A preliminary examination of the speciated $PM_{2.5}$ data from rural and urban SEARCH sites, 1999-2001

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Background

There has recently been considerable interest in the comparison of speciation of fine particulate matter (PM) at urban and rural sites. Using the particulate data from the Interagency Monitoring of PROtected Visual Environments (IMPROVE; rural Class 1 locations) program and the EPA's Speciation Trends Network (STN; mostly urban locations), several investigators have labeled the generally higher levels of carbon species, nitrate (NO_3), sulfate (SO_4), and other ions/elements observed at the urban STN sites as an "urban excess" or "urban increment" (see, for example, presentations available at http://www.epa.gov/air/visibility/meetings.html). A note of caution to this approach is that the IMPROVE and STN networks have different analytical and sample handling/storage protocols; hence, additional analysis is needed to assess how these network differences affect comparisons of concentrations of volatile species including carbon and NO_3.

In order to better compare the PM speciation at "nearby" rural and urban sites, one would ideally consider the data collected and analyzed using identical methodologies. One such database collected as part of the Aerosol Research Inhalation Epidemiology Study (ARIES) and the SouthEastern Aerosol Research and Characterization (SEARCH) programs is available from the Atmospheric Research & Analysis, Inc. (ARA) website (see http://www.atmospheric-research.com). These data consist of 24-hour average speciated $PM_{2.5}$ concentration data from three urban/rural site pairs – Jefferson St. (Atlanta)/Yorkville, GA; Birmingham/Centreville, AL;

and Gulfport/Oak Grove, MS – from 1999-2001. The paired urban and rural locations are within about 80 km of each other, with elevation differences #120 m (see Table 1). The speciated data were reported in two forms – the first method represents what would likely be measured by a Federal Reference Method system ("FRM equivalent"), while the second method represents what actually is in the ambient air ("best estimate"). In this analysis, we considered only the "best estimates" of NO_3, SO_4, ammonium (NH_4), major metal oxides (sum of elemental Al, Ca, Fe, K, Si, and Ti, which are assumed to be predominantly soil-related oxides), elemental carbon (EC), and organic carbon (OC). Note that another advantage to using the ARIES/SEARCH data is that it allows for a comparison of NH_4, a variable that is not routinely reported by IMPROVE.

Table 1. The urban/rural site pairs considered in this analysis

Urban site/Rural site	*Approximate distance between sites (km)*	*Approximate elevation differences between sites (m)*
Gulfport/Oak Grove, MS	67	95
Birmingham/Centreville, AL	83	65
Atlanta/Yorkville, GA	61	120

Analysis and observations

Table 2 lists the annual average concentrations of the six PM components considered in this analysis for each site pair. For a given site pair, only those days on which measurements were reported at both sites were used to compute the averages; there are approximately 500 data points for each average. Note that we did not convert OC to total organic mass (OM). The urban/rural differences were generally small for SO_4; this is not surprising, since SO_4 is a regional pollutant. In terms of contributions to the $PM_{2.5}$ mass, the largest contributor on average was SO_4 (~4-5 μg m^{-3}), followed by OC (~3-5 μg m^{-3}). On the other hand, the metal oxides only

contributed about 0.5-1 μg m^{-3}. The most striking urban/rural contrast by site pair, for species other than SO_4, was observed between Birmingham and Centreville (perhaps related to the amount of industrial activity), whereas the differences between Gulfport and Oak Grove were the smallest. Relatively speaking, the urban EC levels were substantially higher than the corresponding rural EC levels – since EC is often indicative of anthropogenic (e.g. diesel) sources – while the urban/rural contrast in OC levels was not as large.

Table 2. Annual average concentrations at each of the urban/rural site pairs.

Urban site/Rural site	*SO_4*	*NO_3*	*NH_4*	*Metal oxides*	*EC*	*OC*
Gulfport/Oak Grove, MS	4.06 / 3.94	0.42 / 0.31	1.58 / 1.28	0.51 / 0.54	0.84 / 0.55	2.74 / 2.75
Birmingham/Centreville, AL	5.38 / 4.56	0.96 / 0.37	3.38 / 1.56	1.02 / 0.39	2.36 / 0.64	5.15 / 3.11
Atlanta/Yorkville, GA	5.30 / 5.05	1.04 / 0.88	2.80 / 2.55	0.51 / 0.30	1.78 / 0.73	4.39 / 3.38

To examine the issue of urban/rural concentration differences on a finer basis, we computed daily differences (always defined as "urban – rural") and aggregated these differences on a seasonal and annual basis. Figures 1-3 display the average concentration differences and standard deviations of the differences for Gulfport/Oak Grove, Birmingham/Centreville, and Atlanta/Yorkville, respectively. The overall differences (shown in black) and the differences for each of the four seasons are displayed (color-coded: winter = December-February, spring = March-May, summer = June-August, and fall = September-November). These comparisons are only semi-quantitative; although we have plotted means and standard deviations, we have not computed confidence intervals or performed tests of statistical significance. A few observations follow:

- **SO_4**: As expected, at Birmingham/Centreville and Atlanta/Yorkville, the largest differences

were observed during the summer months. At Gulfport/Oak Grove, the differences were negligible during the summer months, but day-to-day variations in the differences were large. At all three site pairs, the spread in the differences was largest during the summer and smallest during the winter.

