value for other elements associated with carbon molecules, such as oxygen and hydrogen, and it relies on the assumption that the average organic molecule contains 70% carbon. The ammonium nitrate and ammonium sulfate algorithms assume that nitrate and sulfate ions are fully neutralized by NH_4^+. The ammonium sulfate algorithm also assumes that all elemental sulfur is in the form of sulfate, and it converts the mass of elemental sulfur to ammonium sulfate using 4.125, which is the ratio of the molecular weight of ammonium sulfate (132 g/mol) to the molecular weight of elemental sulfur (32 g/mol). Similarly, the ammonium nitrate algorithm multiplies the nitrate concentration by the ratio (1.29) of the molecular weight of ammonium nitrate (80 g/mol) to the molecular weight of nitrate (62 g/mol). The non-soil potassium (KNS) algorithm results from the observed ratio (0.6) of potassium to iron in soils. The residual, non-soil potassium (KNS) is assumed to derive from smoke. Lastly, the soil algorithm includes the sum of soil-derived elements, adjusted by coefficients that account for their normal oxides.

The IMPROVE network utilizes the measured mass concentrations of OCM, EC, $(NH_4)_2SO_4$, NH_4NO_3, and soil components to estimate the light extinction resulting from each species. Light extinction values associated with the individual species are summed to reconstruct an overall aerosol extinction parameter (b_{ext}). The IMPROVE extinction calculations account for scattering, absorption, and the effects of relative humidity, as illustrated by equations listed in **Table C-3**. The coefficients represent the dry scattering efficiencies of the compounds, except the coefficient for the EC algorithm, which represents the light absorbing efficiency of EC. $F_T(RH)$ equals an empirically determined relative humidity correction factor that accounts for the hygroscopic nature of the ionic aerosol species.

Table C-3. IMPROVE algorithms for light extinctions of fine aerosol species.

Species	Abbreviation	IMPROVE Calculation
Organic Carbon Mass	OCM Extinction	4*[organic carbon]
Ammonium Nitrate	NH_4NO_3 Extinction	$3*F_T(RH)$*[nitrate]
Ammonium Sulfate	$(NH_4)_2SO_4$ Extinction	$3*F_T(RH)$*[sulfur]
Elemental Carbon	EC Extinction	10*[elemental carbon]
Soil Elements	Soil Extinction	1*[Soil]

C.3 DATA VALIDATION

Data validation helps to prevent serious errors in data analysis and modeling results by identifying erroneous individual data values. The $PM_{2.5}$ Data Analysis Workbook contains the guidelines that we employ for PM data validation (Main and Roberts, 2001). The validation incorporates internal consistency checks of ambient monitoring data, such as the comparison of species concentrations using scatter plots, the calculation of reconstructed particulate mass, and the preparation of material balances. Scatter plots that illustrate the relationships between well characterized species enable data analysts to quickly inspect data and identify any suspect points that may require further attention. Scatter plots also provide a general overview of a data set and preliminary data analysis. Plots that compare species from common sources, such as soil, or from different analytical techniques, such as ion chromatography (IC) or x-ray fluorescence (XRF), can target outlying data points that may indicate an unusual event or an equipment problem. Plots between reconstructed mass and measured mass or between cations and anions help the analyst to visually assess data completeness and to validate data resulting from different measurement techniques. We generated a number of scatter plots using SYSTAT statistical software in an effort to validate the IMPROVE data before performing the comparative analysis. **Table C-4** summarizes the species we inspected using scatter plots, along with their expected relationships and typical sources.

The data quality was good, as IMPROVE data is quality controlled prior to being incorporated into the database; thus, minimal effort was required. The data validation plots explored include 2000 through 2002 data for both Caney Creek and Upper Buffalo Wilderness. The data from both sites exhibit similar relationships between measured species. **Figure C-2** illustrates the comparison between sulfur (S) and sulfate (SO_4^{-2}) for the data set from Upper Buffalo Wilderness. A relatively tight correlation and a slope of roughly three indicate a good

Table C-4. Scatter plot species and expected relationships.

