Chapter 7. Urban Excess in $PM_{2.5}$ Speciated Aerosol Concentrations

7.1 INTRODUCTION AND METHOD

Regulatory efforts designed to reduce aerosol concentrations in the atmosphere, such as the EPA's (Environmental Protection Agency) National Ambient Air Quality Standards (www.epa.gov/air/particlepollution/standards.html) or Regional Haze Rule (U.S. EPA, 1999), rely on an understanding of the sources, lifetimes, and sinks of aerosols in the atmosphere. Emission sources of primary aerosols, secondary aerosol production through atmospheric processes, and aerosol transport are all important considerations for characterizing the impacts of aerosol concentrations on local, regional, and global scales. Primary or secondary aerosols can be transported hundreds or thousands of kilometers from their source region and impact air quality at distant locations. The average regional impact of aerosol sources can be inferred from the spatial distribution of aerosol concentrations; emissions from local sources produce sharper spatial gradients, while emissions from more distant or dispersed sources (e.g., biogenic emissions from vegetation) produce more homogeneous regional spatial patterns. Separating background or regional aerosol concentrations from those emitted locally is important for regulating aerosol sources, especially for meeting air quality standards in nonattainment areas where the regional or background concentrations of a given aerosol species are similar to the standard itself.

We define urban excess as the difference or ratio in aerosol mass concentrations in urban regions compared to nearby remote and rural regions. A schematic depiction of the impact of urban sources on background aerosol concentrations is shown in Figure 7.1. Aerosol concentrations within the city are higher than aerosol concentrations surrounding the city due to the increase in aerosols emitted from anthropogenic activities within the urban corridor. Urban impacts on background or regional aerosol concentrations are influenced by wind direction and mesoscale or synoptic meteorological patterns. We assume that the rural background concentrations refer to the lowest concentrations in a region but may include some impacts from urban emissions. Remote or background aerosol concentrations tend to be aged, well mixed, and regional in extent (depending on the species), whereas urban aerosols tend to originate from local sources, correspond to a younger aerosol, and tend to dilute after some distance from their sources. Both vary as a function of season and region. We also assume that regional contributions to aerosol concentrations of a given species affect the background and urban concentrations similarly, resulting in similar concentrations in the absence of additional urban sources to that species. Urban excess studies provide estimates of the relative magnitude of local versus regional contributions to aerosol concentrations and subsequently increase our understanding of aerosol sources, atmospheric processes, and lifetimes in the atmosphere.

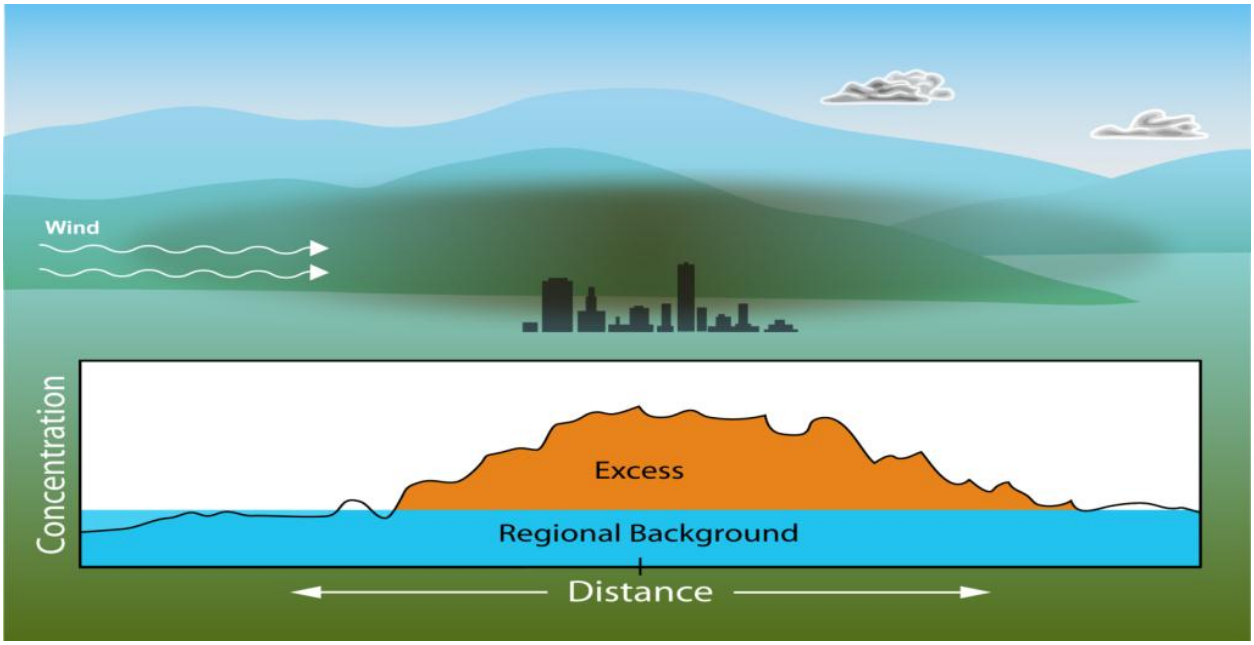

Figure 7.1. Schematic showing urban sources of aerosol concentrations and their impact on surrounding rural concentrations. An arbitrary concentration scale is on the y-axis and distance is on the x-axis. The concentrations levels depicted in orange represent levels above a rural background, depicted as blue.

Different aerosol species correspond to a range in urban excess values, depending on their sources and lifetimes. For example, secondary aerosols, such as sulfate or secondary organic aerosols, form through atmospheric processes that depend not only on sources of precursors, but other meteorological and chemical parameters (e.g., clouds, solar radiation, available reactive aerosol species, chemical equilibrium, etc.). These aerosols can be dispersed over large regions and undergo chemical transformations during their transport. In contrast, primary aerosols, such as light absorbing carbon, are produced from distinct sources, emitted directly, and therefore tend to have the highest concentrations near their source locations. Clearly, both types of aerosols can be entrained in episodic weather patterns that transport them long distances; in general, however, regional aerosols correspond to secondary formation processes, while primary aerosols tend to be associated with local sources.

Urban excess is often characterized by examining the ratios and differences of aerosol concentrations at an urban site and associated remote or rural site(s). One of major challenges to estimating urban excess is determining the rural background concentration at an urban location. One method for computing urban excess is to use data from combinations of urban and nearby rural sites (within a defined elevation or distance). Rao et al. (2003) applied this approach and analyzed urban excess at thirteen CSN sites for one year of data (March 2001- February 2002). They chose nearby IMPROVE sites and performed an inverse-distance-weighted average of the rural concentrations to compare with data from the CSN sites. This approach is straightforward but does depend on the choice of sites and spatial averaging method used to characterize a rural concentration. Additional studies of urban excess were reviewed by Allen and Turner (2008) and the NARSTO (North American Research Strategy for Tropospheric Ozone and Aerosols) Assessment of Fine Particulate Matter Science for Policy Makers (2004). Many of the studies reviewed by Allen and Turner (2008) applied positive matrix factorization (e.g., Liu et al., 2003, 2005; Dutkiewicz et al., 2004; Eatough et al., 2006; Pekney et al., 2006) to data from urban and

rural sites to determine source contribution functions. Comparisons of sources at both sites led to the determination of regional versus local sources. Other studies reviewed by Allen and Turner (2008) and the NARSTO assessment used simpler analyses on data for paired sites to evaluate the relative urban and rural concentrations and determine an urban excess. Most of these studies focused on individual sites or regions (e.g., Kim et al, 2000; Hansen et al, 2003; Rao et al., 2003; U.S. EPA, 2004; Russell et al., 2004; Chow et al. 2006); very few, studies examined urban excess on a continental scale.

The choice of rural site(s) used in the above types of analyses is limited by logistical constraints such as availability and location of nearby sites. These types of issues can be avoided by using spatially-interpolated aerosol concentrations for both the urban and rural values, such as those presented in Chapter 2. Interpolations provide regularly gridded data through a sophisticated weighted averaging technique (a Kriging algorithm was used in Chapter 2). From the interpolated fields a rural aerosol concentration can be obtained at a location corresponding to an urban sampling site that reflects the background concentrations surrounding the site, not just at one or two locations. One major advantage to this method, over choosing a handful of sites in the analyses, is that the rural concentrations are determined from an interpolation scheme that incorporates data from all available nearby sites. The interpolation of both rural and urban data provides gridded urban and rural aerosol fields that can be combined to provide gridded estimates of urban excess for high resolution maps. However, these maps must be interpreted with some caution. Uncertainties introduced by interpolation schemes may bias the results. For example, interpolation schemes tend to smooth concentrations such that high urban concentrations could be biased low, and regions with sparse data may result in gridded concentrations with higher uncertainties.

A third option for estimating urban excess is a combination of the first two. Interpolated fields of rural aerosol concentrations can be used to determine a rural concentration at an urban site location. Measured data from an urban site can be used to compute a ratio or difference between urban and rural concentrations at the site location. These ratios and differences are then interpolated with a Kriging algorithm to provide isopleths of urban excess. An advantage to this method is avoiding the issues surrounding the subjective nature of choosing rural site locations, or the possibility that the chosen sites may not be representative of a regional background. In addition, urban site data are incorporated directly, avoiding the possibility of smoothed data from the interpolation scheme. We apply the third method as a compromise to incorporate actual urban data while retaining the detail in spatial patterns.

Rural concentrations were determined from the interpolated 2005–2008 annual mean IMPROVE data at the grid cell corresponding to the urban CSN site and limited to urban sites with at least one IMPROVE site within 150 km. The urban sites investigated for urban excess were chosen from the 174 CONUS (Contiguous United States) sites that met the completeness criteria outlined in Chapter 2 (sites in Alaska and Hawaii were not included in these analyses). Of these, 114 had a “complete” IMPROVE rural site within 150 km. The 60 sites that did not meet the distance limit were located in Alabama, Georgia, Illinois, Indiana, Iowa, Kentucky, Louisiana, Michigan, Missouri, New York, North Carolina, North Dakota, Ohio, Pennsylvania, South Carolina, Tennessee, Texas, West Virginia, and Wisconsin.

CSN sites are designated as "urban", "suburban", and "rural" by the EPA. We assumed all CSN sites were "urban" for this analysis as the designation of "rural" can have very different meanings than that for the IMPROVE network. No elevation corrections (standard pressure and temperature) were applied to the urban and rural data, with the assumption that if the sites were typically within 150 km, the corrections based on elevation differences would be negligible (it is unlikely that a site at sea level would be 150 km from a site at an elevation of 3 km). In fact, Rao et al. (2003) showed that elevation effects were negligible in their analyses. A more important elevation issue is the possibility that urban and rural sites with a significant elevation difference were actually sampling different air masses, as some IMPROVE monitors could be above the boundary layer in many cases (e.g. Denver and Rocky Mountain National Park).

Caveats to this approach include the uncertainties associated with interpolated aerosol concentrations and other fields. Isopleths serve to guide the eye in observing spatial patterns but obviously are only representations of reality. Site locations are not regularly spaced; regions with high site density from only one network, like in the eastern United States, could affect the derived results. In addition, characterization of "rural" aerosol concentrations assumed that the concentrations at rural sites were not significantly influenced by nearby urban regions, which is likely not the case.