- **NO_3**: The largest NO_3 differences occurred during the cold months, not surprising since the highest concentrations occur during the winter. However, the differences varied little over the year at Atlanta/Yorkville, while the seasonal variation was more pronounced at the other site pairs.
- **NH_4**: The seasonal variation in NH_4 is quite different at the three site pairs. For Gulfport/Oak Grove, the largest excess occurred during the fall; for Birmingham/Centreville, the spring; and for Atlanta/Yorkville, the winter/fall. The largest differences occurred at Birmingham/Centreville, indicating the presence of ammonia (NH_3) sources affecting air quality there. This observation will be discussed later.
- **Metal oxides**: The "crustal" components were very similar at Oak Grove and Gulfport, whereas the urban concentrations were somewhat higher at the other two site pairs (especially during the fall months). The spread in the metal oxide concentrations also was rather different at the three site pairs. Further analysis on an individual species basis, while quite valuable, is not presented here.
- **EC**: The urban EC levels were comparatively higher than their rural counterparts compared to the other species, as EC is a good indicator of motor vehicle emissions. The largest differences occurred on average during the fall months, and the seasonal variation was similar at all three site pairs.
- **OC**: The largest OC differences also occurred during the fall or winter months. The

seasonal variation in OC excess was quite similar to the EC differences at Atlanta/Yorkville and Birmingham/Centreville. Note that during the spring and summer, the OC levels at Oak Grove were higher on average than at Gulfport.

Possible weekday/weekend differences

We also wanted to see how the urban/rural differences on weekdays qualitatively compared with the differences on weekends (see Figures 4-6). At each of the three site pairs, the EC differences were somewhat larger than the weekend differences. This is in qualitative agreement with observations from Toronto, Ontario in which the "diesel motor vehicle" signature is reduced on weekends compared to weekdays (R. Poirot, personal communication). The relatively large differences in weekday/weekend average NO_3 and metal oxides at Birmingham/Centreville and Atlanta/Yorkville are probably related to motor vehicle and industrial activities. Interestingly, the NH_4 results did not mirror the NO_3 results; the relative weekday/weekend differences in NH_4 were minimal. These findings warrant further investigation.

Possible indication of urban NH_3 sources

As mentioned previously, the relatively high urban NH_4 concentrations suggest possible urban NH_3 emission sources. To investigate this issue, we computed the aerosol acidity assuming that NO_3 was fully neutralized and that there are no other significant strong cations and anions. The remaining NH_4 ($=NH_4 - 0.29\times NO_3$ on a mass basis) is, then available to neutralize ambient SO_4. The mass ratio of $NH_4 - 0.29\times NO_3$ to SO_4, then, should vary between 0.19 (all ammonium bisulfate; SO_4 only partly neutralized) and 0.375 (all ammonium sulfate; SO_4 fully

neutralized). Figure 7 displays plots of $NH_4 - 0.29 \times NO_3$ versus SO_4; the broken lines indicate ratios of 0.19 and 0.375, while the solid lines indicate the least-squares regression lines. At two rural sites – Oak Grove and Centreville – and at Gulfport, the data generally fall below the 0.375 lines, except at the lowest values perhaps, indicating slightly acidic aerosols. At the other three sites, relatively high NH_4 levels contributed to a substantial fraction of aerosols in which the ratio of $NH_4 - 0.29 \times NO_3$ to SO_4 actually exceeds 0.375.

These figures indicate that it would be difficult to quantify an "urban excess" since the three site pairs behave somewhat differently. While the data from Oak Grove and Gulfport generally fall between neutral and acidic, Yorkville and Atlanta often denote nearly neutral or exhibit ratios above 0.375. The contrast between Centreville and Birmingham, as noted before, is the most striking; a majority of the time, the ratio exceeds 0.375 at Birmingham.

The assumption of no other major cations or anions does not appear to be valid at times. Although Cl concentrations are usually $<< 1$ μg m^{-3}, they can occasionally reach as high as ~1-2 μg m^{-3}, especially at Birmingham. It does not appear that soluble K and other cations are reported in the public ARA ARIES/SEARCH database. Also, without high temporal resolution data, it is not possible to see how these PM components co-vary over the course of the sampling day. While this analysis is preliminary, it suggests that more work may be needed to understand and characterize urban NH_3 and other precursor emissions, and that strong acidity measurements would be highly desirable.

Discussion

This analysis was undertaken to provide estimates of the potential "urban excess" or "urban increment" associated with the various PM species on an annual and seasonal basis.

Even though the ARIES and SEARCH sites may not have necessarily been established with this goal in mind, such an exploratory analysis can be done since the differences between the PM concentrations at these urban and rural locations is not due to sampling or analytical differences. One limitation of this analysis is that the data are limited geographically to the southeastern US, and the findings cannot necessarily be extended to other regions of the country. However, we feel that the ideas presented here are illustrative of the kinds of analyses that can be performed with compatible data sets, and that this study could serve as a starting point for a more detailed analysis (source attribution, etc.).

The largest urban/rural contrast, in general, was observed between the Birmingham and Centreville, AL sites; the exception is for SO_4, which on average exhibited only slightly higher (< 0.5-1 $\mu g\ m^{-3}$) urban concentrations. The largest urban/rural contrast generally occurred for EC, but higher OC levels were observed throughout the year at Atlanta and Birmingham. Note, however, that the OC levels at Oak Grove and Gulfport, MS were comparable throughout the year, and that the average concentrations during the spring and summer were actually slightly higher at Oak Grove.