Species	Species	Expected Relationship	Source or Reason
S	SO_4^{-2}	3*S ~ SO_4^{-2}	IC vs. XRF
Cl ion	Cl	~ 1:1	IC vs. XRF
Na ion	Na	~ 1:1	IC vs. XRF
K ion	K	~ 1:1	IC vs. XRF
Na	Cl	Correlation	Sea salt
Ca	Si	Correlation	Soil
Al	Si	Correlation	Soil
Fe	Si	Correlation	Soil
Fe	K	Correlation	Soil
OC	Total Carbon (TC)	Correlation	OC large part of TC
EC	TC	Some Correlation	EC part of TC
Se	SO_4^{-2}	Some Correlation	Coal Emissions
Fe	Zn	Some Correlation	Smelter Emissions
Ni	V	Some Correlation	Oil Combustion
K	EC	Some Correlation	Wood Smoke
b_{abs}	EC	Correlation	EC absorbs most light
Cations	Anions	Near 1:1	Neutralized Aerosol
$PM_{2.5}$	Reconstructed Mass	Good Correlation	Should be equal

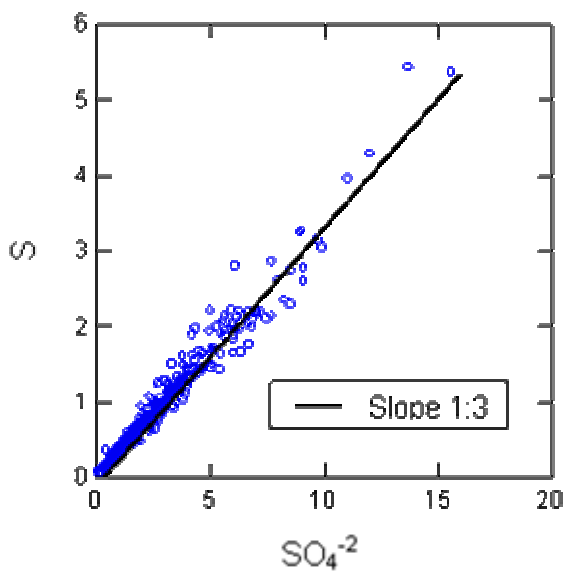
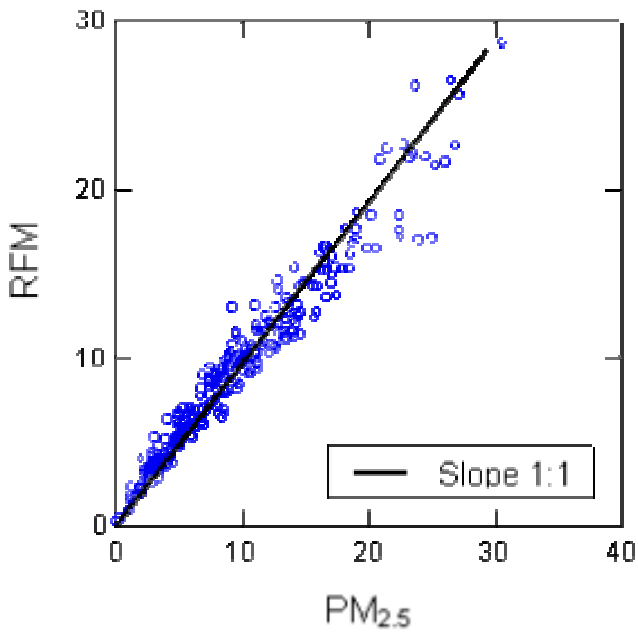


Figure C-2. Concentrations of XRF sulfur (S) versus IC sulfate (SO_4^{-2}) from the Upper Buffalo Wilderness IMPROVE station (µg/m^3). The line has a slope of one third, representing the expected 1:3 ratio between sulfur and sulfate.

comparison between the data obtained from the XRF and IC analyses. The slope equals 3 because the molecular mass of sulfate (96 g/mol) is three times the molecular mass of sulfur (32 g/mol). **Figure C-3** highlights the good correlation between the measured fine particulate mass ($PM_{2.5}$) and the reconstructed fine particulate mass (RFM). According to IMPROVE protocol, RFM equals the sum of SO_4^{-2}, NO_3^-, EC, OCM, and soil components. The good correlation between $PM_{2.5}$ and RFM indicates the overall reliability of the data sets and measurement techniques. The correlation exhibited between iron (Fe) and potassium (K) in **Figure C-4** is confounded by several data points of high K and low Fe, which suggests an additional source of K, possibly wood smoke, since both species commonly derive from soils. Overall this indicates that most K is from soil, which suggests influence from the non-soil sources is infrequent and contributes only a small amount of the



K.

