

Atmospheric Aerosol over Two Urban-Rural Pairs in the Southeastern United States: Chemical Composition and Possible Sources

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ABSTRACT: Positive matrix factorization (PMF) was used to infer the sources of PM_{2.5} observed at four sites in Georgia and Alabama. One pair of urban and rural sites in each state is used to examine the regional and urban influence on PM_{2.5} concentrations in the Southeast. Eight factors were resolved for the two urban sites and seven factors were resolved for the two rural sites. Spatial correlations of factors were investigated using the square of correlation coefficient (R^2) calculated from the resolved G factors. Fourier transform was used to define the temporal characteristics of PM_{2.5} factors at these sites. Factors were normalized by using aerosol fine mass concentration data through multiple linear regression to obtain the quantitative factor contributions for each resolved factor. Common factors include: (1) secondary sulfate dominated by high concentrations of sulfate and ammonium with a strong seasonal variation peaking in summer; (2) nitrate and the associated ammonium with a seasonal maximum in winter; (3) “coal combustion/other” factor with presence of sulfate, EC, OC, and Se; (4) soil represented by Al, Ca, Fe, K, Si and Ti; and (5) wood smoke with the high concentrations of EC, OC and K. The

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motor vehicle factor with high concentrations of EC and OC and the presence of some soil dust components is found at the urban sites, but cannot be resolved for the two rural sites. Among the other factors, two similar industry factors are found at the two sites in each state. For the wood smoke factor, different seasonal trends are found between urban and rural sites, suggesting different wood burning patterns between urban and rural regions. For the industry factors, different seasonal variations are also found between urban and rural sites, suggesting that this factor may come from different sources or a common source may impact the two sites differently. Generally, sulfate, soil, and nitrate factors at the four sites showed similar chemical composition profiles and seasonal variation patterns reflecting the regional characteristics of these factors. These regional factors have predominantly low frequency variations while local factors such as coal combustion, motor vehicle, wood smoke, and industry factors have high frequency variations in addition to low frequency variations.

KEYWORDS: Receptor modeling; PM_{2.5}; PMF; Urban; Rural; SEARCH; Factor contribution; Factor profiles; Fourier transform; Correlation coefficient.

INTRODUCTION

High concentrations of particulate matter (PM) are an important air pollution issue in the United States (Vedal, 1997; Rudell et al., 1999). Particles in the air may arise from a wide variety of natural or anthropogenic sources. Health effects of airborne particles have been studied extensively, and significant and positive associations between human mortality/morbidity and PM concentrations or some PM components have been observed in some studies but not in others (Dockery et al., 1993; Schwartz et al., 1993; Lipfert et al., 1995.). More recent studies indicate that fine particles (PM_{2.5}, < 2.5µm in diameter) are more likely associated with adverse health effects (Gilliland et al., 2001; Peters et al., 2001; Pope et al., 2002) than other PM fractions.

In an effort to better characterize and understand the factors controlling near-surface PM concentrations in the Southeast, a multi-year study, the Southeastern Aerosol Research and Characterization project (SEARCH), was initiated in August 1998 and is scheduled to operate through

2005 (e.g. Hansen et al., 2003). SEARCH consists of 8 monitoring stations in 4 urban-rural pairs in four states: Alabama (North Birmingham [BHM] and Centreville [CTR]), Georgia (Atlanta [JST] and Yorkville [YRK]), Mississippi (Gulfport [GFP] and Oak Grove [OAK]), and Florida (Pensacola [PNS] and suburban Pensacola [OLF]). Measurements at each site include a wide range of gases (O_3 , NO, NO_2 , NO_y , HNO_3 , SO_2 , CO), PM mass ($PM_{2.5}$, $PM_{10-2.5}$), PM composition (elemental carbon (EC), organic carbon(OC), sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), and trace metals), and meteorological parameters (wind speed, wind direction, temperature, relative humidity, barometric pressure, solar radiation, and rainfall).

Two objectives of the SEARCH study are to: (1) estimate the source contributions and (2) better understand the chemical composition of each source (Hansen et al., 2003). Source apportionment study using factor analysis have been previously conducted for the observations at the JST site from August, 1998 to August, 2000 (Kim et al., 2003 (a,b); Kim et al., 2004). These investigations provided important insight in the source apportionment at this site and showed some innovative use of speciated carbon fraction measurements.

Our main interests in the current study are to understand the urban-rural difference, the regional-local contrast, and the seasonal variations of the source-related factors. We apply positive matrix factorization (PMF) analysis (Paatero and Tapper, 1993, 1994; Paatero, 1997; Polissar et al., 1998, 1999, 2001) to SEARCH $PM_{2.5}$ observations at four sites (two urban-rural pairs) in Alabama (urban BHM and rural CTR) and Georgia (urban Atlanta and rural Yorkville) from January, 2000 to December, 2002. By analyzing the urban-rural pairs, we examine their correlations defined by regional sources and the factors contributing to urban-rural concentration gradients. To further examine the seasonal variations of the $PM_{2.5}$ factors, we make use of Fourier transforms to define the frequency variation of the factors. The power spectra provide a simple way to analyze the periodicity of time series data (Hies et al., 2000; Sebald et al., 2000). We expect the regional factors to have higher correlations among the sites and

variations in lower frequencies than the local factors.