Clearly, the degree of "urban increment" at each of the paired sites varies by species and season, so that a characterization of the urban/rural differences requires more information than simply the concentrations. One such variable that could be considered is population, as higher populations imply higher emissions and ambient pollutant levels. According to the 2000 Census Bureau estimates for the three metropolitan areas (see http://www.census.gov). The Atlanta CMSA has the highest population of about 4.1 million, followed by Birmingham (~920,000) and Biloxi-Gulfport-Pascagoula (~360,000). Note that the highest concentrations were generally observed at Birmingham compared to the other urban sites, especially for metal oxides,

suggesting that local and regional emissions inventories need to be examined. Also, if NO_x emissions are proportional to population, it is not surprising that the highest NO_3 levels were observed at Atlanta; however, they were only slightly higher than at Birmingham. In fact, the NO_3 levels at Yorkville were only slightly lower than those at Birmingham, illustrative of the effect of emissions from the Atlanta area. Also, the urban NH_4 levels were somewhat higher than their corresponding rural counterparts, suggesting that a careful examination of the NH_3 emissions in these particular regions is needed. While the results of this study are preliminary and the analysis cursory, we suggest that caution be used when attempting to characterize an "urban increment" based solely upon comparisons or nearby urban and rural PM concentrations.

Acknowledgments

All particulate data considered in this analysis were obtained from the ARA public data archive site (http://www.atmospheric-research.com), while the 2000 population estimates were obtained from the Census Bureau site (http://www.census.gov). Discussions with R. Poirot (VT DEC) were particularly helpful.

Figures

Figure 1. The mean and standard deviations of the urban/rural concentration differences for (a) SO_4, (b) NO_3, (c) NH_4, (d) metal oxides, (e) EC, and (f) OC for Gulfport/Oak Grove, MS. The black lines denote all data, while the seasons are color-coded: winter, spring, summer, and fall.

Figure 2. Same as Figure 1, except for Birmingham/Centreville, AL.

Figure 3. Same as Figure 1, except for Atlanta/Yorkville, GA.

Figure 4. The mean and standard deviations of the urban/rural concentration differences on average weekdays and weekends for (a) SO_4, (b) NO_3, (c) NH_4, (d) metal oxides, (e) EC, and (f) OC for Gulfport/Oak Grove, MS, color-coded as weekday and weekend.

Figure 5. Same as Figure 4, except for Birmingham/Centreville, AL.

Figure 6. Same as Figure 4, except for Atlanta/Yorkville, GA.

Figure 7. Plots of $NH_4 - 0.29 \times NO_3$ versus SO_4 at (a) Oak Grove, (b) Gulfport, (c) Centreville, (d) Birmingham, (e) Yorkville, and (f) Atlanta. For a given urban/rural site pair, only common sampling days are displayed. The broken lines indicate aerosol acidity ratios of 0.19 (acidic) and 0.375 (neutral), while the solid line represents the least-squares regression.

Figure 1.