Figure C-3. Concentrations of reconstructed fine mass (RFM) versus fine particulate mass ($PM_{2.5}$) from the Caney Creek IMPROVE station ($\mu g/m^3$). The line has a slope of one, representing a one to one ratio between RFM and $PM_{2.5}$.

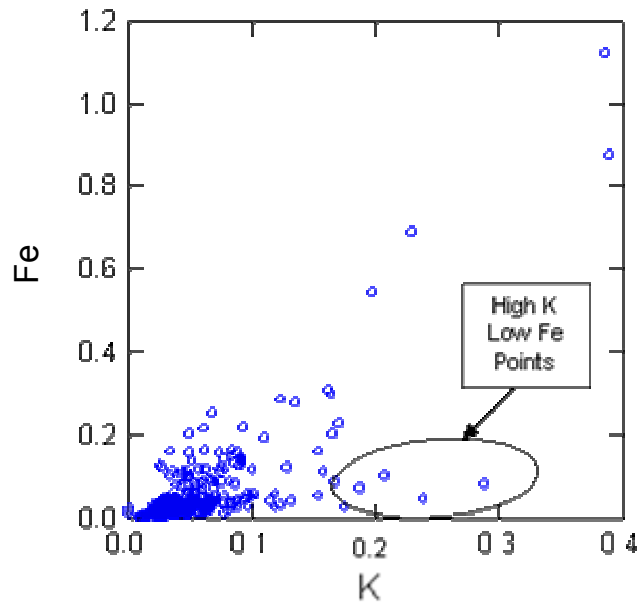


Figure C-4. Concentrations of iron (Fe) versus potassium (K) from the Upper Buffalo Wilderness IMPROVE station ($\mu g/m^3$). Points that exhibit higher than normal K to Fe ratios are highlighted.

C.4 CHARACTERIZING $PM_{2.5}$ DATA

It is important to first characterize the typical seasonal concentrations of and ratios between species to understand what comprises the "normal" composition of $PM_{2.5}$ before identifying whether specific source influences such as prescribed burning can be determined. **Figure C-5** depicts seasonal proportions of the median mass concentrations of OCM, EC, NH_4NO_3, $(NH_4)_2SO_4$, and soil influences for Caney Creek; Upper Buffalo Wilderness showed similar results. Summary statistics are given in Appendix A. At both sites, $(NH_4)_2SO_4$ and OCM comprise the dominant fractions of $PM_{2.5}$ in all seasons except winter, when NH_4NO_3 also contributes a significant fraction. The larger fraction of NH_4NO_3 in winter is consistent with nitrate formation mechanisms which favor cold, wet conditions, and the dominant fractions of $(NH_4)_2SO_4$ are consistent with observations made at other eastern IMPROVE sites (Malm, 1999). EC is a small component of the mass in all seasons.

Figure C-6 illustrates the proportions of light extinction attributed to OCM, EC, NH_4NO_3, $(NH_4)_2SO_4$, and soil for each season at Caney Creek; Upper Buffalo Wilderness showed similar results. Summary statistics are given in Appendix A. The dominant portion of light extinction derives from $(NH_4)_2SO_4$ in all seasons except winter, when NH_4NO_3 also contributes significantly. This is consistent with other analyses of $PM_{2.5}$ aerosol in the Midwest and CENRAP region (http://www2.nature.nps.gov/air/studies/bravo/bravo2003factsheet.htm)