SAMPLE COLLECTION AND CHEMICAL ANALYSIS

PM_{2.5} composition data analyzed in this study consist of the measurements taken at four sites of the SEARCH network (Figure 1) (Hansen et al., 2003). In Georgia, the urban (JST) monitoring site is located 4 km northwest of downtown Atlanta; the rural (YRK) monitoring site is located 60 km northwest of the center of Atlanta. In Alabama, the urban (BHM) site is located 4 km north of downtown Birmingham; the rural (CRT) site is located about 70 km southwest of center Birmingham.

Daily integrated PM_{2.5} samples were collected at the JST site. PM_{2.5} samples were collected every third day at the BHM, CRT and YRK sites. Samples were collected by using particulate composition monitors (PCM, Atmospheric Research and Analysis, Inc., Durham, NC) that have three sampling lines (air flow rate 16.7 l/min) with inlets at 5 m above ground. More detailed descriptions can be found elsewhere (e.g., Kim et al., 2003a).

A total of 932 samples for the JST site, 336 samples for the BHM site, 347 samples for the YRK site and 338 samples for the CTR site were obtained and analyzed, covering the time period from January 2000 through December 2002. For each sample, concentrations of the following 19 chemical species were usually available: SO₄²⁻, NO₃⁻, NH₄⁺, EC, OC (OC was calculated as OC1+OC2+OC3+OC4+OP and EC as EC1+EC2+EC3-OP), As, Ba, Br, Cu, Mn, Pb, Se, Ti, Zn, Al, Si, K, Ca, and Fe, although there are occasional “missing data” (no reported measurement) for one or more species. The total PM_{2.5} mass concentration for each sample, the analytical uncertainty and detection limit for each chemical species were also obtained.

METHODOLOGY

In this study, PMF was used to analyze PM_{2.5} data at the four sites. Application of PMF requires that error estimates for the data be chosen judiciously to reflect the quality and reliability of each data point. This feature provides one of the important advantages of PMF: the ability to handle missing and below

detection limit data by adjusting the corresponding error estimates. In the four data sets for the present study, there were missing and below detection limit values for different chemical species in different samples. The summary for the PM_{2.5} mass and 19 component concentrations used for PMF analysis was shown in Table 1. In this work, missing data were replaced by the geometric mean of corresponding elements and four times of geometric mean as the corresponding error estimates (Polissar et al., 1998). Half of the detection limit was used for the values below the detection limit and 5/6 of the detection limit was used for the corresponding error estimate (Polissar et al., 1998).

With the total PM_{2.5} mass concentration measured for each sample, multiple linear regression (MLR) was performed to regress the mass concentration against the factor scores obtained from PMF. Because of the uncertainties introduced by the measurement matrix, PMF results always have a portion of unexplained variation. The mass concentration minus the unexplained variation portion from G factors (the factor loading matrix) was used to regress the factor scores so that the contribution by each resolved factor was obtained. The regression coefficients were used to transform the factor profiles into those with physically meaningful units. Spatial differences and urban-rural concentration gradients were also examined using the factor contributions estimates from PMF.

Frequency separation in a pollutant time series is important as discussed by several studies (Eskridge et al., 1997; Rao et al., 1997) since the dynamic processes operate on different frequencies. Fourier transformation was employed to find the time-frequency relationship of the factor contributions estimated by PMF. Only the factor contribution results for the JST data were used to perform Fourier transform since daily samples were taken only at the JST site.

As done in a previous spectral analysis of air pollutant concentrations (Hies et al., 2000), we apply a logarithmic transformation for variance stabilization. Average concentrations (in log space) were subtracted from all values to obtain a zero mean for the series, and the missing values were set to zero. Discrete Fourier transform using a fast Fourier transform (FFT) of the time series was calculated to construct the periodogram, an estimate of the spectral density function for a finite time series.

The discrete Fourier transform $X(k)$ is defined as

$$X(k) = \frac{1}{\sqrt{N}} \sum_{t=0}^{N-1} x_t \exp(-2\pi v_k t) \quad k=0, 1, \dots, N-1 \quad (1)$$

where N is the number of observations, $x(t)$ is the original time series, and $v_k = k/N$. The periodogram is calculated at frequency v_k as the squared magnitude of the discrete Fourier transform, or

$$P(v_k) = |X(k)|^2 \quad (2)$$

The spectral density function indicates the strength of the signal as a function of frequency, and the integral of the spectral density function over frequency equals the variance of the time series data.

RESULTS

Apportionment

A critical step in PMF analysis is the determination of the number of factors. The normal practice is to experiment with different numbers of factors and find the optimal one with the most physically meaningful results. Analysis of the model fit, Q , can be used to help determine the optimal number of factors (Yakovleva et al., 1999). Assuming that reasonable error estimates of individual data points are available, fitting each value should add one to the sum and the theoretical value of Q should be approximately equal to the number of data points in the data sets. However, the resulting solution also needs to be physically meaningful within the system of interest. Based on the evaluation of the resulting factor profiles, the selected final PMF solutions in this study were determined by trial and error with different numbers of factors as well as different uncertainty estimates. Eight factors were resolved for the two urban sites and seven factors were determined for the two rural sites. Five factors are common among the four sites. They are secondary sulfate, nitrate, soil, wood smoke, and coal combustion/other. In order to find the spatial variations contributed by different factors among the four sites, the square of correlation coefficient (R^2) was calculated from the G factors that were common for the four sites (Table 2).