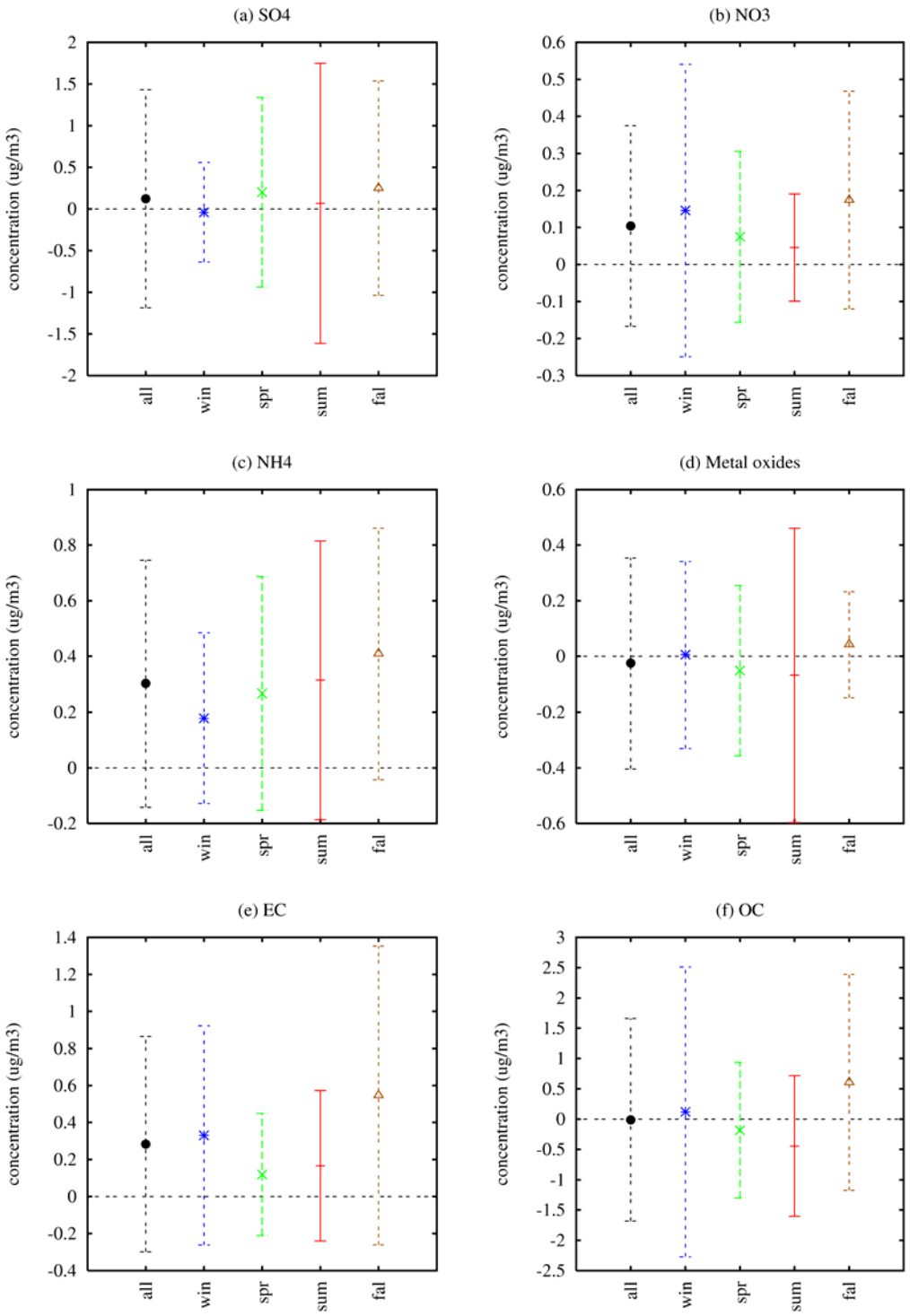

(a) SO4
(b) NO3
(c) NH4
(d) Metal oxides
(e) EC
(f) OC
concentration (ug/m3)
all
win
spr
sum
fal

Figure 2.

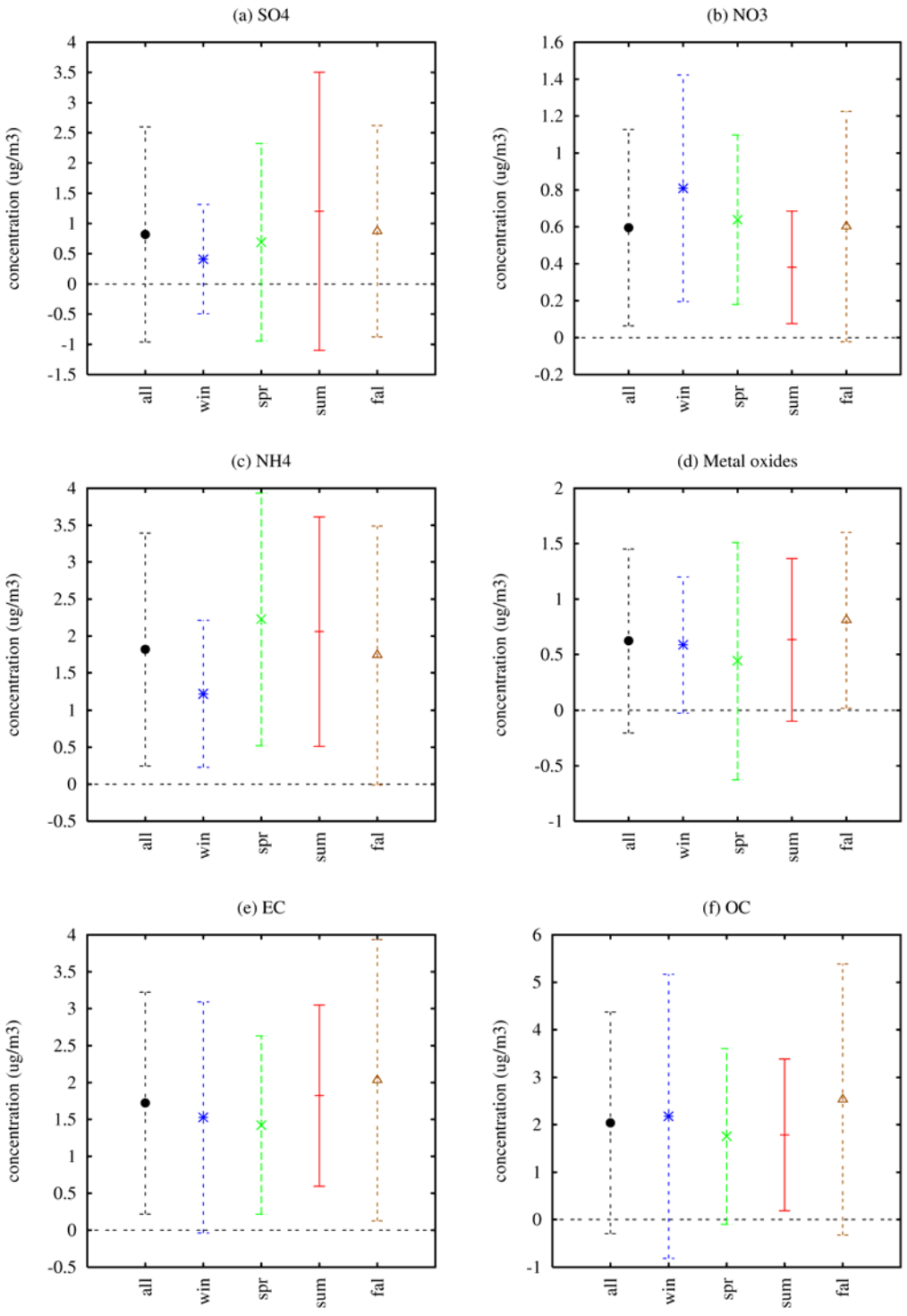

(a) SO4
(b) NO3
(c) NH4
(d) Metal oxides
(e) EC
(f) OC
concentration (ug/m3)
all
win
spr
sum
fal

Figure 3.