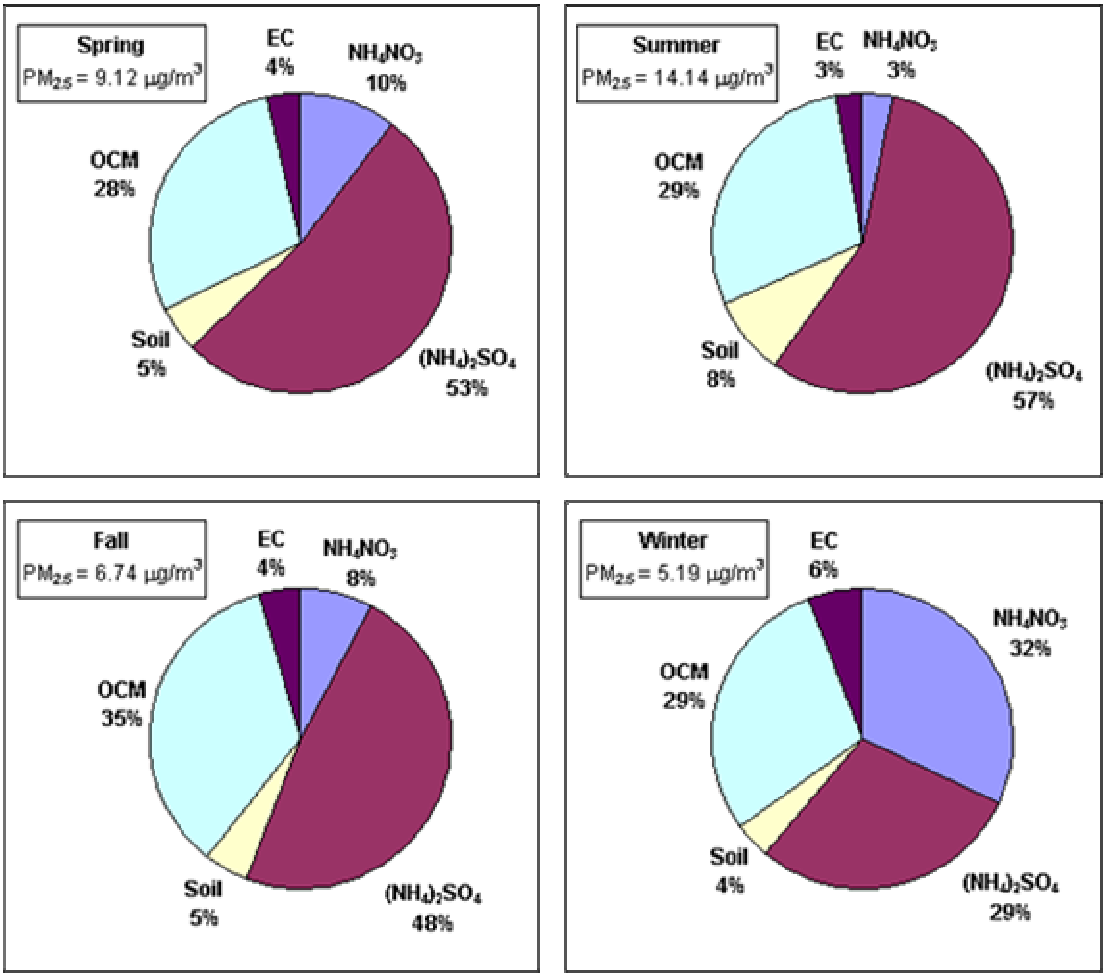


Figure C-5. Median mass and composition of $PM_{2.5}$ by season (spring is March to May, summer is June to August, fall is September to November, and winter is December to February) at Caney Creek for 2000 through 2002.

(Coutant et al., 2003; Coutant et al., 2002; Georgoulias and Dattner, 2002; Sisler and Malm, 2000; Malm, 1999). $PM_{2.5}$ composition at other Class 1 areas in the CENRAP region will likely be similar. The light extinction proportions resemble the mass concentration proportions, because the extinction calculations directly depend on mass concentrations. $(NH_4)_2SO_4$ has a large effect on visibility due to its extremely hygroscopic nature and large contribution to the overall mass. The effect of EC on visibility is most pronounced during the winter months when the effect of $(NH_4)_2SO_4$ is at a minimum, though it only accounts for about 5% of the total extinction.