The secondary sulfate factor has high concentrations of sulfate and ammonium. Figure 2 shows the

factor profiles and factor contributions resolved from PMF at these four sites. OC and a small amount of EC were associated with this factor. The EC content probably reflects an increase in those concentrations under more stagnant conditions, and suggests that any resolved factor does not purely represent one source. The OC association was consistent with several previous studies (Ramadan, et al., 2000; Kim et al., 2004). In the Phoenix study (Ramadan, et al., 2000), the high particulate content of OC in this factor profile was explained as a result of coating of sulfur particles by OC from motor vehicles. However, secondary organic aerosol formation may also coincide with the secondary sulfate formation during the transport of the materials emitted from primary sources to the receptor sites. Molar ratios of ammonium to sulfate were 2.3, 2.0, 2.1 and 1.6 for the JST, YRK, BHM, and CTR site, respectively. Considering the possibility of evaporation of ammonium during sample analysis and the uncertainty from the PMF model, sulfate is likely present primarily as ammonium sulfate at these four receptor sites, though sulfate at CTR is probably not fully neutralized much of the time. This factor shows a strong seasonal variation with high concentrations in summer, reflecting photochemically enhanced gas-phase and heterogeneous cloud processing of sulfate production from SO₂ during summer. The bottom panel in Figure 2 shows the periodogram for this factor at the JST site. There is a large peak at low frequency for the annual cycle and almost no peak at higher frequencies, which suggests the importance of the seasonal dependence of sulfate formation. Significant correlations (Table 2) were found for this factor at the four sites reflecting, the regional nature of sulfate formation and transport.

The “coal combustion/other” factor has strong signals of sulfate, EC, OC, and particularly Se at all sites (Figure 3). The prior studies by Polissar et al. (2001) and Kim et al. (2003) in the eastern US suggest that the "coal" factor may represent the variability in sulfur photochemical transformation, with the large mass contribution factor in summer and the higher Se/S ratio factor in winter. Therefore, this factor probably represents the higher Se/S ratio factor during winter, likely also including some contributions by local coal combustion emissions (Edgerton, 2001). The ratios of OC to Se were 139.5, 179.4, 134.9 and 162.3 for the JST, YRK, BHM, and CTR site, respectively. The OC/Se ratios were

much higher than the previous resolved coal boiler source profiles (Watson et al., 2001). There is now increasing evidence that acid particulate matter can catalyze the formation of secondary organic aerosol (Jang et al., 2002). Thus, the increased OC associated with these particles could arise either by condensation of urban OC onto the particles as suggested by Ramadan et al. (2000) or it could also represent the acid catalyzed conversion of adsorbed precursors including isoprene and other less volatile material. The ratios of EC to Selenium were 47.9, 4.09, 25.6 and 5.52 for the JST, YRK, BHM, and CTR site, respectively. The reported EC/ Se ratio varies from 1 to 24 depending on boiler type and efficiency (Watson et al., 2001). The high variation in industrial boilers from different industrial sources in urban areas may explain the different EC/Se ratios between the rural and urban sites. The periodogram for this factor at the JST site is shown at the bottom panel of Figure 3. The large peak at low frequency corresponds to an annual cycle, and the little peak at high frequency relates to a weekly cycle. The annual cycle may reflect the seasonal variation and the weekly cycle may represent the weekday-weekend activity for this factor. The weekly fluctuation suggests that other industrial sources in addition to power plants are involved in this factor as power plant operation would not be expected to have such a pronounced weekly variation. Seasonal trends between urban and rural sites, i.e., JST vs. YRK and BHM vs. CTR, were apparently different except for some sporadic periods. It is also reflected by the low correlation coefficients of this factor among the four sites (Table 2), indicating the predominant local impact.

Figure 4 shows the factor profile and contribution results for the secondary nitrate factor. This factor is represented by high concentrations of nitrate and ammonium. OC and a small amount of EC were also associated with this factor. This can also be explained by the secondary aerosol formation process as previously mentioned. Molar ratios of ammonium to nitrate were 1.1, 0.9, 1.4 and 1.2 for the JST, YRK, BHM, and CTR site, respectively. Considering the possibility of evaporation of ammonium during sample analysis, the mixed sulfate in this factor and the uncertainty of the PMF model, the nitrate is probably present as ammonium nitrate. Nitrate is formed in the atmosphere mostly through the

oxidation of NO_x . The particulate partitioning of total nitrate ($\text{HNO}_3(\text{g}) + \text{NO}_3^-$) depends on ambient temperature, relative humidity, and the presence of ammonia or alkaline PM. Nitric acid gas tends to condense to particulate NH_4NO_3 at low temperature and high humidity. High peaks of nitrate occurred mainly during wintertime in part because of low temperature. The bottom panel in Figure 3 shows the periodogram for this factor at the JST site. The seasonal dependence of nitrate formation is reflected by a large peak at low frequency. Similar seasonal variations of ammonium nitrate at the four sites reflect the regional nature of ammonium nitrate formation and transport. The localized character in the urban areas was reflected by the small monthly peak. The R^2 values for the nitrate factor among the four sites are not as high as those of sulfate factors. The larger heterogeneity in the nitrate as compared to the sulfate factor is partly due to the shorter lifetime of NO_x than SO_2 .