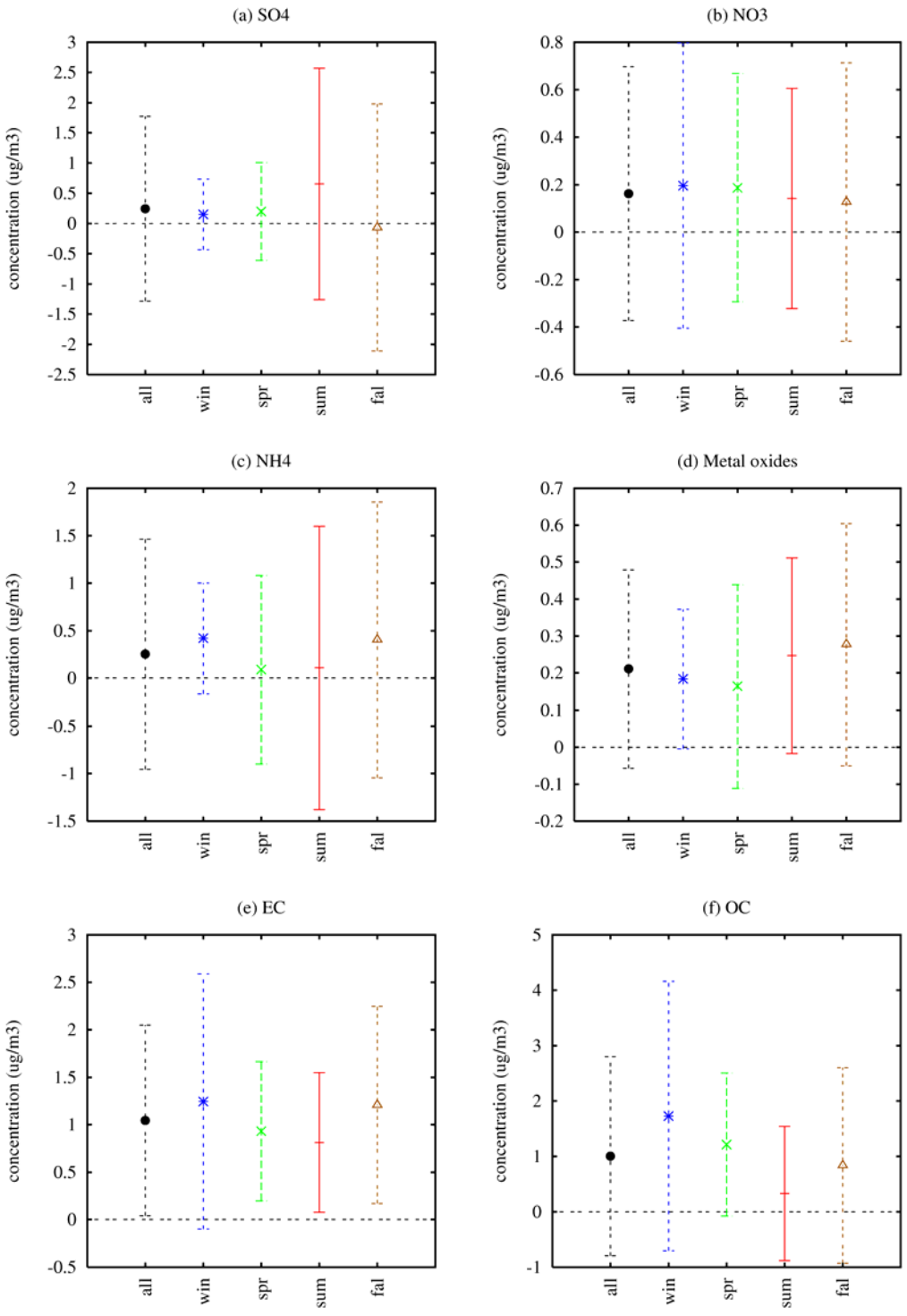

(a) SO4
(b) NO3
(c) NH4
(d) Metal oxides
(e) EC
(f) OC
concentration (ug/m3)
all
win
spr
sum
fal

Figure 4.