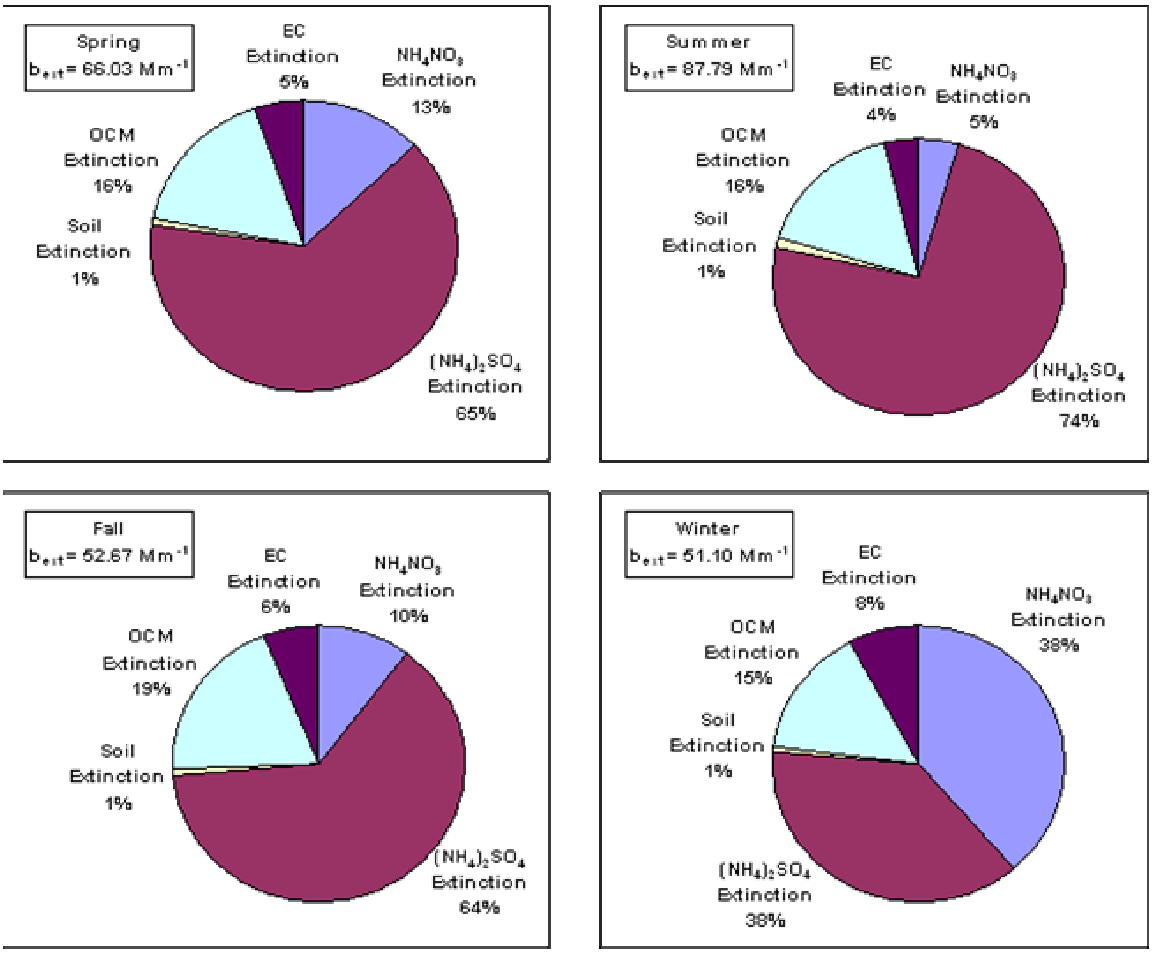


Figure C-6. Median extinction and composition of extinction by season (spring is March to May, summer is June to August, fall is September to November, and winter is December to February) at Caney Creek for 2000 through 2002.

C.5 CHARACTERIZATION OF VISIBILITY

In order to determine which species are most responsible for poor visibility, we isolated the top and bottom 20% visibility days in 2000 through 2002 by aerosol extinction at each site. Summary statistics of the best visibility data, worst visibility data, and overall data for Caney Creek and Upper Buffalo Wilderness were calculated. The median mass compositions for the best and worst visibility days, as well as the annual median from Caney Creek are depicted in **Figure C-7**; results for Upper Buffalo Wilderness are similar to those for Caney Creek. At both sites, days with poor visibility are dominated by $(NH_4)_2SO_4$ and show a decrease in the fractions of the other species, especially OCM and NH_4NO_3. The fractions of EC and Soil components vary to a lesser extent between the good visibility and poor visibility days and are minor contributors to mass and extinction.