The soil factor has high concentrations of Al, Si, Ca, Fe, K, and Ti, representing wind-blown crust dust and re-suspended road dust. Figure 5 shows that the soil factors are fairly consistent among the four sites. This factor has high source contribution peaks during April, 2001, July, 2001 and July, 2002. These are likely intercontinental dust transport events as observed in a number of other analyses across the eastern US. The April 2001 event is due to transport from Asia (EPA, 2003). The July episodes in these two years are probably from Saharan based on back trajectory analysis as well as prior studies. Prospero (2001) showed that the summer trade winds carry African dusts into southeastern United States. The mixed EC content in this factor also suggests that the resolved factor mixed with some other sources during the long-range transport. The bottom panel in Figure 5 shows the periodogram for this factor at the JST site. The large peak at low frequency for the annual cycle indicated the seasonal variation of this factor. There is almost no peak at high frequency except a monthly variation, suggesting that local dust has limited impact on this factor at the JST site. Similar seasonal trends of this factor at the four sites and the significant correlations among the four sites imply that this factor is regional.

A wood smoke factor was also resolved at each of the four sites. This factor is represented by high

concentrations of OC, EC and K (Figure 6). The wood smoke factor is probably related to local residential and commercial wood burning, local agricultural burning, and occasional forest fires. For the two urban sites, this factor has a seasonal trend with high values in winter and short-term peaks in spring and summer. The winter peaks likely indicate residential wood burning and other urban wood burning activity, and the spring and summer events are likely to be related to local agricultural field and forest management through burning. The periodogram for this factor is shown at the bottom panel of Figure 5 for the JST site. The different wood burning activity in winter and summer is represented by large annual and semi-annual cycles. Compared to the urban sites, this factor at the rural sites had more peaks during spring and summer and fewer peaks in winter, suggesting that the rural areas are more likely impacted by forest fires and agricultural burning, and the urban sites are more likely impacted by local residential and other wood burning. The correlation coefficients of this factor among the four sites were substantially lower, indicating that different sites are influenced by different sources for this factor.

A motor vehicle factor was resolved at the two urban sites (JST and BHM). It is represented by high concentrations of OC, EC and the inclusion of some soil dust constituents (Fe, Ca, Si). Some sulfate and ammonium may be mixed in this factor during the formation and transport of particles. The bottom panel in Figure 7 shows the periodogram for this factor at the JST site. The characteristic weekly driving cycle is reflected by the weekly peak. The complicated driving patterns and emission characteristics for this factor were echoed by large peaks for semi-annual, seasonal (90 days), monthly, and other weekly-seasonal cycles. The apparently different temporal variability and the low correlation coefficients between the two sites may indicate that this factor is strongly influenced by local traffic sources.

At the JST and YRK sites, an industrial factor with high OC and calcium concentrations along with some dust elements, "Industry Factor 1/ dust", was resolved (Figure 8). This factor is likely the result of a cement kiln located in Atlanta (Kim et al., 2003; Kim et al., 2004 (a,b)) along with some local dust sources. The bottom panel of Figure 8 shows the periodogram for this factor at the JST site. The large peak at low frequency corresponded to an annual cycle and the peaks at higher frequencies were related

to the monthly and weekly cycles for this factor. The weekly cycle was related to weekday-weekend activity. The factor contribution peak matched well during spring and fall between JST and YRK site with a R^2 value of 0.23 (Table 2). This indicates that the two sites are affected by some common sources under certain meteorological conditions.

A factor with high mass fractions of Zn, Fe, and Pb, “Industry Factor 2”, was also resolved at both the JST and YRK sites (Figure 9). A metal recycling facility found by previous JST site studies (Kim et al., 2003 (a,b); Kim et al., 2004) may be the origin of this factor for JST site, but it would be unlikely that the YRK site be impacted by this source. Thus, this factor more likely represents a more general industrial source. The bottom panel of Figure 9 shows the periodogram for this factor at the JST site. The large peak at low frequency corresponded to the annual cycle, and the peak at high frequencies was related to a weekly cycle. The high weekly peak suggested this factor was much dominated by weekday-weekend activity. The temporal variabilities between these two sites are not correlated, consistent with the very low R^2 value (Table 2) between the two sites. It emphasizes that this factor may come from different sources or represents a more general set of industrial sources near the YRK site.

At the BHM and CTR sites, “Industry Factor 3” with high concentrations of Zn, Fe, Cu, Pb, and Mn was resolved (Figure 10). The factor profiles were similar between these two sites except that there is less EC at the CTR site. However, the correlation between the two sites was low (Table 2) and there were no similar time variations for this factor between these two sites. It suggests that this factor may come from different sources or a common source that has different impacts at the two receptor sites.