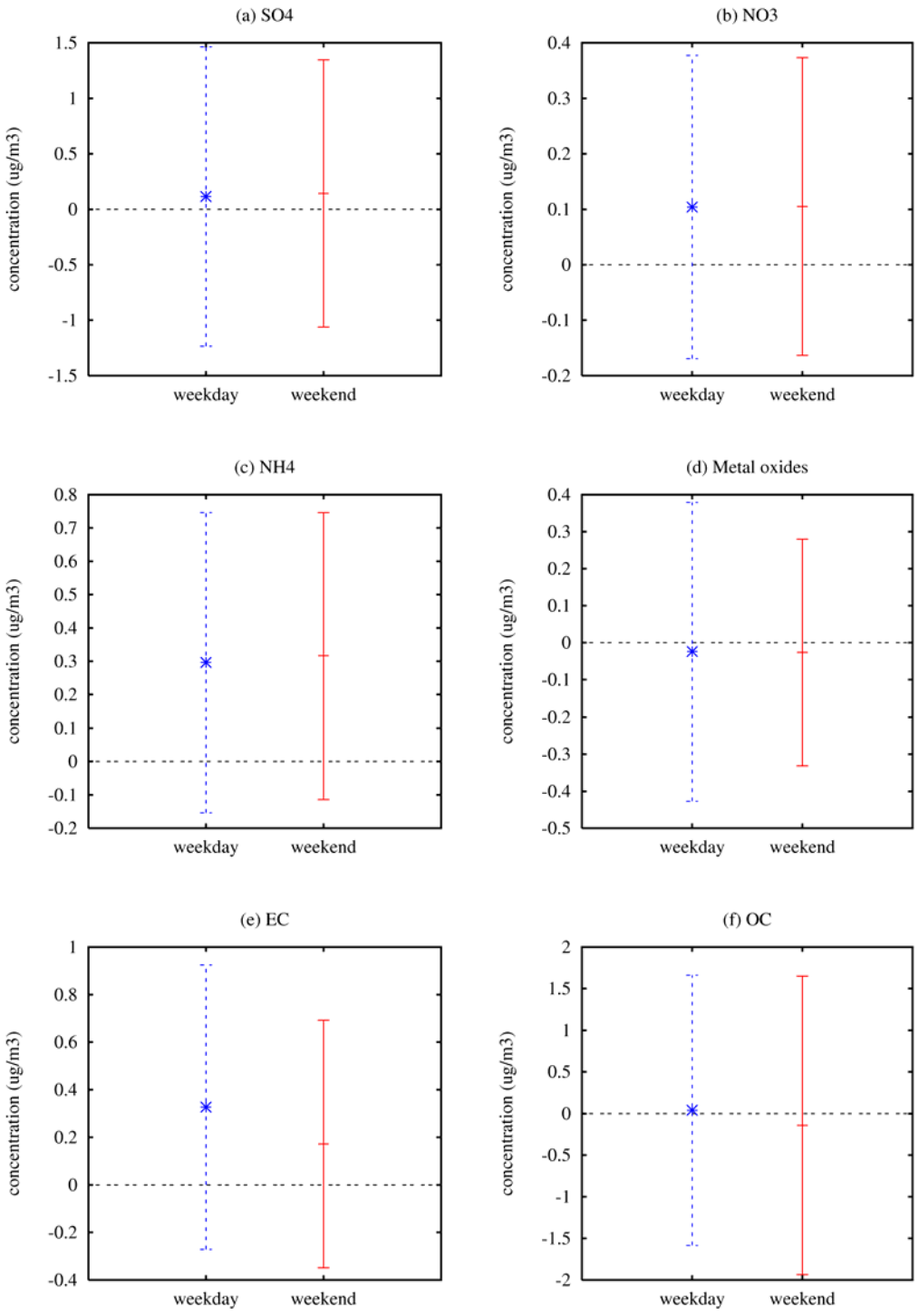

(a) SO4
concentration (ug/m3)
1.5
1
0.5
0
-0.5
-1
-1.5
weekday
weekend
(b) NO3
concentration (ug/m3)
0.4
0.3
0.2
0.1
0
-0.1
-0.2
weekday
weekend
(c) NH4
concentration (ug/m3)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
weekday
weekend
(d) Metal oxides
concentration (ug/m3)
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
weekday
weekend
(e) EC
concentration (ug/m3)
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
weekday
weekend
(f) OC
concentration (ug/m3)
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
weekday
weekend

Figure 5.