Urban excess was investigated for 2005–2008 annual mean ammonium sulfate (AS), ammonium nitrate (AN), particulate organic matter (POM), light absorbing carbon (LAC), and $PM_{2.5}$ gravimetric fine mass (FM). Sea salt or fine soil were not included because of the relative biases derived for those species from analyses of data from collocated IMPROVE and CSN sites (see Table 1.8). Coarse mass also was not included, as CSN does not monitor for it. We computed differences and ratios in annual mean urban and rural concentrations from 2005 to 2008, although urban excess undoubtedly varies temporally, as the seasonal aerosol concentration for urban and rural sources can be very distinct (see Chapter 4). Differences in urban and rural concentrations emphasized relatively higher concentrations, while ratios revealed patterns in both low and high concentrations. For example, urban and rural LAC concentrations of 0.2 $\mu g\ m^{-3}$ and 0.1 $\mu g\ m^{-3}$, respectively, resulted in a difference of 0.1 $\mu g\ m^{-3}$ and a ratio of 2, while urban and rural FM concentrations of 20 $\mu g\ m^{-3}$ and 10 $\mu g\ m^{-3}$, respectively, result in a difference of 10 $\mu g\ m^{-3}$ but the same ratio of 2.

Isopleths maps of aerosol concentrations for both the IMPROVE and CSN networks are presented to remind the reader of the spatial patterns and magnitudes in concentrations for the species under consideration. The urban and rural aerosol concentration isopleths were created with the same scales to emphasize the differences in urban and rural concentrations. Maps of ratios and differences in urban and rural concentrations are also presented. Finally, results are summarized by comparing urban excess estimates for each species.

7.2. AMMONIUM SULFATE

Recall from Chapter 2.2.1 that the 2005–2008 annual mean AS concentrations were fairly regional in spatial extent. Figure 7.2.1 shows interpolated annual mean AS concentrations for rural IMPROVE sites, compared to the isopleths for IMPROVE plus CSN sites in Figure 7.2.2. The maximum concentration level listed on the scale corresponds to the 95th percentile for the combined IMPROVE and CSN data. Both maps were created with the same scale. The spatial

extent of AS concentrations was similar, with higher AS concentrations in the eastern United States for both networks. Higher urban concentrations in the eastern United States were associated with the Ohio River valley and Appalachian Mountains. Notice the difference in site density between the IMPROVE and CSN networks, with many additional eastern CSN sites that provide enhanced detail to the spatial patterns of AS in this area.

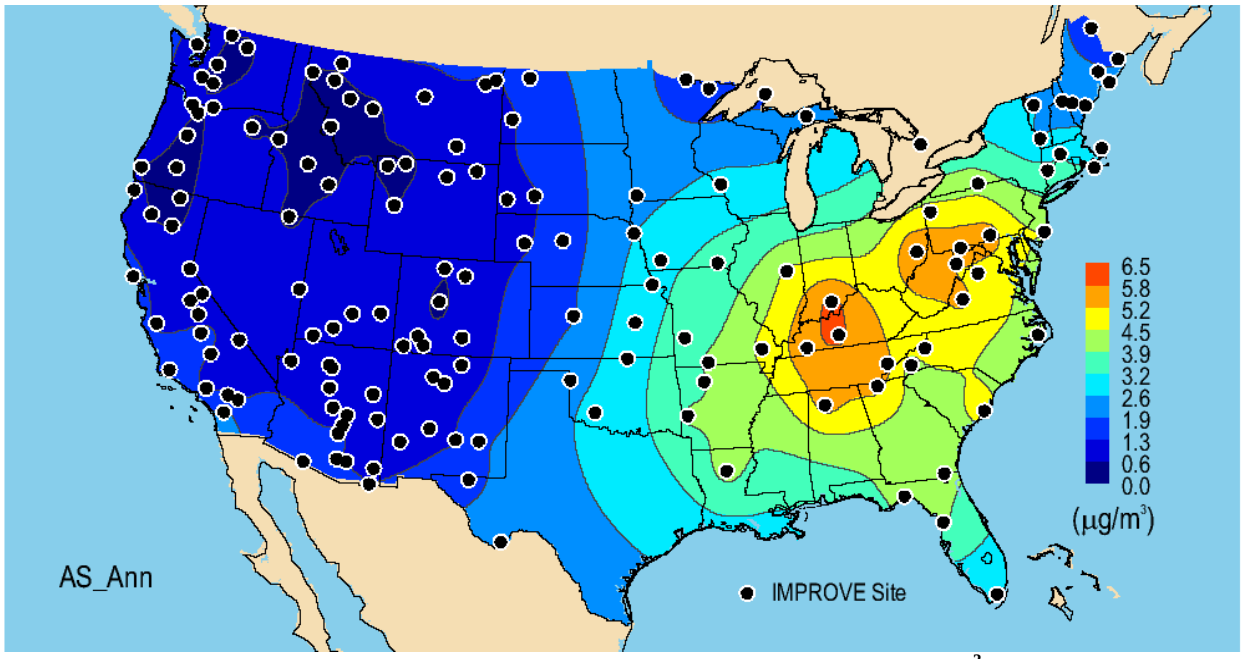

Figure 7.2.1. Interpolated annual mean ammonium sulfate (AS) concentrations (µg m^{-3}) for the rural IMPROVE network for 2005–2008. IMPROVE site locations are shown as black circles.

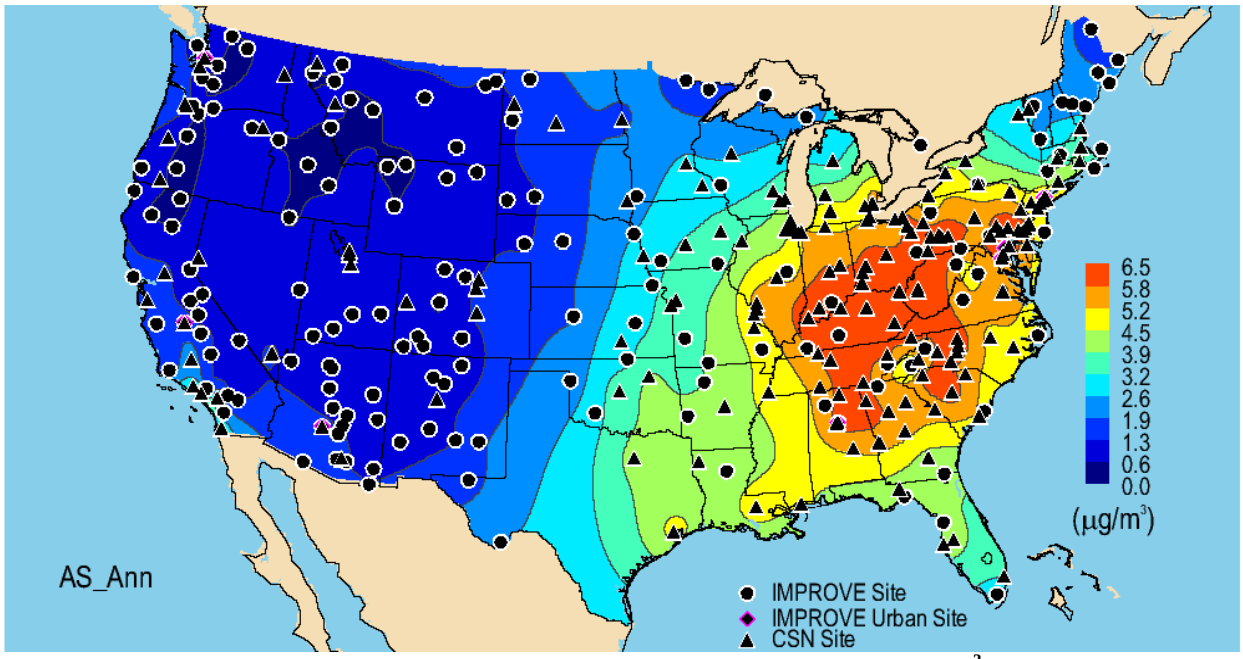

Figure 7.2.2. Interpolated annual mean ammonium sulfate (AS) concentrations (µg m^{-3}) for the rural IMPROVE and urban CSN networks for 2005–2008. IMPROVE site locations are shown as black circles, CSN sites are shown as black triangles, and urban IMPROVE sites are shown as magenta diamonds.

The ratio of urban to rural AS concentrations is shown in Figure 7.2.3. CSN site locations with an IMPROVE monitor within 150 km are depicted as black squares, and CSN sites that were not used in the analyses are shown as black triangles. The isopleth scale ranges from <1.26 to >2.0. The ratios ranged from 0.6 in Spokane (#530630016) to 2.9 in Los Angeles (#060371103). In addition to the southern California area, higher ratios occurred for a swath of area southeast of the Appalachian Mountains and the Ohio River valley. The lowest ratios occurred in the central, western, northwestern, and northeastern United States. The mean and one standard deviation in the ratio was 1.4 ± 0.3. Recall the relative bias of 7% in AS concentrations between CSN and the IMPROVE network, with CSN having larger concentrations (Table 1.9).

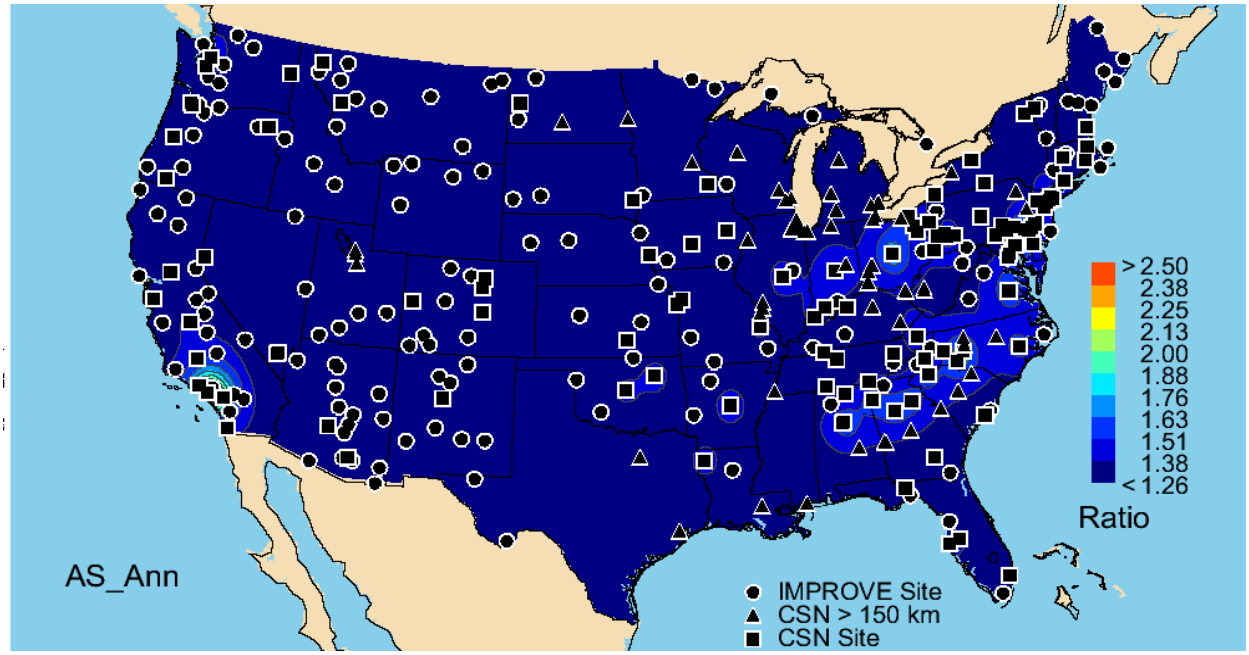

Figure 7.2.3. Interpolated ratios of urban (CSN) to rural (IMPROVE) annual mean ammonium sulfate (AS) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

The difference between urban and rural annual mean AS concentrations is shown in Figure 7.2.4. The scale ranges from <0.82 to >2.50 μg m^{-3}. Differences ranged from -0.7 μg m^{-3} in Spokane to 3.4 μg m^{-3} in Liberty, Pennsylvania (#420030064), with a mean of 1.3 ± 0.9 μg m^{-3}. Patterns in urban-rural differences highlight regions in the eastern United States, most likely because AS concentrations were higher there compared to the Southern California region. Higher differences corresponded to the Ohio River valley and Washington, D.C./Philadelphia Corridor and southeast of the Appalachian Mountains. Differences in these regions were ~2 μg m^{-3} or less. Most of the United States corresponded to differences less than 1 μg m^{-3}. The higher differences in the eastern United States may reflect the impact of site density and location on this type of analysis. While we focused on urban sites within 150 km of rural sites, the location of those sites could be important. For example, notice that the urban sites near the Appalachia Mountains region have rural sites to the north and west but no nearby sites in the southeast, corresponding to where ratios and differences were highest.