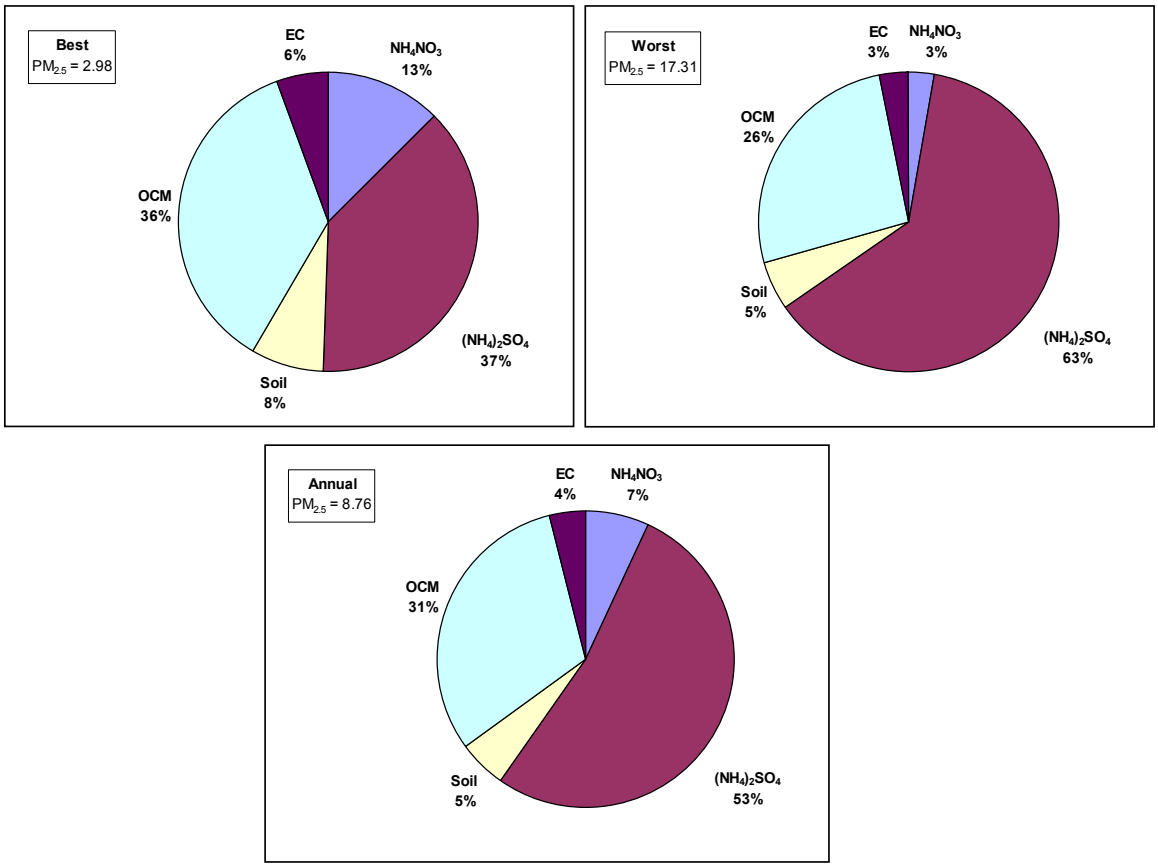


Figure C-7. Median $PM_{2.5}$ composition for the 20% best and worst aerosol extinction days and the median annual composition at Caney Creek from 2000 to 2002.

C.6 FIRE HISTORY DATA

In order to evaluate the effect of prescribed fires on visibility, we analyzed fire history data with the 2002 IMPROVE data for Caney Creek and Upper Buffalo Wilderness. We isolated the dates with IMPROVE data that corresponded to the day of or the day after prescribed burning occurred within a specific radius (i.e., range of influence) of each site. The range of influence around each site was established by using data from nearby meteorological stations: the radius around each site was calculated as the sum of the 24 hourly averaged wind speeds for each date, which represented an estimate of the distance that a parcel of air could have traveled on a given day. Theoretically, emissions from fires located within the range of influence could have been detected by the IMPROVE station if transport conditions were conducive. We then analyzed dates when the most extensive burning (with respect to acreage) occurred.

Due to the proximity of the two IMPROVE sites, several of the dates selected for each site overlap. The OCM, EC, K and KNS mass concentrations from overlapping dates that correspond to the day of or the day after extensive burning within the vicinity of both sites are compared to the springtime and annual mean concentrations from 2000 to 2002 for each site in **Figures C-8** and **C-9**. Error bars representing the 95% confidence limits for the mean concentrations of EC and KNS for the springtime and annual data sets are also plotted. In

Appendix A, mass concentrations of EC, KNS and the other key species for the selected dates and whether the EC and KNS concentrations significantly exceed the springtime are presented.