Another factor, “Industry Factor 4 / dust”, with high elemental carbon and dust elements was also resolved for the BHM and CTR sites (Figure 11). This factor most likely represents emissions from coke plants near Birmingham along with some local dust sources. The component of this factor is a little different between these two sites. Some OC from other sources may have been mixed with this factor during the transport. The low correlation between the two sites (Table 2) suggests that these two sites may be influenced by different sources or common sources have different impacts on the two sites.

It is obviously desirable to understand better the potential source locations for the identified factors. In general, backtrajectory analysis can be effectively combined with receptor modeling such as this study for this purpose. In particular, Potential Source Contribution Function (PSCF) and Conditional Probability Function (CPF) have previously been used (Gao et al. 1993, 1996; Ashbaugh et al., 1985; Kim and Hopke., 2004). These investigations are beyond the scope of this current investigation. Results from CPF and the backtrajectory based analyses will be reported in a later paper (Liu et al., 2004).

Factor Contributions

The factor contributions were calculated using MLS as described previously. However, Kim et al. (2003a) identified a mass balance problem that about a third of the samples had measured mass values less than the sum of the components. We compared in Table 3 the source contribution results using our approach and the method by Kim et al. (2003a). The results using these methods are quite similar considering the errors in the measurements and the receptor model.

The sample-to-sample and site-to-site variations in daily PM_{2.5} mass concentrations from 2000 to 2002 are shown in Figure 12. The PM_{2.5} mass concentrations correlation coefficients among the four sites were calculated (Table 2). Figures 13 and 14 present the reconstructed mass contributions by the factors obtained by PMF for different seasons at the four sites.

The temporal variability of PM_{2.5} mass was similar at the four sites, suggesting that regional sulfate, nitrate, and soil factors dominated the PM_{2.5} mass concentrations. These factors are of regional nature because their temporal variations at the rural–urban pair sites are correlated well.

Differences between PM concentrations measured at urban-rural pairs are seasonal, peaking in winter when local urban pollution events are more frequent due to a poorly mixed boundary layer. During the periods with high urban and low rural PM concentrations, the high PM concentrations at urban sites are likely due to intense local sources. The strongest local contributing factor to the primary fine particle masses at the two urban sites is traffic, which on average contributed 2.9 and 3.0 $\mu\text{g}/\text{m}^3$ to the total PM_{2.5} masses for the JST and BHM sites, respectively. The strongest local contributing factor to the fine

particle masses at rural sites is wood smoke, which on average contributed 2.8 and 3.7 $\mu\text{g}/\text{m}^3$ to the total $\text{PM}_{2.5}$ mass for the YRK and CTR sites, respectively. In comparison, it contributed only 2.1 and 1.5 $\mu\text{g}/\text{m}^3$ for the JST and BHM sites, respectively.

The four industry factors showed some urban-rural gradients between urban and rural sites. On average, the urban-rural gradients are as follows: “Industry Factor 1 / dust” (JST, 1.1 $\mu\text{g}/\text{m}^3$ ~ YRK, 0.7 $\mu\text{g}/\text{m}^3$); Industry Factor 2 (JST, 0.4 $\mu\text{g}/\text{m}^3$ ~ YRK, 0.3 $\mu\text{g}/\text{m}^3$); Industry Factor 3 (BHM, 0.5 $\mu\text{g}/\text{m}^3$ ~ CTR, 0.3 $\mu\text{g}/\text{m}^3$); “Industry Factor 4 / dust” (BHM, 1.3 $\mu\text{g}/\text{m}^3$ ~ CTR, 1.2 $\mu\text{g}/\text{m}^3$). Coal combustion related factors also showed some urban-rural gradients at the BHM~CTR pair (BHM, 1.5 $\mu\text{g}/\text{m}^3$ ~ CTR, 0.6 $\mu\text{g}/\text{m}^3$). However, the opposite was somewhat true for the JST~YRK pair (JST, 0.5 $\mu\text{g}/\text{m}^3$ ~ YRK, 0.8 $\mu\text{g}/\text{m}^3$).

Figure 15 shows the average factor contributions of fine particles at urban and rural sites. For the JST site, the sum of the average contributions by sulfate and coal combustion factors are smaller than that by Kim et al., (2003ab) and Kim et al. (2004), which may reflect the SO_2 emission reduction during the years of 2001 and 2002. The average contribution by the nitrate and motor vehicle factors are in agreement with Kim et al., (2003ab) and Kim et al. (2004). The average contribution from the wood smoke factor is larger than that by Kim et al. (2003a). The sum of average contributions from “industry factor 1 / dust” and industry factor 2 are larger than the sum of Cement kiln and metal recycling factors by Kim et al. (2003a), probably because the two industry factors resolved in this study are mixed with some other factors such as local dusts.

In general, fine particles at the urban sites consisted mainly of sulfate (37% for the JST site and 30% for the BHM site), nitrate (8% for the JST site and 9% for the BHM site), motor vehicle (17% for both of the JST and BHM sites), wood smoke (13% for the JST site and 9% for the BHM site), industry factors (9% for the JST site and 10% for the BHM site), “coal combustion/other” (3% for the JST site and 8% for the BHM site), and soil (2% for the JST site and 3% for the BHM site) factors. The main components at the rural sites were the same as for the urban sites except for the traffic factor. At the

corresponding rural sites, the relative contributions by the sulfate factor (45% for the YRK site and 36% for the CTR site) and wood smoke (20% for the YRK site and 29% for the CTR site) factors were higher than those at the urban sites. The relative contributions by the soil factor (2% for each of the rural sites) were almost the same as the urban sites. The relative contributions by industry factors at the rural YRK site (7%) is lower than those at the corresponding urban JST site, while it is higher at the rural CTR site (12%) than that at the urban BHM site. The relative contribution by the “coal combustion/other” factor at the rural YRK site (6%) is higher than that at the corresponding urban JST site (3%), while it is lower at the rural CTR site (6%) than that at the urban BHM site (8%).