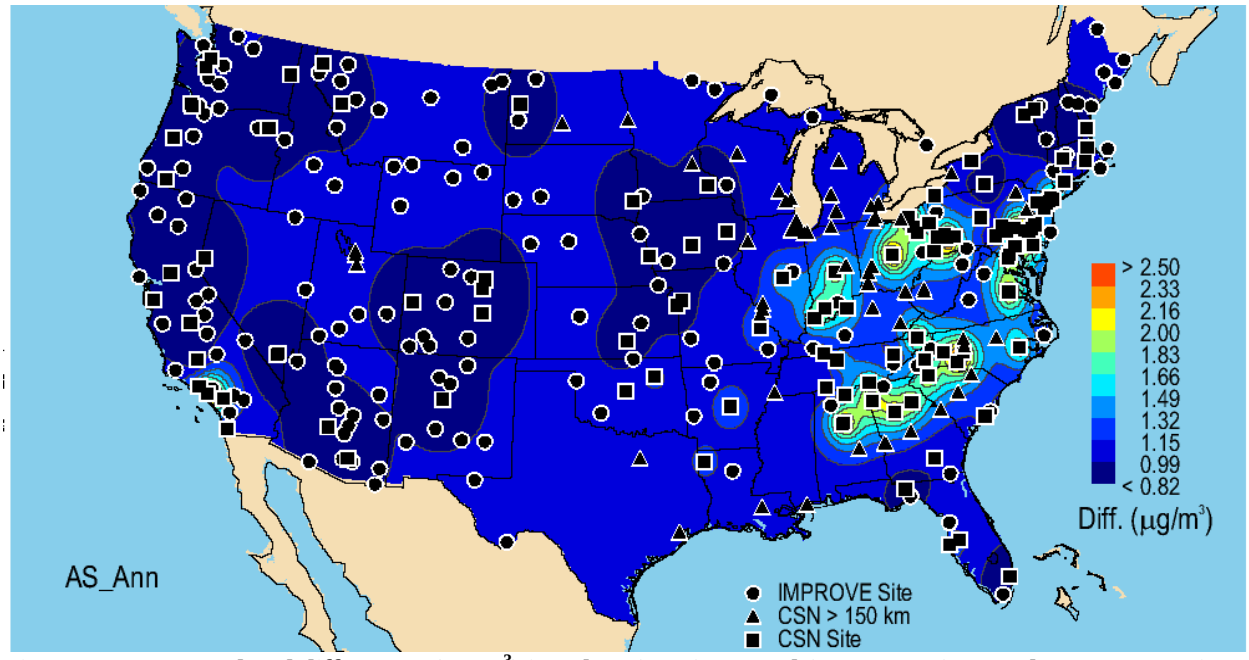

Figure 7.2.4. Interpolated differences (µg m^{-3}) in urban (CSN) to rural (IMPROVE) annual mean ammonium sulfate (AS) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

Rao et al. (2003) reported lower differences compared to those we derived; the over-all mean difference for the thirteen sites they investigated was 0.41 µg m^{-3} (we converted their sulfate ion mass difference to AS mass difference) and ranged from 0 to 1.4 µg m^{-3}. Our values at the same cities (although different time periods) ranged from -0.6 µg m^{-3} to 2.7 µg m^{-3}, with a mean of 1.8 ± 1.1 µg m^{-3}. We assumed we were using data from the same sites, although they did not list specific site ID. They also computed higher differences in sulfate ion mass for three western sites compared to ten eastern sites. In contrast, our analyses demonstrated larger differences in the eastern United States. Some of the discrepancy between our estimates and that of Rao et al. (2003) includes the different time periods of data used in the analysis and the calculation of rural aerosol concentration, as we applied a Kriging algorithm and they used a simple inverse weighting technique. The NARSTO (2004) assessment suggested that sulfate was strongly regional in the eastern United States. Urban excess ratios ranging from 1.05 to 1.33 were reported by the NARSTO assessment in a review of Hansen et al. (2003) for four urban-rural pairs of SEARCH (Southeastern Aerosol Research and Characterization Study) sites in Mississippi, Alabama, Georgia, and Florida from 1999 to 2001, consistent with our results. Allen and Turner (2008) also reported an urban to rural sulfate ratio of 1.05 in Saint Louis in 2001.

7.3 AMMONIUM NITRATE

Emissions of precursors to AN are higher in agricultural regions in the Midwest, resulting in the highest 2005–2008 annual mean concentrations of AN for rural sites (Figure 7.3.1). Elevated rural AN concentrations are also found in southern California in the West and near Baltimore and Washington, D.C. in the East, perhaps due to urban sources. Urban concentrations (Figure 7.3.2) were also higher in the Midwest and were considerably higher than rural concentrations in the same region. Relatively high urban AN concentrations in the Midwest

extended farther east to include several sites in Michigan, Indiana, Ohio, and Wisconsin. In addition, urban sources resulted in several localized areas with relatively high AN concentrations, such as cities in southern California, Salt Lake City, Denver, and cities in the northeastern United States.

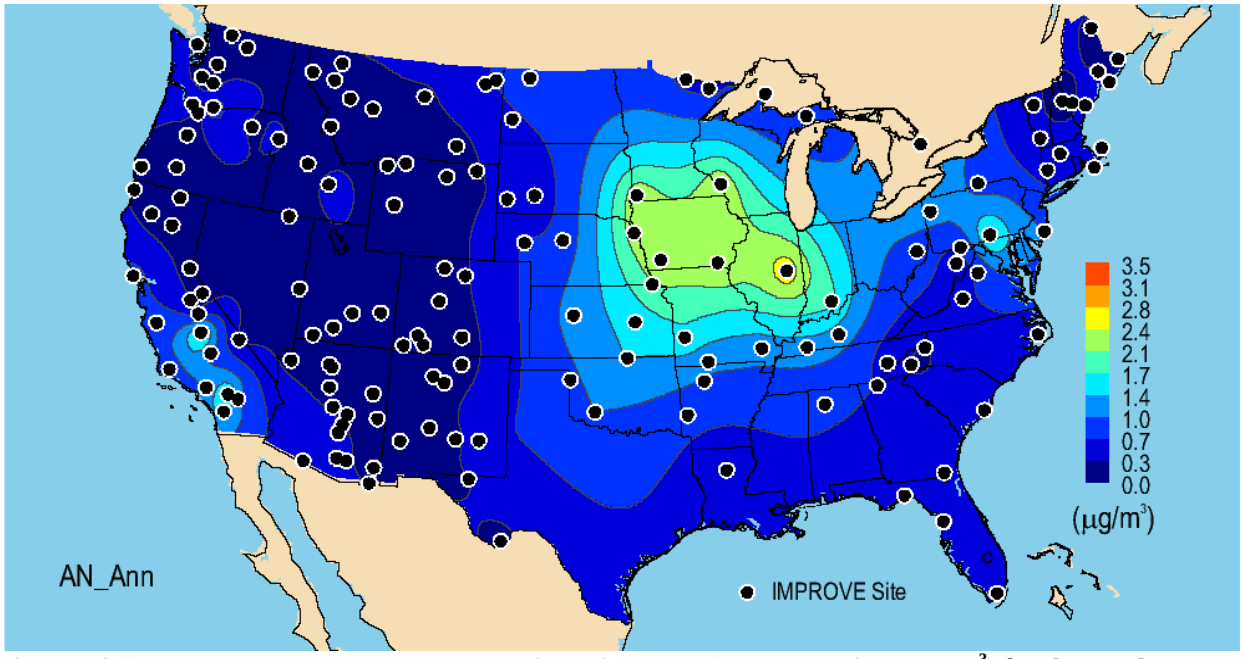

Figure 7.3.1. Interpolated annual mean ammonium nitrate (AN) concentrations (µg m^{-3}) for the rural IMPROVE network for 2005–2008. IMPROVE site locations are shown as black circles.

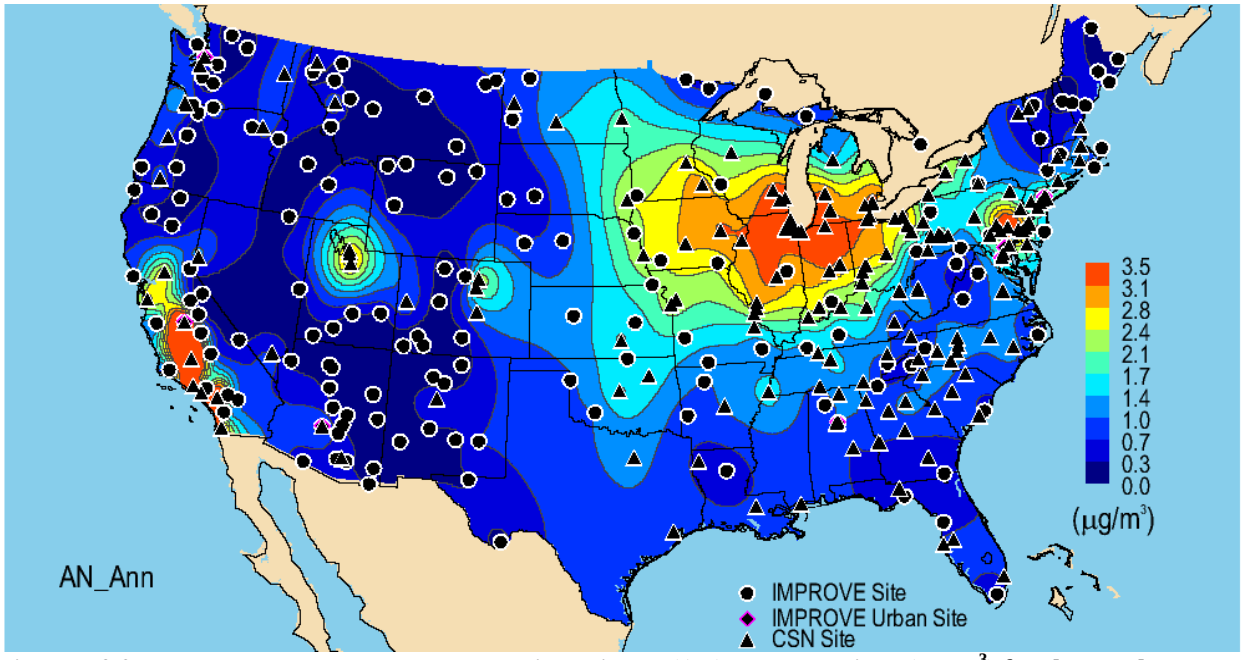

Figure 7.3.2. Interpolated annual mean ammonium nitrate (AN) concentrations (µg m^{-3}) for the rural IMPROVE and urban CSN networks for 2005–2008. IMPROVE site locations are shown as black circles, CSN sites are shown as black triangles, and urban IMPROVE sites are shown as magenta diamonds.