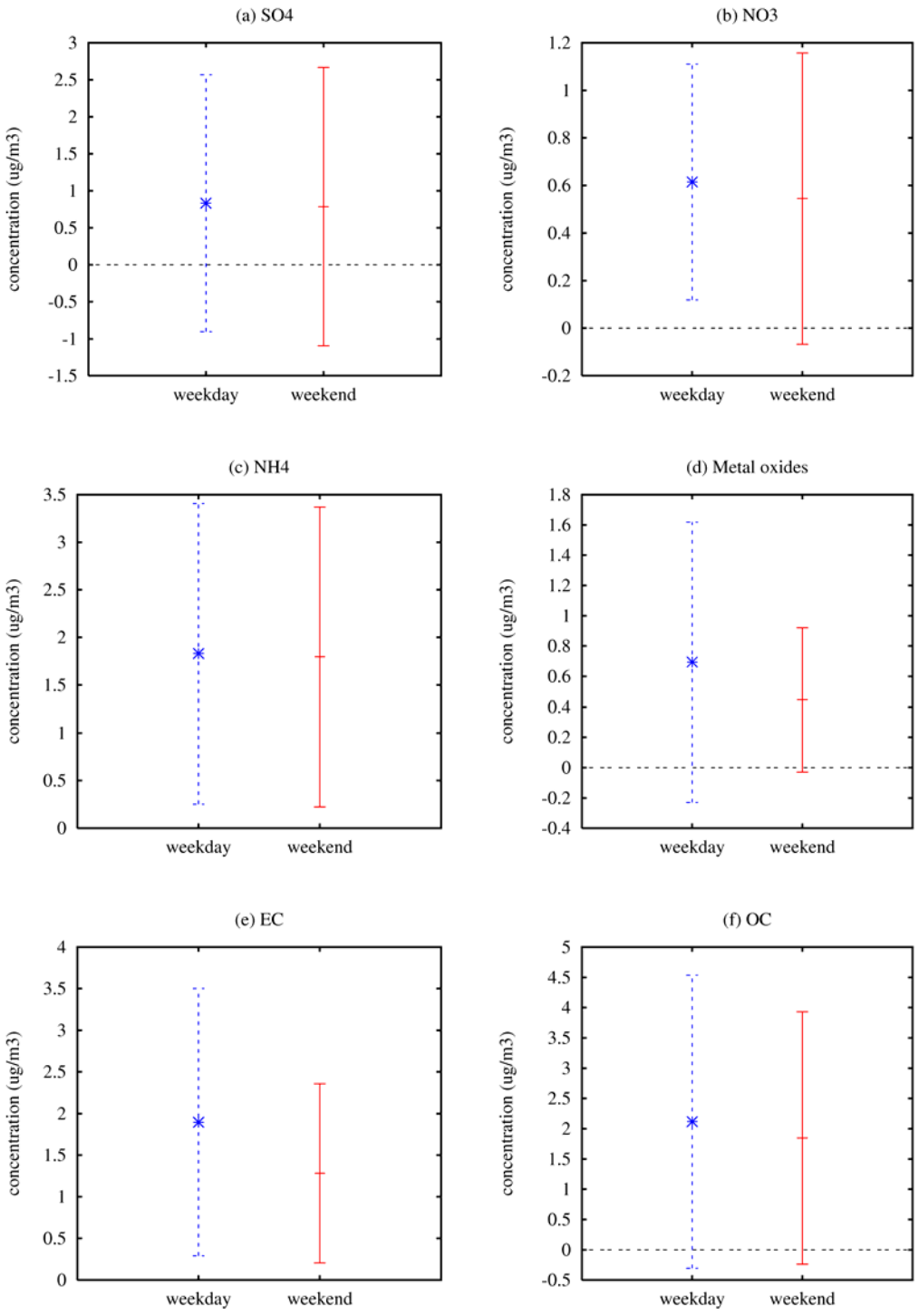

(a) SO4
concentration (ug/m3)
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
weekday
weekend
(b) NO3
concentration (ug/m3)
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
weekday
weekend
(c) NH4
concentration (ug/m3)
3.5
3
2.5
2
1.5
1
0.5
0
weekday
weekend
(d) Metal oxides
concentration (ug/m3)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
weekday
weekend
(e) EC
concentration (ug/m3)
4
3.5
3
2.5
2
1.5
1
0.5
0
weekday
weekend
(f) OC
concentration (ug/m3)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
weekday
weekend

Figure 6.