CONCLUSIONS

Positive matrix factorization (PMF) was used to identify possible source-related factors contributing to the PM_{2.5} masses at four sites, representing two urban-rural pairs in Georgia and Alabama. Eight source factors were resolved for the two urban sites. Seven factors were resolved for the two rural sites. Spatial differences and correlations were analyzed using the factor contribution results. Fourier transform was also employed to define the frequency variations of the above factors.

Sulfate, nitrate, and soil factors show regional characteristics with similar seasonal variation patterns and low frequency variations at the four sites. Sulfate and nitrate mainly exist as ammonium sulfate and ammonium nitrate in the receptor sites. The soil factor has high source contribution peaks during April 2001, July 2001, and July 2002. The April event likely reflects the intercontinental dust transport from Asia and the two July events likely reflect dust transport from Sahara. The sulfate and soil factors have the highest correlations among the four sites. The R² values of the nitrate factors among the sites are lower than those of sulfate factors due in part to the shorter lifetime of the precursor gas NO₂ than SO₂. The regional factors contribute to about 40-50% of the total PM_{2.5} masses.

The correlations among different sites are poor for the wood smoke, coal combustion, motor vehicle, and industry factors. The periodograms using Fourier transform for these factors show large high-frequency variations. Therefore these factors are dominated by local sources. The seasonal patterns of

the wood smoke factors are different between urban and rural sites. The dominant wood smoke source for the urban areas is residential wood burning characterized by high concentration in winter and that for the rural areas is local agricultural burning with high contributions during spring time. Two similar industry factors are found for the JST-YRK urban-rural pair and another two similar industry factors are also found for the BHM-CRT urban-rural pair. The strongest local contributing factor to the primary fine particle masses for the two urban sites is traffic, which on average contributes 17% to the PM_{2.5} masses for the JST and BHM sites. The strongest local contributing factor to the fine particle masses for the rural sites is wood smoke, which on average contributes 20 and 29% to the PM_{2.5} masses for the YRK and CTR sites, respectively.

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Table 1. Summary of the PM_{2.5} mass and compositions ($\mu\text{g}/\text{m}^3$) used in the PMF analysis

| Species | JST | | YRK | | BHM | | CTR | |
|-------------------|-------------------|-------------------|-------|-------|-------|-------|-------|-------|
| | A.M. ^a | G.M. ^b | A.M. | G.M. | A.M. | G.M. | A.M. | G.M. |
| PM _{2.5} | 16.72 | 15.04 | 13.88 | 12.05 | 17.92 | 15.68 | 12.60 | 10.88 |
| SO ₄ | 4.55 | 3.840 | 4.42 | 3.58 | 4.63 | 3.87 | 4.02 | 3.38 |
| NO ₃ | 0.96 | 0.703 | 0.92 | 0.65 | 0.98 | 0.74 | 0.34 | 0.24 |
| NH ₄ | 2.39 | 2.127 | 2.27 | 1.86 | 2.54 | 2.18 | 1.33 | 1.22 |
| EC | 1.44 | 1.19 | 0.56 | 0.48 | 1.82 | 1.41 | 0.52 | 0.37 |
| OC | 4.05 | 3.58 | 2.81 | 2.44 | 4.31 | 3.59 | 2.73 | 2.34 |
| As | 0.001 | 0.001 | 0.001 | 0.001 | 0.004 | 0.002 | 0.001 | 0.001 |
| Ba | 0.016 | 0.015 | 0.016 | 0.015 | 0.017 | 0.016 | 0.016 | 0.015 |
| Br | 0.004 | 0.003 | 0.003 | 0.002 | 0.005 | 0.003 | 0.002 | 0.002 |
| Cu | 0.003 | 0.001 | 0.001 | 0.001 | 0.007 | 0.003 | 0.001 | 0.001 |
| Mn | 0.002 | 0.001 | 0.001 | 0.001 | 0.015 | 0.007 | 0.001 | 0.001 |
| Pb | 0.005 | 0.003 | 0.002 | 0.002 | 0.026 | 0.011 | 0.002 | 0.001 |
| Se | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Ti | 0.003 | 0.003 | 0.002 | 0.002 | 0.003 | 0.003 | 0.002 | 0.002 |
| Zn | 0.013 | 0.010 | 0.006 | 0.005 | 0.119 | 0.058 | 0.009 | 0.004 |
| Al | 0.022 | 0.011 | 0.011 | 0.006 | 0.021 | 0.010 | 0.016 | 0.007 |
| Si | 0.089 | 0.066 | 0.049 | 0.034 | 0.166 | 0.115 | 0.068 | 0.028 |
| K | 0.059 | 0.049 | 0.045 | 0.037 | 0.118 | 0.082 | 0.062 | 0.041 |
| Ca | 0.043 | 0.035 | 0.025 | 0.019 | 0.114 | 0.080 | 0.032 | 0.015 |
| Fe | 0.074 | 0.060 | 0.024 | 0.020 | 0.178 | 0.122 | 0.030 | 0.019 |

^aA.M. denotes arithmetic mean.