The impacts of urban sources of AN to surrounding rural regions were apparent by examining the ratio of urban to rural AN concentrations as shown in Figure 7.3.3. Western cities such as Denver, Missoula, and Medford, Oregon, corresponded to relatively high ratios with sharp spatial gradients. Most of California corresponded to higher ratios. Based on the differences in the rural and urban concentrations in the Great Lakes region of the Midwest presented in Figures 7.3.1 and 7.3.2, respectively, one would expect significant urban excess in that region. However, none of the urban sites in that area were associated with rural sites within 150 km (notice the sites depicted as triangles in that region); therefore low urban excess in that area was most likely due to lack of data. The urban to rural ratio ranged from 0.8 in Wilmington, New York, (#360310003) to 7.9 in Bakersfield, California (#060290014). The mean ratio (one standard deviation) was 2.5±1.3. Recall the relative bias in AN concentrations of 17.2% with CSN having higher concentrations.

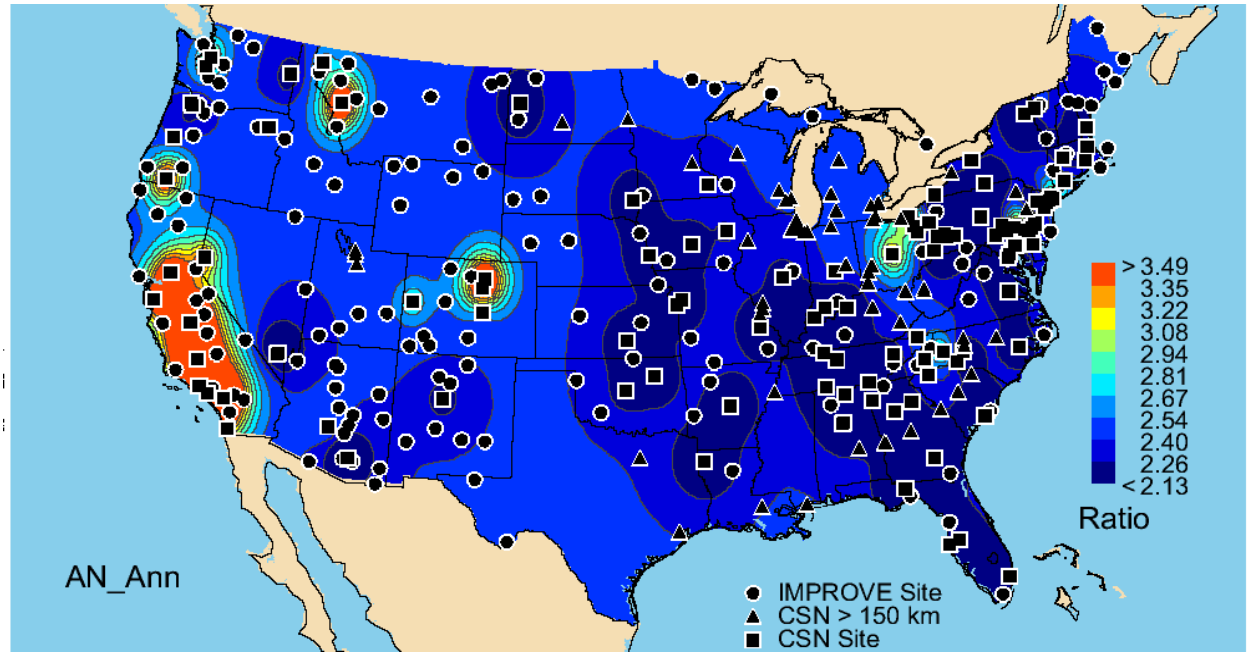

Figure 7.3.3. Interpolated ratios of urban (CSN) to rural (IMPROVE) annual mean ammonium nitrate (AN) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

The difference in urban and rural AN ranged from -0.11 μg m^{-3} in Wilmington to 7.8 μg m^{-3} in Rubidoux, California (#060658001). The mean difference was 1.2 ± 1.3 μg m^{-3}. The spatial pattern in the urban-rural difference is shown in Figure 7.3.4. Higher differences were associated with Denver, Rochester, Minnesota, Cedar Rapids, Iowa, Decatur, Illinois, Indianapolis, Columbus, Ohio, and New York City. Unlike urban to rural ratios, the differences in Medford, Oregon, were relatively low, probably because concentrations there were also relatively low (see Figure 7.3.2). Most of central and southern California corresponded to differences in AN concentrations around 1.9 μg m^{-3} or greater.

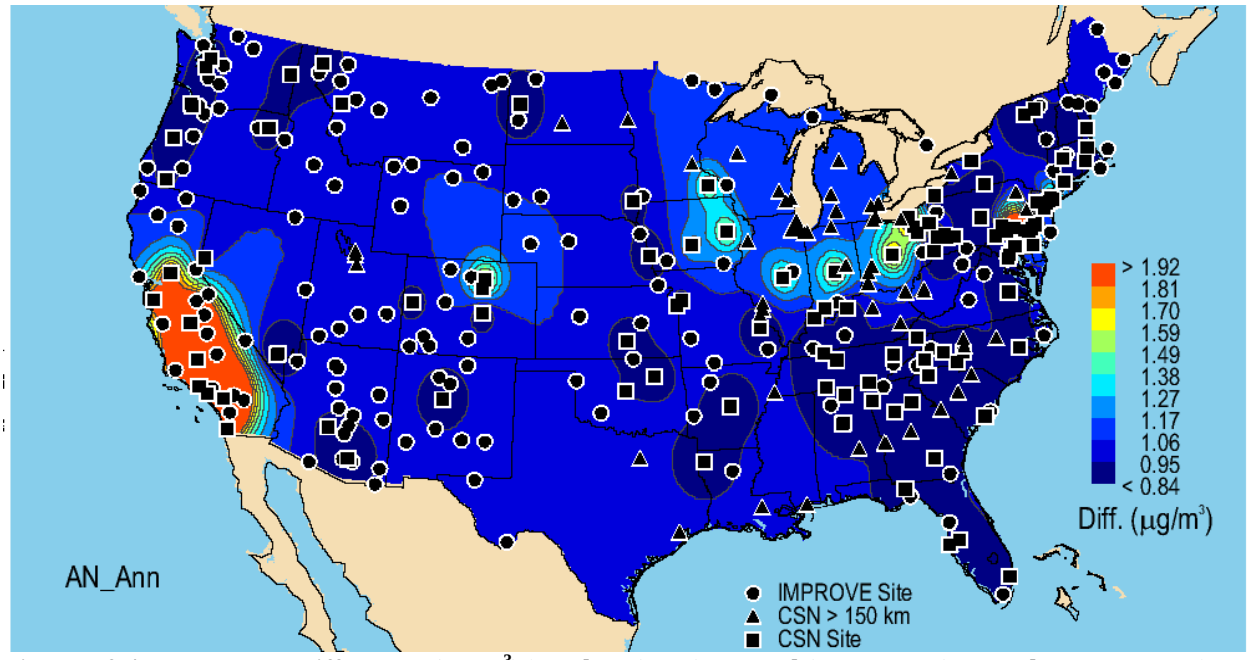

Figure 7.3.4. Interpolated differences (µg m^{-3}) in urban (CSN) to rural (IMPROVE) annual mean ammonium nitrate (AN) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

A similar range in urban to rural difference was computed by Rao et al. (2003). Their values ranged from 0.52 µg m^{-3} to 8.4 µg m^{-3}, with an average of 1.9 µg m^{-3} for thirteen sites. They found that higher values corresponded to western U.S. cities (Fresno and Salt Lake City) and in the central (Cleveland) and northeastern United States (Baltimore and the Bronx), similar to the spatial patterns shown in Figure 7.3.4. For the same cities we computed a difference range from 0.3 µg m^{-3} to 6.0 µg m^{-3} with a mean of 1.6 ± 1.5 µg m^{-3}. These estimates were in closer agreement than those for AS. Recall that estimates by Rao et al. (2003) correspond to a different time period.

Other studies in the central Midwest suggested regional-scale nitrate events with smaller urban excess (Allen and Turner, 2008, and references therein). In addition, the region-wide nitrate influence in the San Joaquin Valley in California was also observed during the CRPAQS study (Central California Regional PM10/PM2.5 Air Quality Study, Chow et al. 2006; Turkiewicz et al. 2006). While AN is secondary in nature, its spatial extent may be limited by its specific sources or equilibrium behavior in the atmosphere.

7.4 PARTICULATE ORGANIC MATTER

Urban excess estimates for POM did not account for different types of organic aerosols known to exist in urban versus rural settings. Urban organic aerosols from local sources are less aged and correspond to lower molecular weight per carbon weight ratios compared to rural aerosols (e.g., Turpin and Lim, 2001). We did not account for differences in the organic carbon multiplier for urban versus rural aerosols in this analysis (a value of 1.8 was applied to both), although Malm et al. (2011) suggested that the urban organic multiplier was 5–15% lower than

that for rural sites after investigating biases in fine mass data from the IMPROVE network and the CSN (also see Chapter 8).

The highest 2005–2008 rural annual mean POM concentrations corresponded to a large regional area in the southeastern United States (Figure 7.4.1), most likely associated with biogenic emissions and perhaps biomass smoke emissions (Tanner et al., 2004; Bench et al., 2007). The western United States was associated with more localized regions of higher rural POM concentrations. The impact of urban POM sources on local and regional POM concentrations was significant, as shown in Figure 7.4.2. In the southeastern United States, the regional extent of higher rural POM concentrations increased and the spatial pattern became more resolved with the addition of urban sites, especially to the southeast of the Appalachian Mountains. Higher POM concentrations and more localized impacts of urban POM sources were apparent in the western United States, such as for cities in Colorado, Utah, Nevada, Arizona, California, Oregon, Idaho, Montana, and Washington, with sharper gradients compared to the eastern United States.

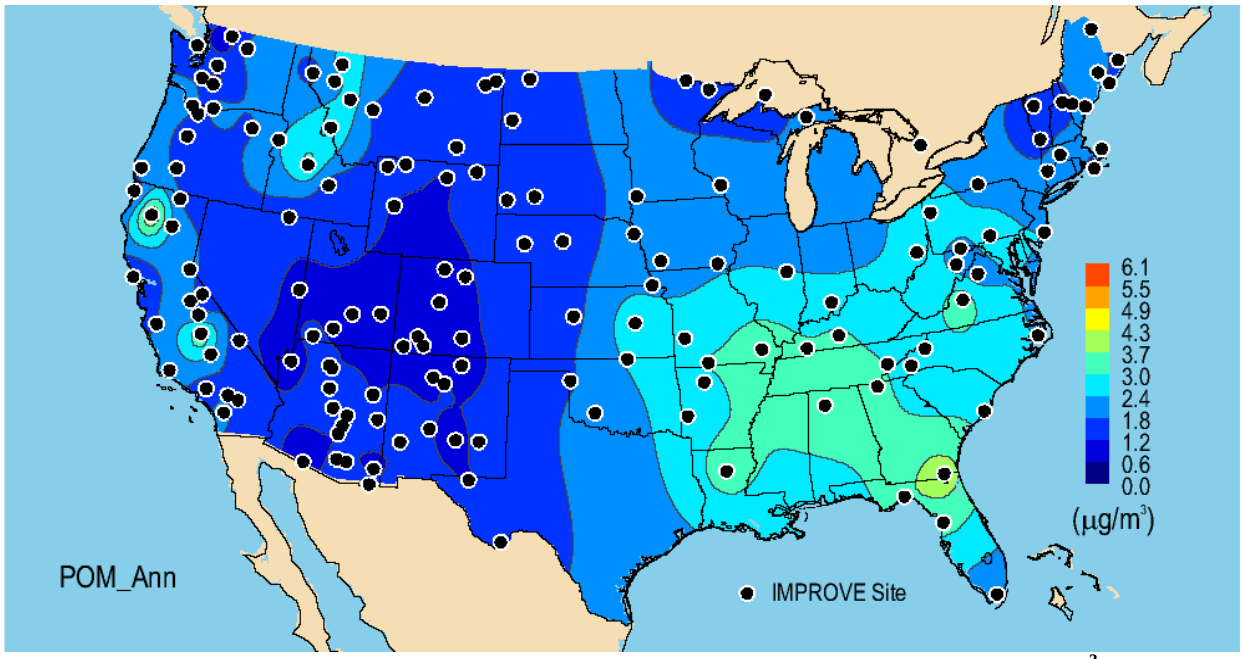

Figure 7.4.1. Interpolated annual mean particulate organic matter (POM) concentrations (µg m^{-3}) for the rural IMPROVE network for 2005–2008. IMPROVE site locations are shown as black circles.