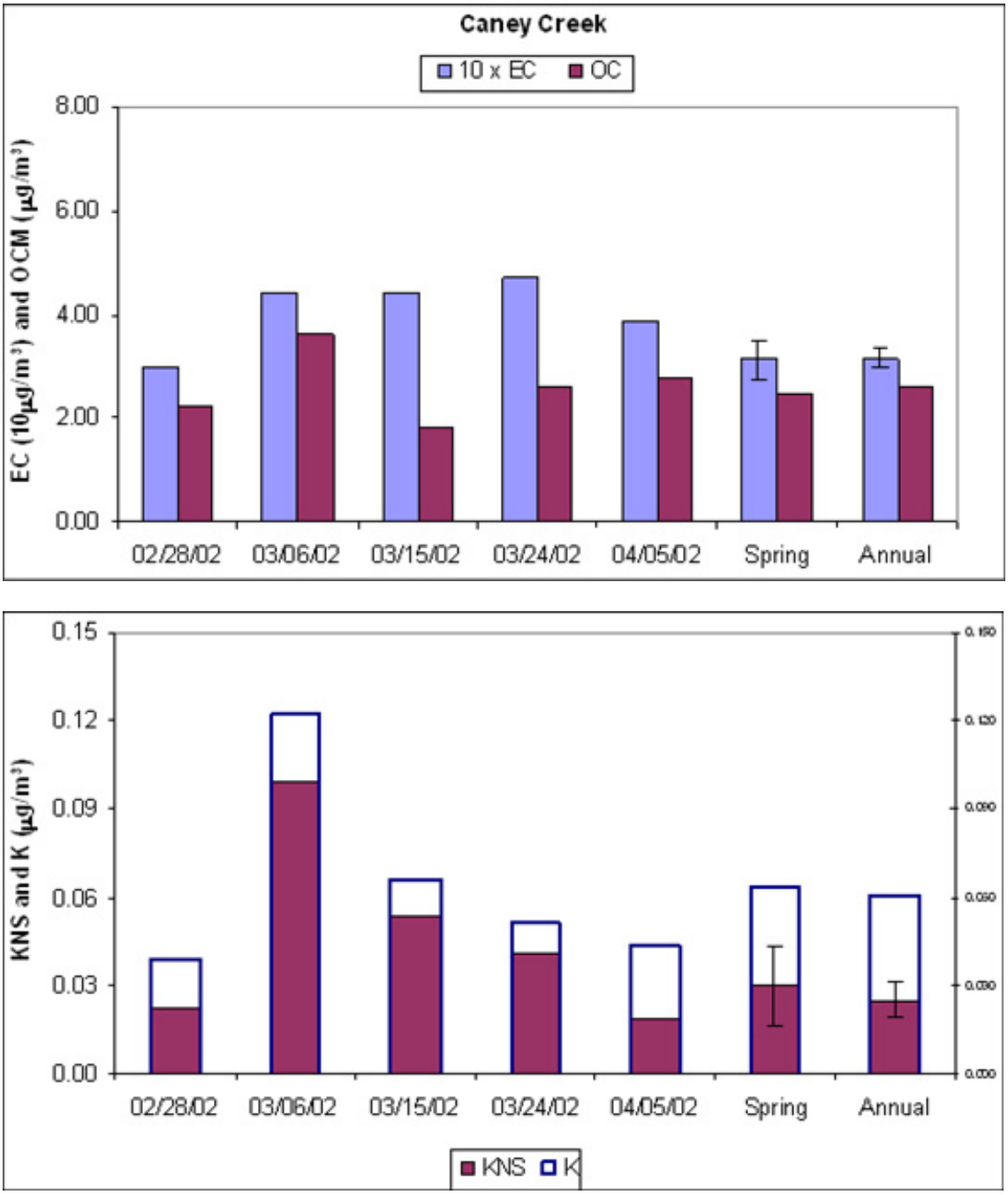


Figure C-8. EC, OCM, K and KNS mass concentrations (µg/m^3) for select dates compared to the spring and annual means for Caney Creek.