^bG.M. denotes geometric mean.

Table 2. Squared correlation coefficients (R^2) for the factors by PMF at the four sites

| | JST vs. YRK | JST vs. BHM | JST vs. CTR | BHM vs. YRK | BHM vs. CTR | YRK vs. CTR |
|------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Sulfate | 0.77 | 0.38 | 0.34 | 0.54 | 0.37 | 0.44 |
| Nitrate | 0.33 | 0.22 | 0.28 | 0.29 | 0.21 | 0.26 |
| Soil | 0.77 | 0.48 | 0.70 | 0.34 | 0.64 | 0.65 |
| Coal | 0.03 | 0.03 | 0.00 | 0.15 | 0.05 | 0.04 |
| Wood smoke | 0.17 | 0.08 | 0.06 | 0.19 | 0.19 | 0.25 |
| Motor vehicle | N.A. | 0.13 | N.A. | N.A. | N.A. | N.A. |
| Industry source 1 | 0.23 | N.A. | N.A. | N.A. | N.A. | N.A. |
| Industry source 2 | 0.02 | N.A. | N.A. | N.A. | N.A. | N.A. |
| Industry source 3 | N.A. | N.A. | N.A. | N.A. | 0.00 | N.A. |
| Industry source 4 | N.A. | N.A. | N.A. | N.A. | 0.08 | N.A. |
| PM _{2.5} mass | 0.75 | 0.49 | 0.42 | 0.45 | 0.62 | 0.52 |

Table 3. Average factor contributions using different apportionment methods for the JST site

| | Kim et al. (2003) | This work |
|--------------------------|----------------------|-----------|
| Sulfate | 30.0% | 37.0% |
| Nitrate | 6.0% | 8.0% |
| Soil | 3.0% | 2.0% |
| Coal | 6.0% | 3.0% |
| Wood smoke | 14.0% | 13.0% |
| Motor vehicle | 20.0% | 17.0% |
| Industry factor 1/ dust | 8.0% | 6.0% |
| Industry factor 2 | 6.0% | 3.0% |
| Industry factor 3 | N.A. | N.A. |
| Industry factor 4 / dust | N.A. | N.A. |
| Undetermined | 7.0% | 11.0% |

Figure captions

Figure 1. Locations of SEARCH monitoring sites.

Figure 2. Profiles of and contributions by the sulfate factors resolved by PMF at the four sites. The bottom panel shows the Periodogram of the mean-subtracted factor contribution (in log space) at JST site.

Figure 3. Same as Fig. 2 but for the coal combustion/other factors.

Figure 4. Same as Fig. 2 but for the nitrate factors.

Figure 5. Same as Fig. 2 but for the soil factors.

Figure 6. Same as Fig. 2 but for the wood smoke factors.

Figure 7. Same as Fig. 2 but for the motor vehicle factors.

Figure 8. Profiles of and contributions by the “Industry factor 1/dust” factors resolved from the JST and YRK sites

Figure 9. Same as Fig. 8 but for the “Industry factor 2” factors.

Figure 10. Profiles of and contributions by the “Industry factor 3” factors resolved from the BHM and CTR sites.

Figure 11. Same as Fig. 10 but for the “Industry factor 4 / dust” factors.

Figure 12. PM_{2.5} mass time series at the four sites.

Figure 13. Seasonal averaged factor contributions for the JST and YRK sites. The error bars represent measurement uncertainties.

Figure 14. Same as Fig. 13 but for the BHM and CTR sites.

Figure 15. Average factor contributions during 2000-2002 for the four sites.