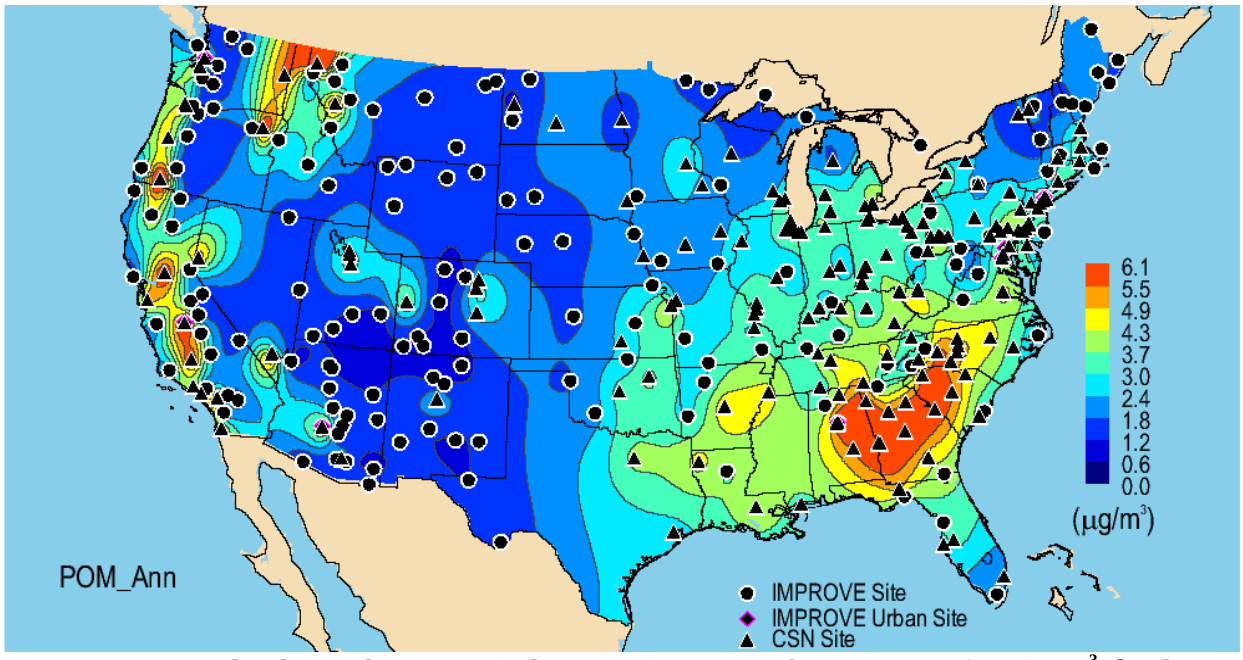

Figure 7.4.2. Interpolated annual mean particulate organic matter (POM) concentrations (µg m^{-3}) for the rural IMPROVE and urban CSN networks for 2005–2008. IMPROVE site locations are shown as black circles, CSN sites are shown as black triangles, and urban IMPROVE sites are shown as magenta diamonds.

This pattern of localized influence is displayed more clearly as the urban to rural concentration ratio in Figure 7.4.3. Several western cities were associated with higher ratios (urban concentrations over 2.5 times higher than rural concentrations), including Denver, Grand Junction, Phoenix, and Las Vegas. Several northwestern U.S. sites as well as most of California were associated with higher ratios. In the southeastern United States, a swath of area to the southeast of the Appalachian Mountains corresponded to ratios of ~2.3. This area was associated with the highest POM urban concentrations and the fewest number of rural IMPROVE sites. Urban concentrations were 1.9 ± 0.9 higher than rural concentrations on average. Ratios ranged from 0.6 in Wilmington, New York (#360310003, designated as a "rural" site), to 6.7 in Libby, Montana (#300530018).

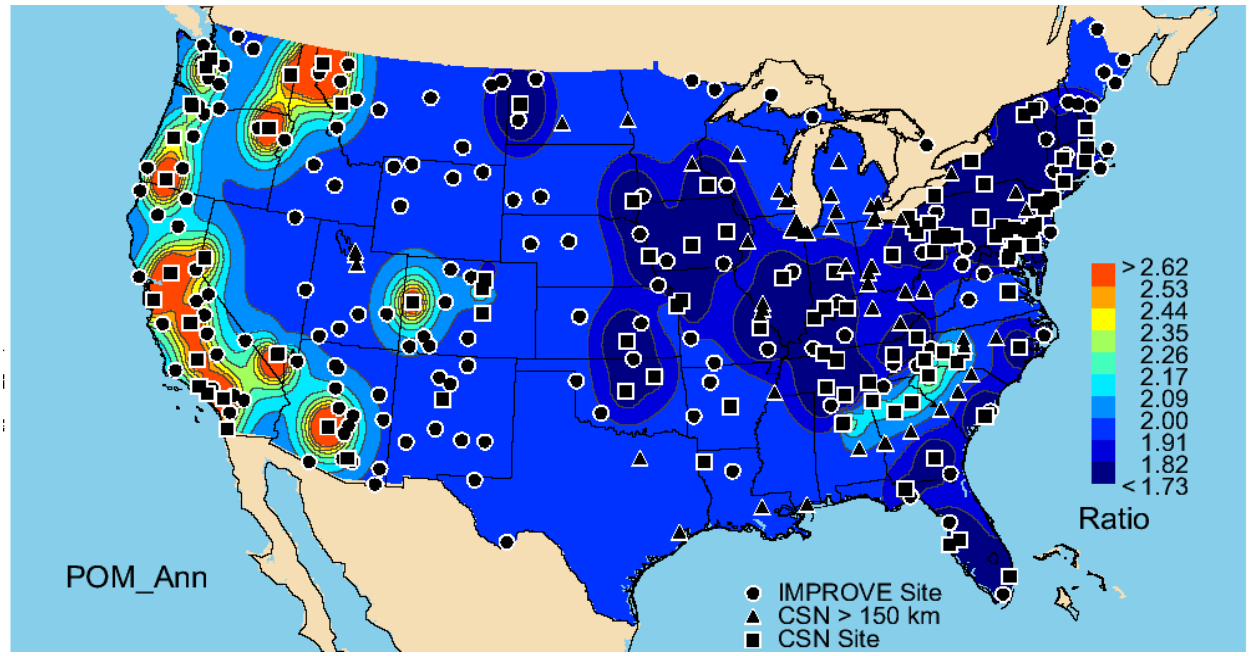

Figure 7.4.3. Interpolated ratios of urban (CSN) to rural (IMPROVE) annual mean particulate organic matter (POM) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

Similar spatial patterns were associated with urban-rural POM differences (Figure 7.4.4). Higher differences (over 3 μg m^{-3}) corresponded to sites along the western coast and in the northwestern United States. The differences in some western cities, such as Denver, Grand Junction, Phoenix, and Las Vegas were not as pronounced as for the ratio patterns, probably because concentrations were lower in those areas in general (see Figure 7.4.2). Higher differences were associated with the same swath of area in the southeastern United States as was observed in the ratio isopleths, but extended over a larger area. Differences ranged from -0.7 μg m^{-3} (Wilmington) to 9.9 μg m^{-3} (Libby), with an average urban to rural difference in annual mean POM concentration of 1.9 ± 1.6 μg m^{-3}. In general the impacts of urban POM sources were fairly local and contained within the first set of surrounding rural sites.

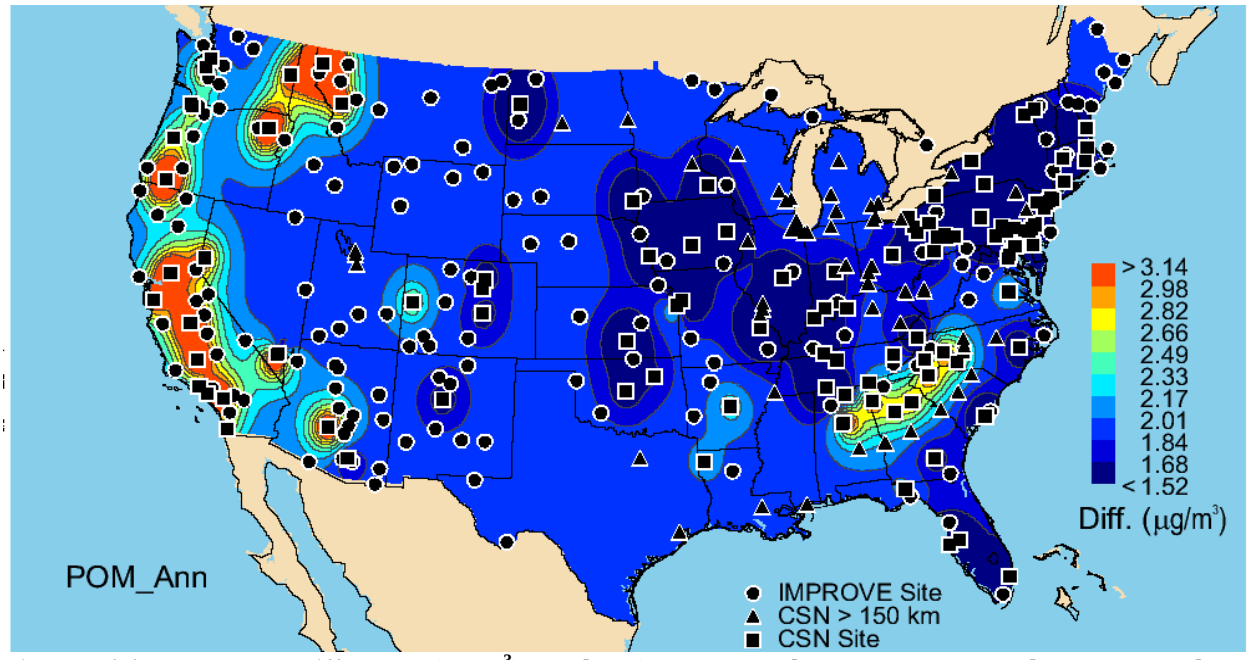

Figure 7.4.4. Interpolated differences (µg m^{-3}) in urban (CSN) to rural (IMPROVE) annual mean particulate organic matter (POM) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

The NARSTO assessment reported urban to rural ratios of 1.33–1.67 in the eastern United States, corresponding to SEARCH sites in Mississippi, Alabama, Georgia, and Florida, consistent with our findings (Hansen et al., 2003). Studies in California (Kim et al., 2000; Chow et al, 2006) suggested POM sources that were strongly local. An urban to rural ratio of 1.8 was computed at the Saint Louis Supersite during a 3-month study in 2001 (Allen and Turner, 2008). Rao et al. (2003) computed urban excess for total carbon, not POM and light absorbing carbon separately. We discuss those estimates at the end of the next section.