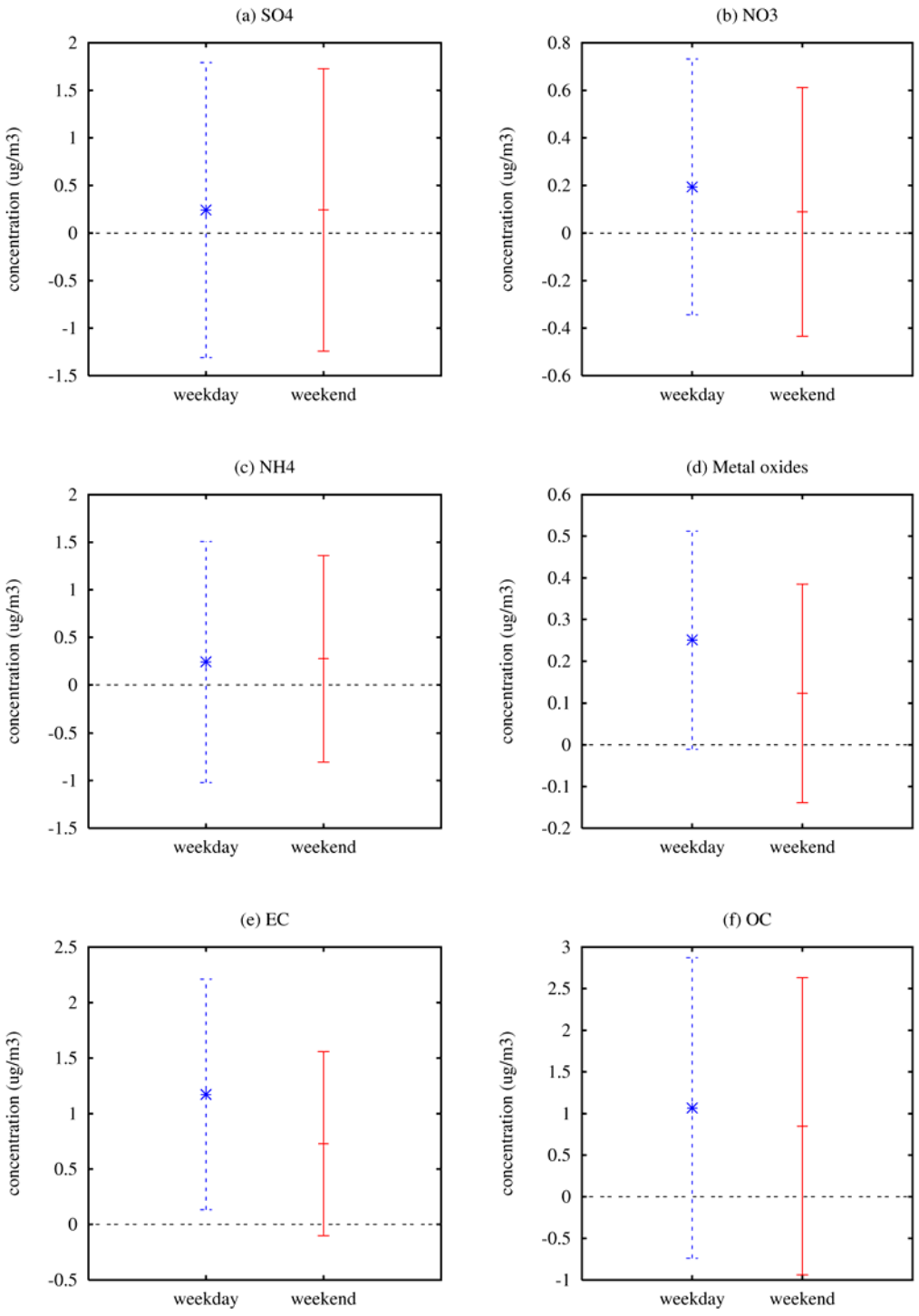
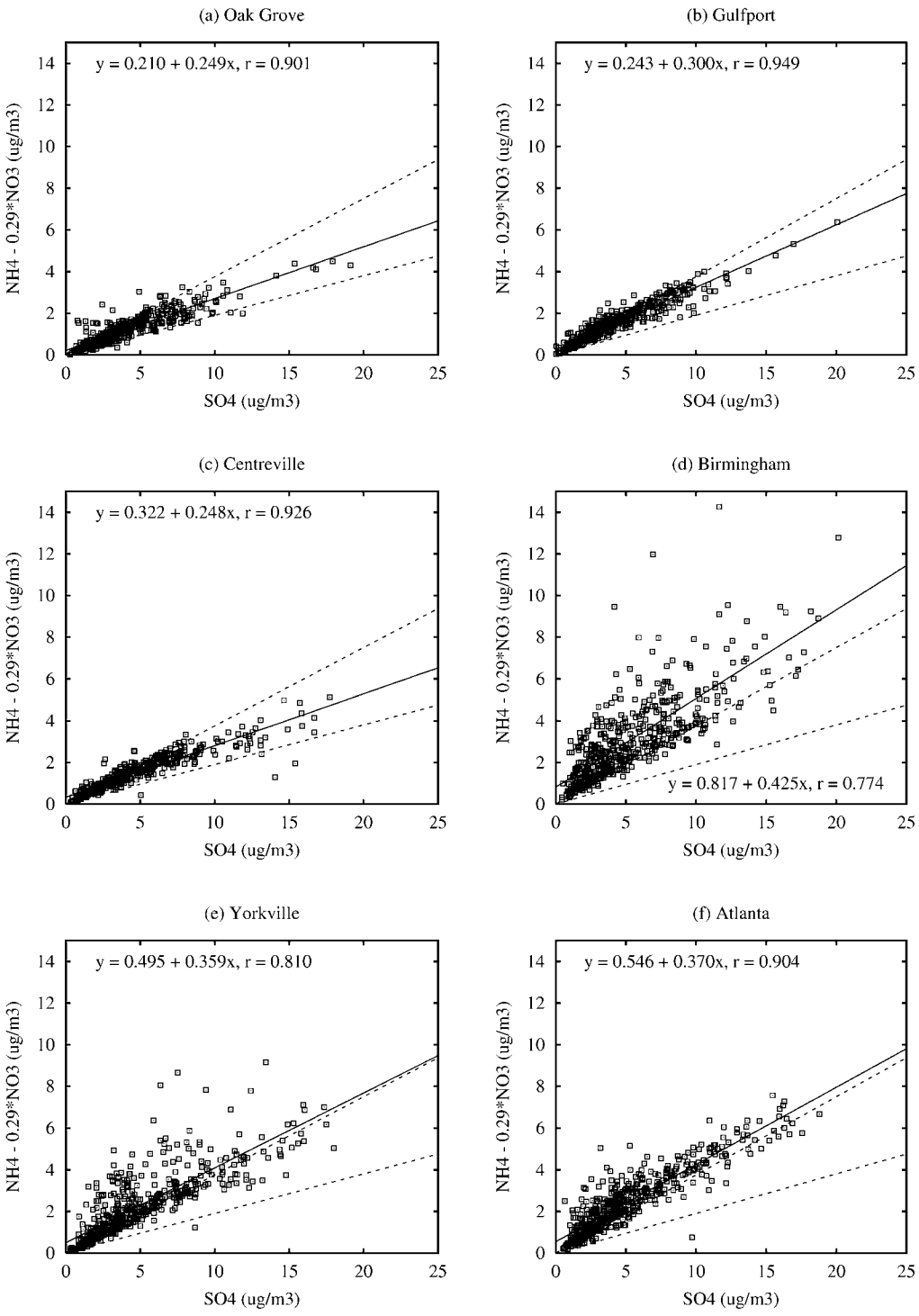

(a) SO4
concentration (ug/m3)
2
1.5
1
0.5
0
-0.5
-1
-1.5
weekday
weekend
(b) NO3
concentration (ug/m3)
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
weekday
weekend
(c) NH4
concentration (ug/m3)
2
1.5
1
0.5
0
-0.5
-1
-1.5
weekday
weekend
(d) Metal oxides
concentration (ug/m3)
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
weekday
weekend
(e) EC
concentration (ug/m3)
2.5
2
1.5
1
0.5
0
-0.5
weekday
weekend
(f) OC
concentration (ug/m3)
3
2.5
2
1.5
1
0.5
0
-0.5
-1
weekday
weekend

Figure 7.


(a) Oak Grove
y = 0.210 + 0.249x, r = 0.901
(b) Gulfport
y = 0.243 + 0.300x, r = 0.949
(c) Centreville
y = 0.322 + 0.248x, r = 0.926
(d) Birmingham
y = 0.817 + 0.425x, r = 0.774
(e) Yorkville
y = 0.495 + 0.359x, r = 0.810
(f) Atlanta
y = 0.546 + 0.370x, r = 0.904
NH4 - 0.29*NO3 (ug/m3)
SO4 (ug/m3)
0
2
4
6
8
10
12
14
0
5
10
15
20
25