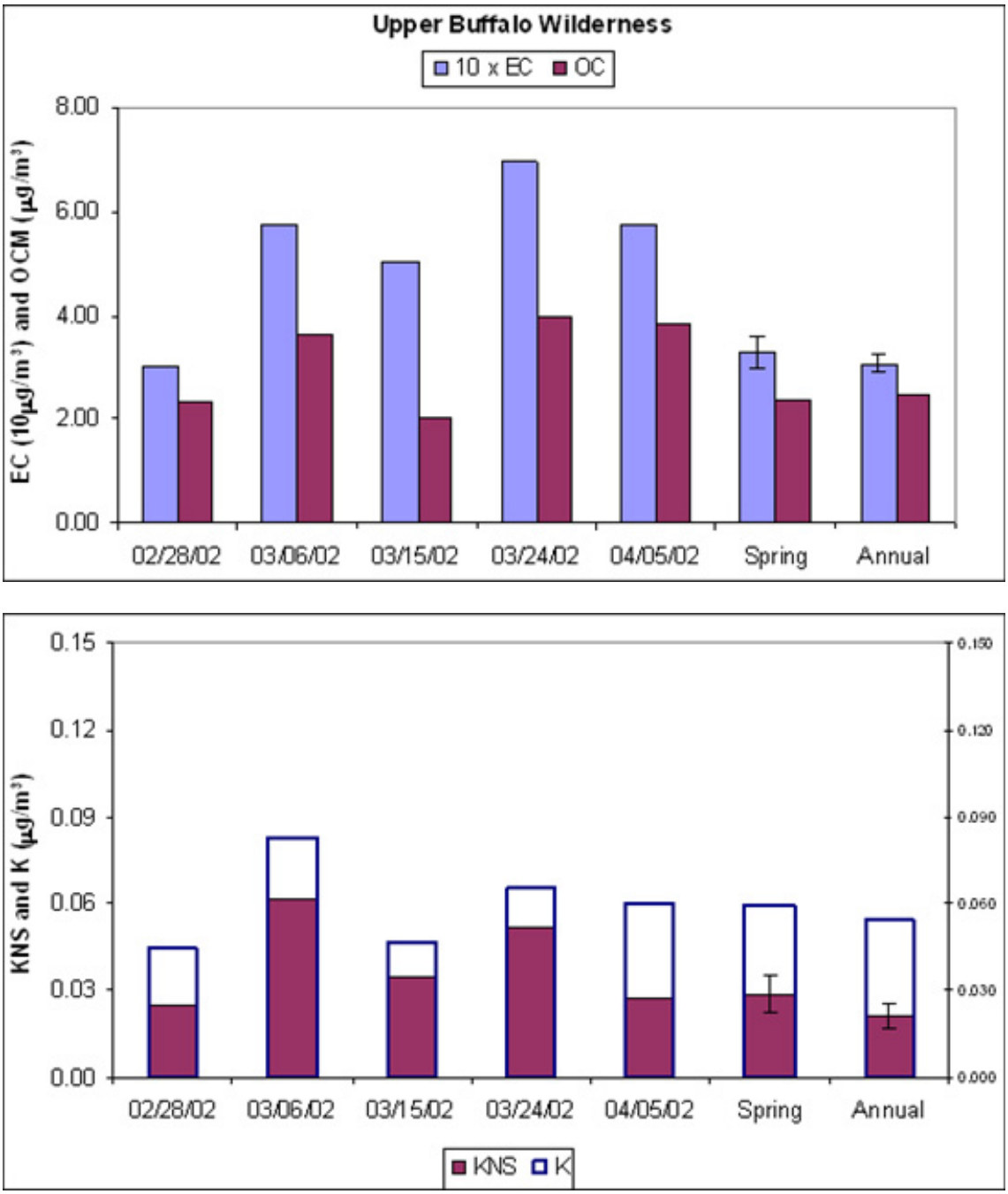


Figure C-9. EC and KNS mass concentrations (μg/m^3) for select dates compared to the spring and annual means for Upper Buffalo Wilderness.

Extensive burns occurred on the days before March 6, 15, 24, and April 5. On these dates, the measured EC significantly (at a 95% confidence level) exceeds the springtime and annual means for both sites. On March 15 and 24, the contributions of EC in relation to OC are significantly higher than the springtime and annual average EC contributions for both sites. The elevated EC emissions observed on March 6, 15, 24, and April 5 could derive from the extensive