7.5 LIGHT ABSORBING CARBON

Spatial patterns in 2005–2008 annual mean rural concentrations of LAC were largely indistinguishable in Figure 7.5.1 when using the same scale as the urban map, suggesting that urban LAC concentrations were much larger than rural values. Urban LAC concentrations generally were localized around individual site locations in the western United States and more regional in extent in the eastern United States, although not to the degree of POM (see Figure 7.5.2). Western U.S. urban sites that corresponded to higher LAC concentrations also corresponded to higher POM concentrations (e.g., Denver, Las Vegas, and Phoenix and sites in California and the northwestern United States).

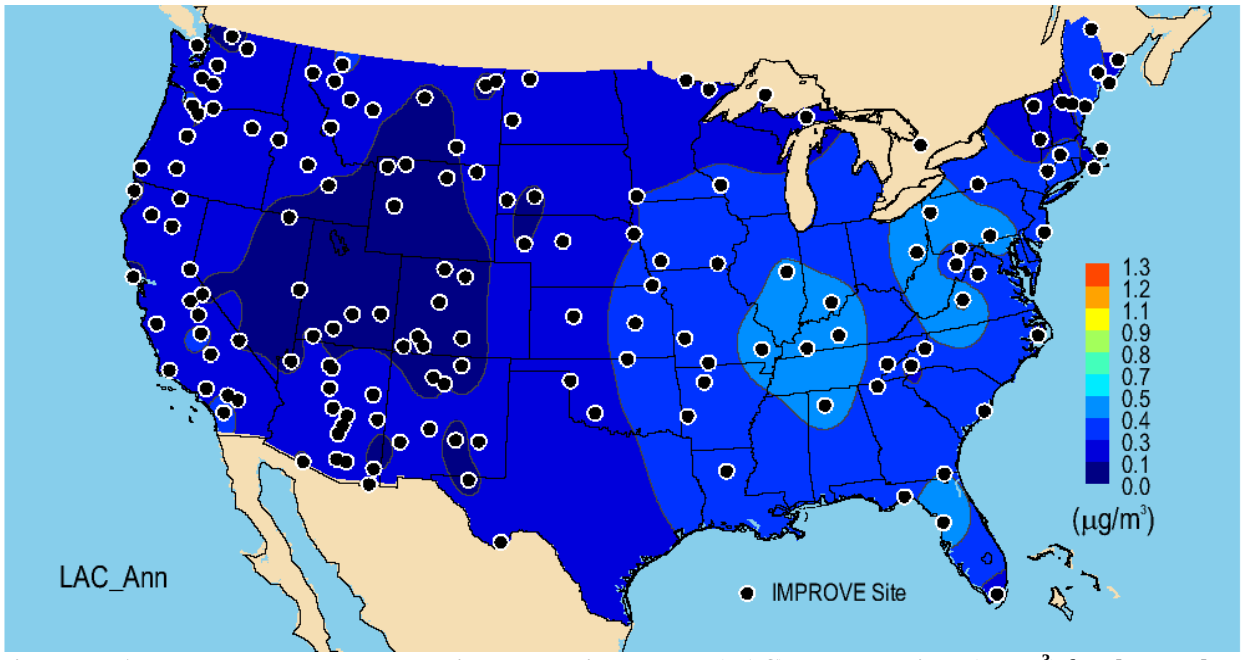

Figure 7.5.1. Interpolated annual mean light absorbing carbon (LAC) concentrations (µg m^{-3}) for the rural IMPROVE network for 2005–2008. IMPROVE site locations are shown as black circles.

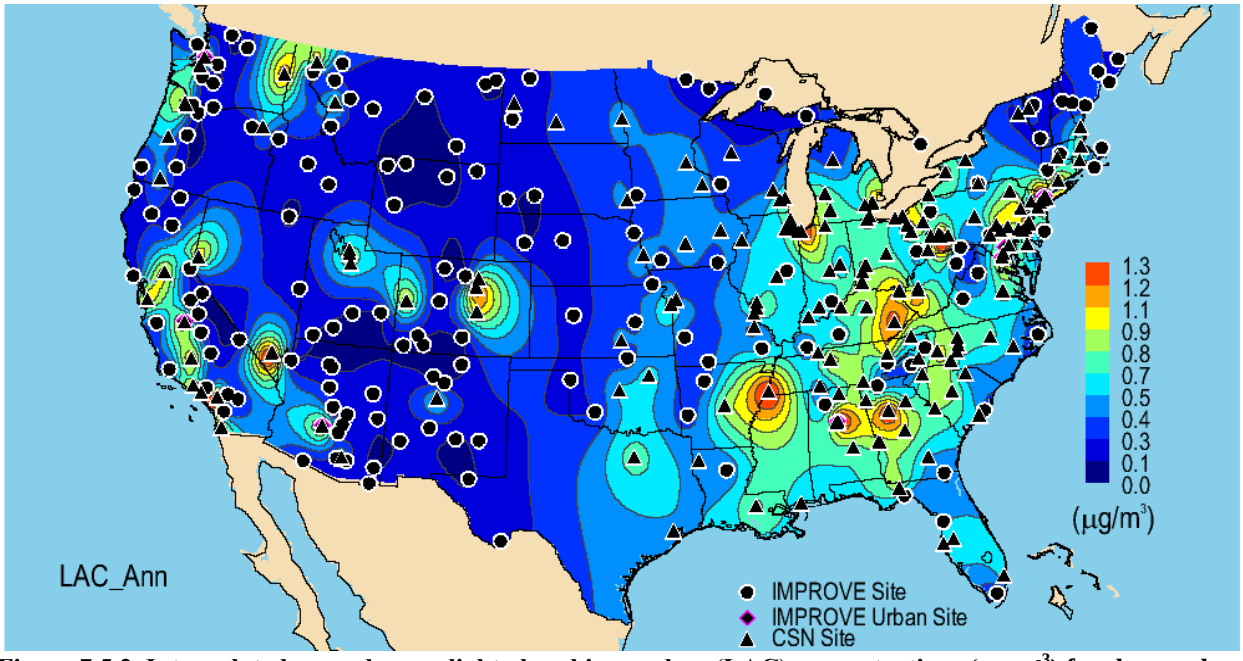

Figure 7.5.2. Interpolated annual mean light absorbing carbon (LAC) concentrations (µg m^{-3}) for the rural IMPROVE and urban CSN networks for 2005–2008. IMPROVE site locations are shown as black circles, CSN sites are shown as black triangles, and urban IMPROVE sites are shown as magenta diamonds.

The ratio of urban to rural LAC concentrations demonstrated the localized impact of LAC on surrounding rural regions. Fewer eastern U.S sites were associated with higher ratios compared to the western United States (Figure 7.5.3). Western U.S. sites in Colorado, Arizona, Nevada, California, Montana, and Washington were associated with high ratios with small spatial extent. In California the LAC excess was more localized compared to the spatial extent of

POM excess. Although the locations associated with high ratios were similar for POM and LAC, LAC ratios were much larger, suggesting urban LAC sources were significantly larger than rural sources and less regional in extent than POM. Ratios ranged from 0.8 in Watford City, North Dakota (#380530002, designated as a "rural" CSN site), to 10.5 in Las Vegas (#320030561). The mean ratio was 3.3 ± 1.9 and was much larger than the mean ratio for AS, AN, or POM.

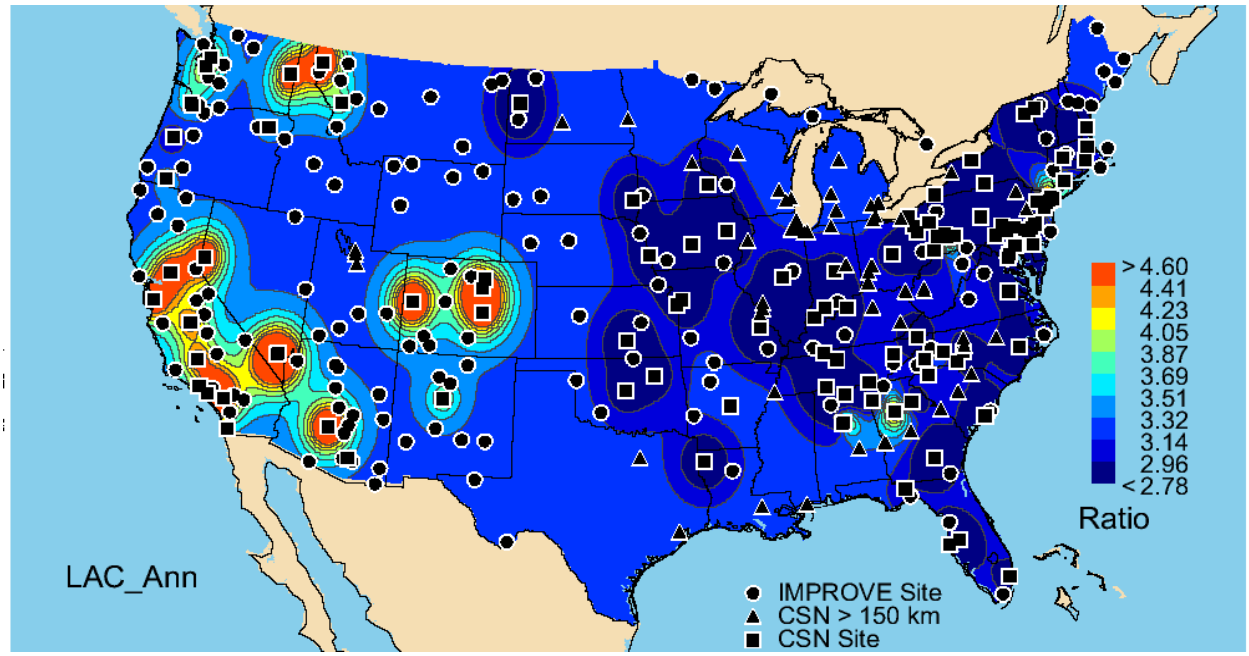

Figure 7.5.3. Interpolated ratios of urban (CSN) to rural (IMPROVE) annual mean light absorbing carbon (LAC) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

The urban to rural difference in LAC ranged from -0.05 μg m^{-3} in Watford City, North Dakota, to 2.2 μg m^{-3} in Liberty, Pennsylvania (#420030064). The mean difference was 0.6±0.4 μg m^{-3}, the lowest difference of all the species examined, but recall that LAC concentrations were relatively low. Patterns in urban to rural differences were similar to ratios for most western U.S. locations, but several additional locations emerged in the eastern United States (Figure 7.5.4). For most eastern U.S. locations, the differences were associated with tight gradients surrounding individual sampling sites. The spatial pattern in LAC difference was similar to POM differences but differed in the spatial extent, with the impact of urban LAC sources spatially localized.

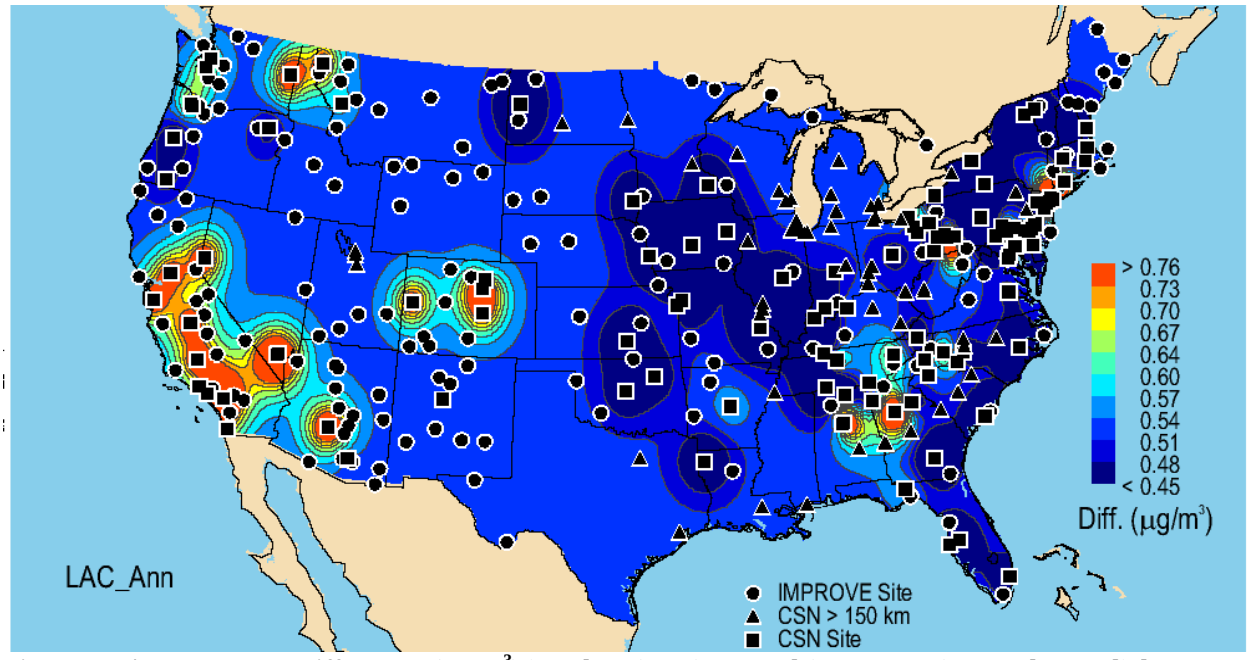

Figure 7.5.4. Interpolated differences (µg m^{-3}) in urban (CSN) to rural (IMPROVE) annual mean light absorbing carbon (LAC) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

As mentioned in the previous section, Rao et al. (2003) investigated urban excess in total carbon (TC) instead of POM and LAC separately, due to the differences in analytical methods and monitoring equipment between the CSN and IMPROVE networks. They computed TC by assuming an organic multiplier of 1.8 and derived differences in TC that ranged from 2.9 µg m^{-3} to 13.2 µg m^{-3} with a mean of 5.1 µg m^{-3}. Values were higher for cities in the western, northwestern, and southeastern United States. Combining our LAC and POM differences at the same sites resulted in a range of TC differences from 1.9 µg m^{-3} to 6.0 µg m^{-3} with a mean of 3.3±1.3 µg m^{-3}.

7.6 $PM_{2.5}$ GRAVIMETRIC FINE MASS

FM 2005–2008 annual mean concentrations for IMPROVE and CSN are shown in Figures 7.6.1 and 7.6.2, respectively. Plotting isopleths with the same scale reduced peaks in FM for the rural network, resulting in a less resolved pattern of FM concentrations in the eastern United States. In the western United States, urban regions with higher FM were associated with sites in southern California, Montana, Utah, Colorado, Nevada, and Arizona. Discussions from previous sections suggested that these hotspots were most likely associated with AN and POM concentrations. Higher FM concentrations in the eastern United States were associated with sites in the New York City-Philadelphia area and the Ohio River valley and Appalachian Mountains, probably associated with AS, POM, and AN.

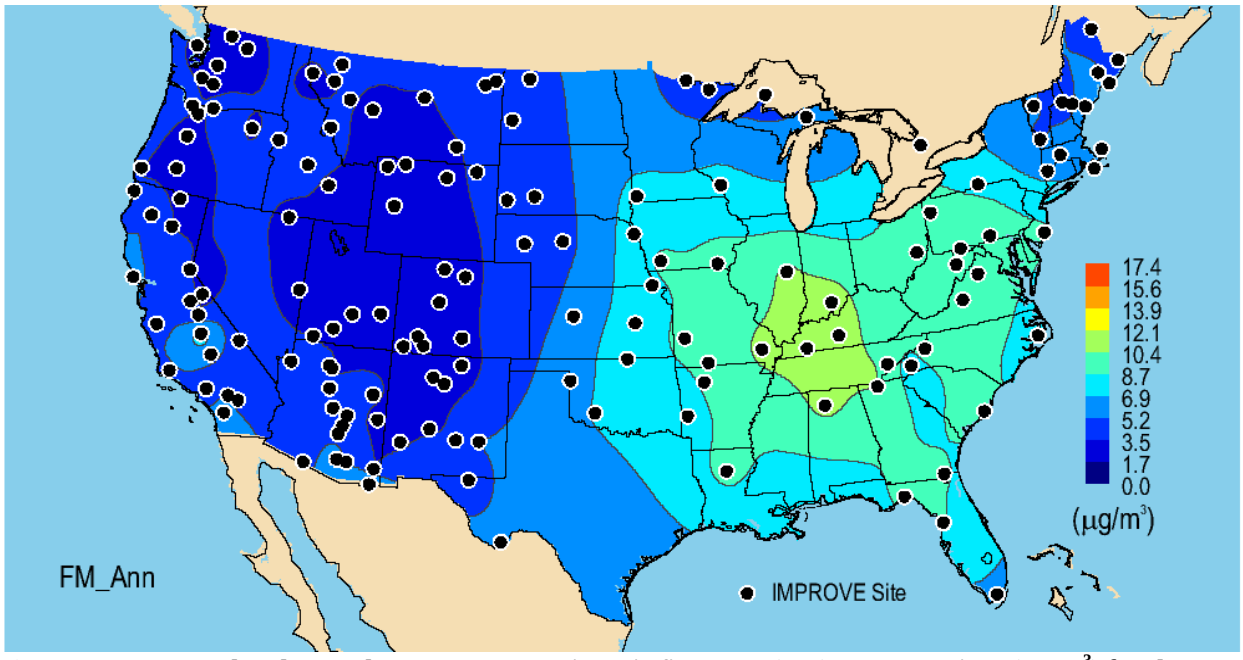

Figure 7.6.1. Interpolated annual mean $PM_{2.5}$ gravimetric fine mass (FM) concentrations (µg m^{-3}) for the rural IMPROVE network for 2005–2008. IMPROVE site locations are shown as black circles.

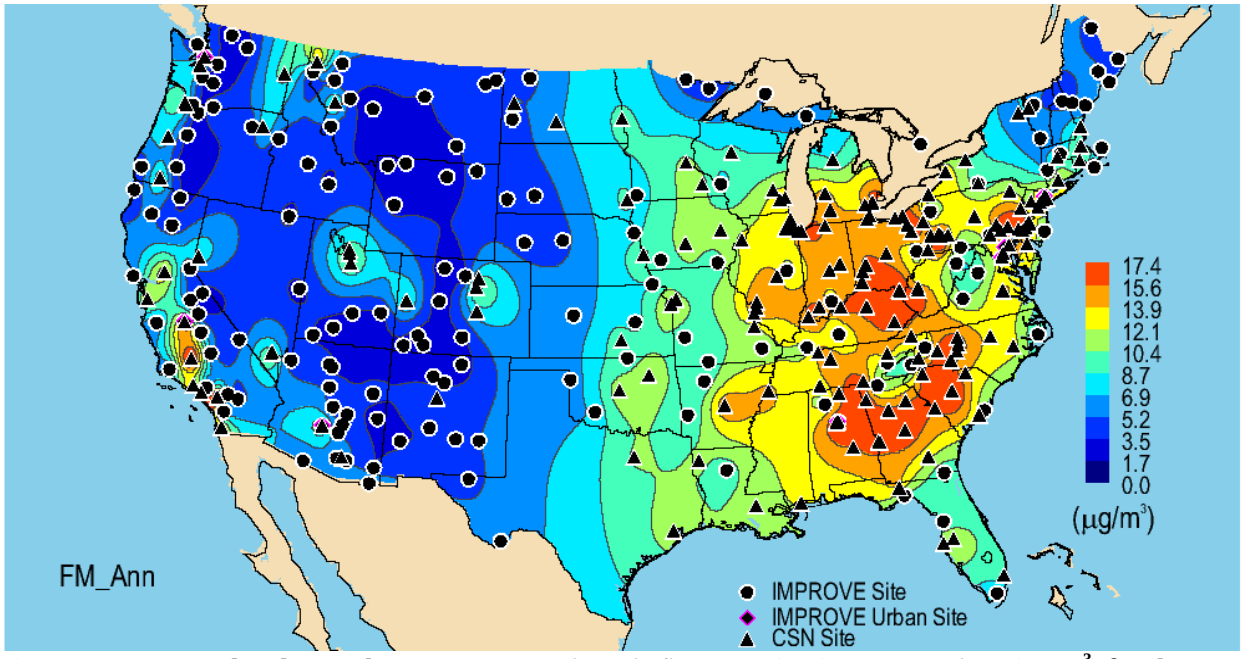

Figure 7.6.2. Interpolated annual mean $PM_{2.5}$ gravimetric fine mass (FM) concentrations (µg m^{-3}) for the rural IMPROVE and urban CSN networks for 2005–2008. IMPROVE site locations are shown as black circles, CSN sites are shown as black triangles, and urban IMPROVE sites are shown as magenta diamonds.

Ratios of urban to rural FM concentrations ranged from 1.0 (Wilmington, New York, #360310003) to 4.3 (Libby, Montana, #300530018), with a mean of 2.0 ± 0.6 and were highest at sites in central and southern California, Montana, Washington, Oregon, and Colorado (Figure 7.6.3). Patterns of high ratios in California were most likely associated with AN (see Figure 7.3.3), whereas patterns of high FM ratios in Washington, Oregon, Montana, Colorado, and Utah

were most likely due to a combination of POM and AN (see Figure 7.4.3). In the eastern United States, the patterns in FM were similar to those of AS (especially southeast of the Appalachian Mountains and the Ohio River Valley, see Figure 7.2.3), and POM (e.g., southeast of the Appalachian Mountains, Figure 7.4.3). Recall the relative bias of 18.4% between CSN and IMPROVE data, with CSN having higher FM concentrations.

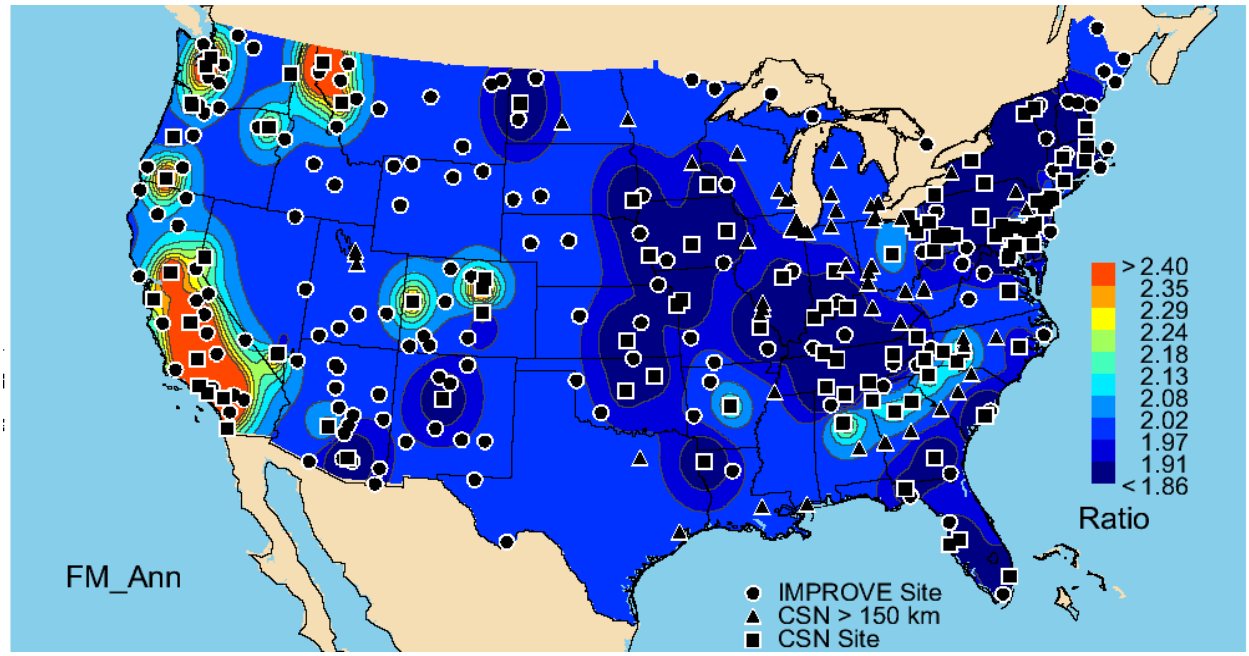

Figure 7.6.3. Interpolated ratios of urban (CSN) to rural (IMPROVE) annual mean $PM_{2.5}$ gravimetric fine mass (FM) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

Differences in FM concentrations ranged from 0.2 μg m^{-3} in Wilmington, New York, to 15.7 μg m^{-3} in Rubidoux, California (#060658001), with a mean of 7 ± 3 μg m^{-3}. The largest difference in FM corresponded to central and southern California, near Libby, Montana, near the Appalachian Mountains, and the Ohio River valley (see Figure 7.6.4). Excess values greater than 8 μg m^{-3} along the Appalachian Mountains were perhaps due to differences in POM (~3 μg m^{-3}, see Figure 7.4.4) and AS (~2 μg m^{-3}, see Figure 7.2.4).

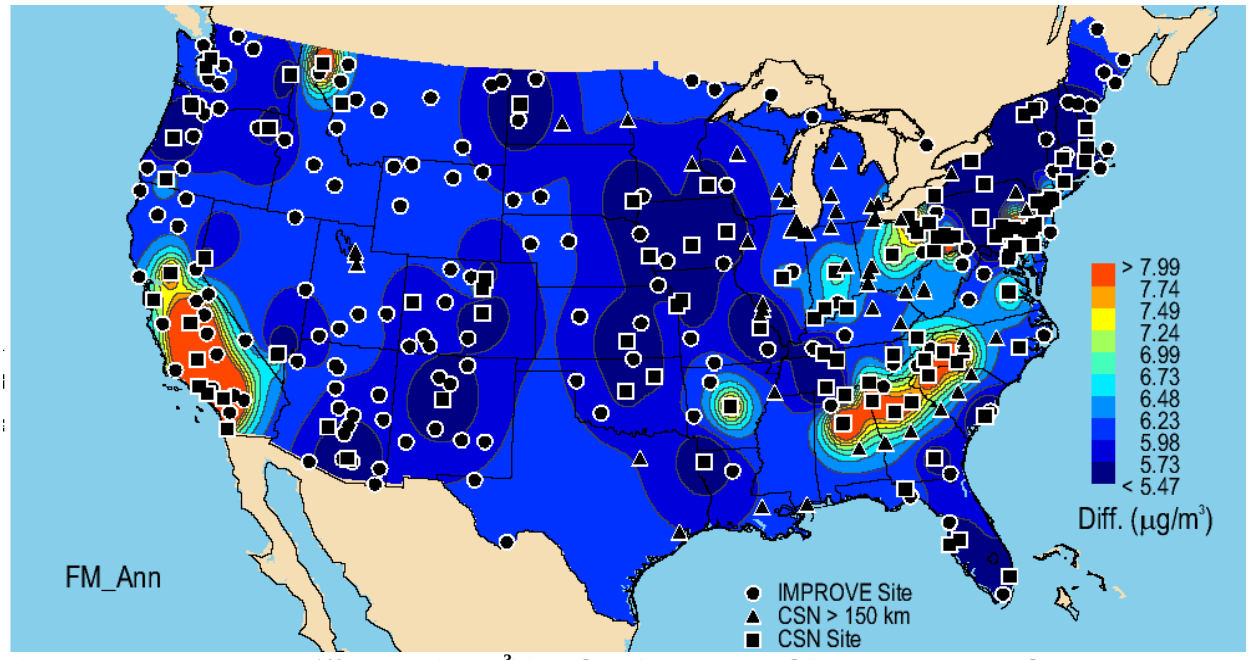

Figure 7.6.4. Interpolated differences (µg m^{-3}) in urban (CSN) to rural (IMPROVE) annual mean $PM_{2.5}$ gravimetric fine mass (FM) concentrations for 2005–2008. IMPROVE sites are shown as circles, CSN sites with an IMPROVE monitor within 150 km are depicted as squares, and CSN sites not used in the analyses are shown as triangles.

Although Rao et al. (2003) included FM in their analyses, they did not report urban excess values for it specifically so we were not able to perform comparisons with those results. However, the graphical display of their data suggested that the FM excess ranged from 4-16 µg m^{-3} (mean of ~8 µg m^{-3}), with higher values corresponded to western sites compared to sites in the East.

7.7 SUMMARY

The spatial patterns and magnitudes of urban excess (defined as either the urban to rural ratio or difference) differed significantly depending on species. This is not unexpected based on the differences in spatial patterns and seasonality of mass concentrations presented here and in Chapter 2 and Chapter 4. Scatter plots of urban and rural concentrations are shown in Figure 7.7.1a and Figure 7.7.1b and correspond only to the sites used in these analyses. The urban concentrations correspond to CSN data, while the rural concentrations correspond to the interpolated IMPROVE data at the CSN site location. Both figures present the same data but with a linear scale (Figure 7.7.1a) and a logarithmic scale (7.7.1b) to enhance the lower magnitude concentrations mainly associated with LAC. The relationship between rural and urban concentrations suggested that the magnitude of rural background concentrations is changing in response to regional influences and perhaps to local sources at nearby urban sites. The mass concentrations corresponding to different species separated according to their relative magnitudes and increased in order from LAC, AN, POM, and AS. These results suggested that the urban excess in AS increased for AS concentrations, as lower AS concentrations were in closer agreement. It was expected that the urban and rural AS concentrations would be similar, given the regional extent of sulfate sources in the area, when in fact the AS urban concentrations were higher than rural concentrations, with an average ratio of 1.4.

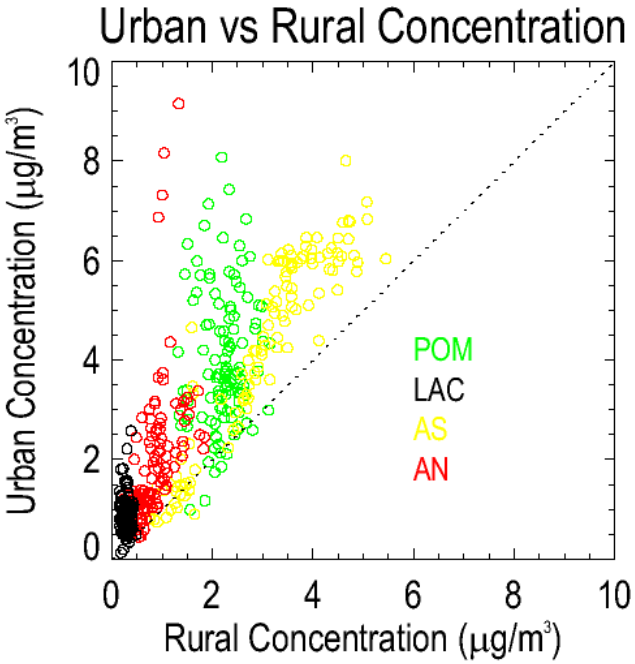

Figure 7.7.1(a). Comparisons of 2005–2008 annual mean IMPROVE rural concentration (interpolated) on the x-axis and CSN urban concentration (data) on the y-axis for ammonium sulfate (AS, yellow), ammonium nitrate (AN, red), particulate organic matter (POM, green), and light absorbing carbon (LAC, black). Concentrations are in µg m^{-3}.

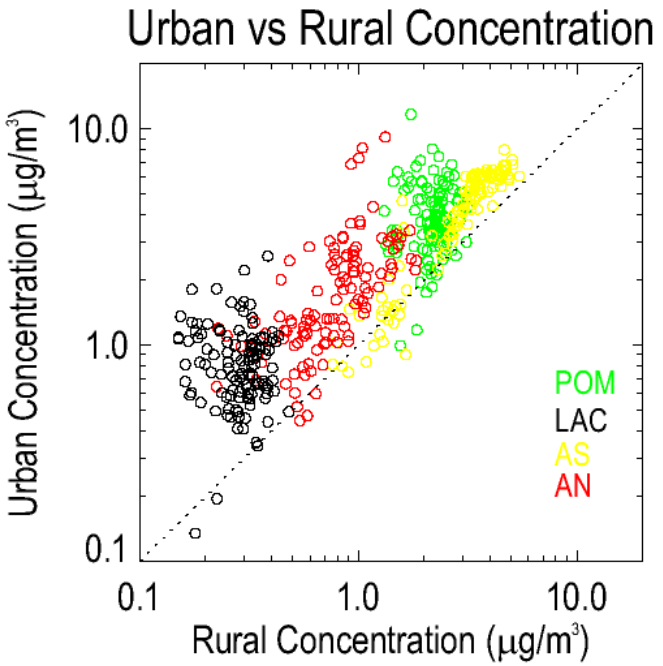

Figure 7.7.1(b). Same as part (a) but with a logarithmic scale.

Although the investigation was constrained to urban sites with rural sites within 150 km, site location (including elevation) and density could bias estimates of urban excess, especially when complicating factors such as wind direction were not accounted for. In addition to the issue

of site coverage, CSN site classification and location could also introduce uncertainties in urban excess estimates. While the CSN designates some sites as "rural", locations vary widely regarding the degree of remoteness of the location. In addition, some rural IMPROVE sites are located near urban sites, with urban influences being inevitable. All CSN sites were assumed to be "urban" and all IMPROVE sites were assumed to be "rural" in this analysis (urban IMPROVE sites were not considered in this analysis), but sites with locations that are not strictly classified into either category could introduce uncertainty into derived estimates. Furthermore, remote sites with elevations above the boundary layer could be sampling very different air masses compared to the urban sites to which they were compared.

These analyses provided urban excess estimates with spatial patterns for the United States. For certain species, such as POM, LAC, and AN, annual mean urban concentrations were considerably higher than rural concentrations. As a summary, the 2005–2008 annual mean AS urban excess mean ratio and difference (and one standard deviation) were 1.4 ± 0.3 and 1.3 ± 0.9 $\mu g\ m^{-3}$, respectively. The AN mean ratio and difference were 2.5 ± 1.3 and 1.2 ± 1.3 $\mu g\ m^{-3}$, respectively. The mean ratio and difference in POM urban to rural concentrations were 1.9 ± 0.9 and 1.9 ± 1.6 $\mu g\ m^{-3}$, respectively, while for LAC they were 3.3 ± 1.9 and 0.6 ± 0.4 $\mu g\ m^{-3}$, respectively. The mean FM ratio and difference were 2.0 ± 0.6 and 7 ± 3 $\mu g\ m^{-3}$, respectively. These estimates varied widely as a function location.

While the isopleths of urban excess were representative of actual concentrations only, they indicate the spatial extent of urban impacts on surrounding rural and remote areas as a function of species. For example, while LAC corresponded to the highest mean urban to rural concentration ratio, its spatial extent was generally the lowest and associated with sharp spatial gradients. In contrast, the spatial patterns in urban excess associated with species such as AS, POM, and FM were more regional in extent, especially in the eastern United States, although impacts from local sources were also apparent.

This type of analysis is simplistic in approach and subject to uncertainty but provides information that improves our understanding of the impact of regional and local urban sources to rural areas and potentially informs more effective regulatory efforts. A more thorough characterization of urban excess requires investigations into seasonal variability as well incorporating source emissions and back trajectory information.

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