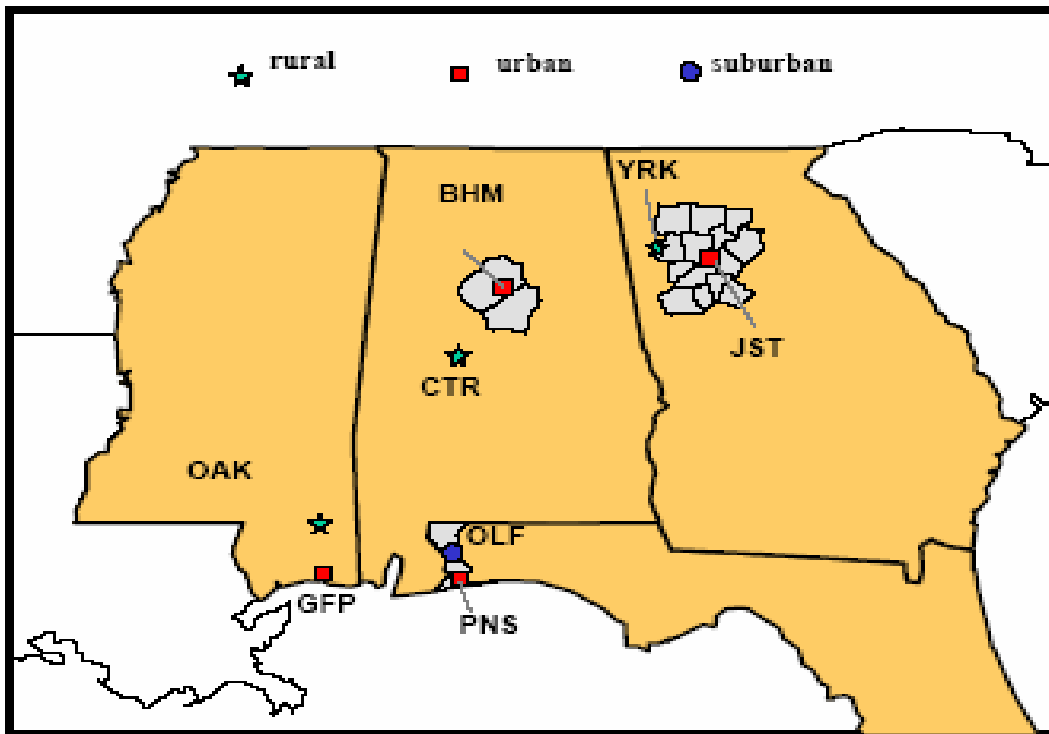


Figure 1

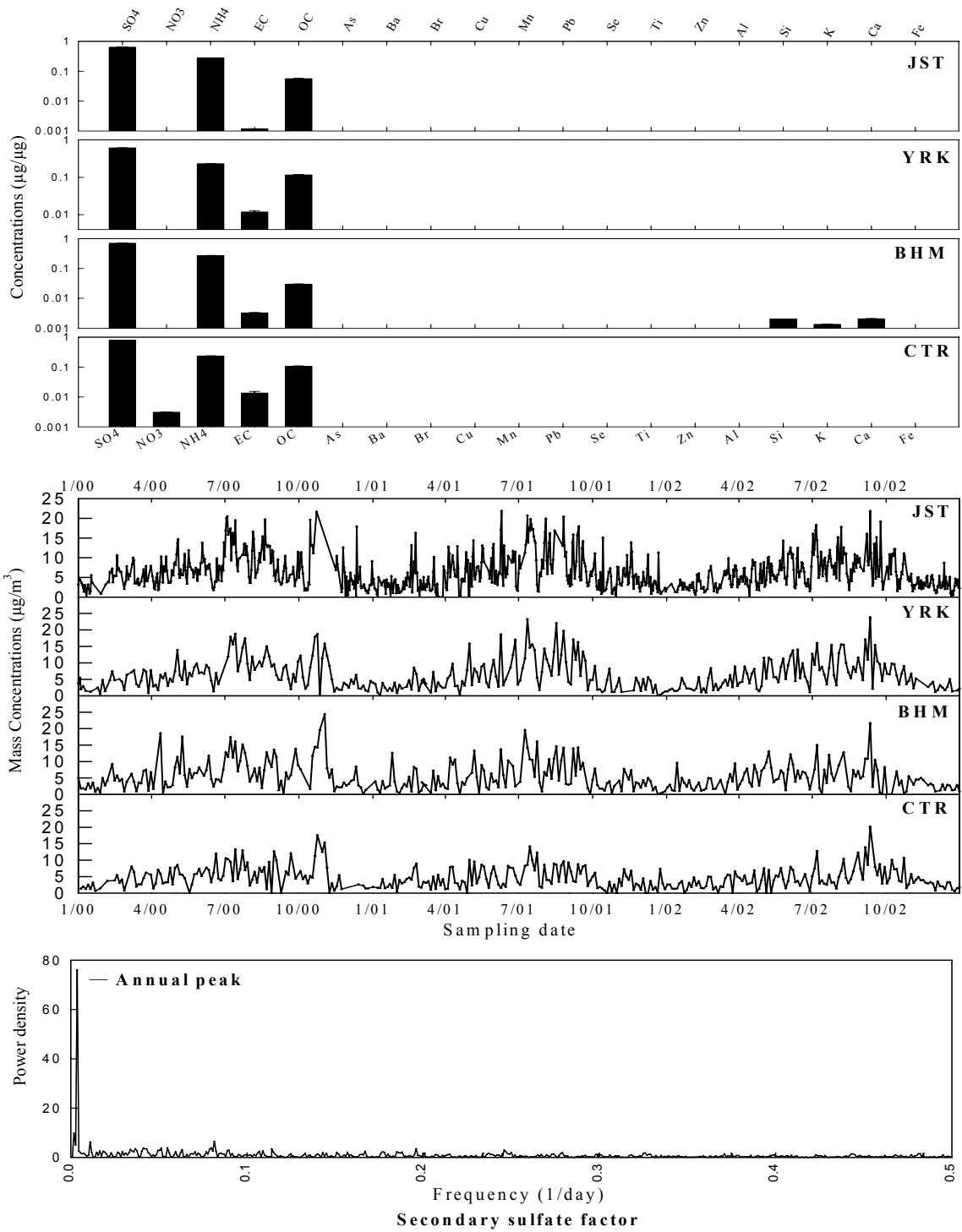


Figure 2

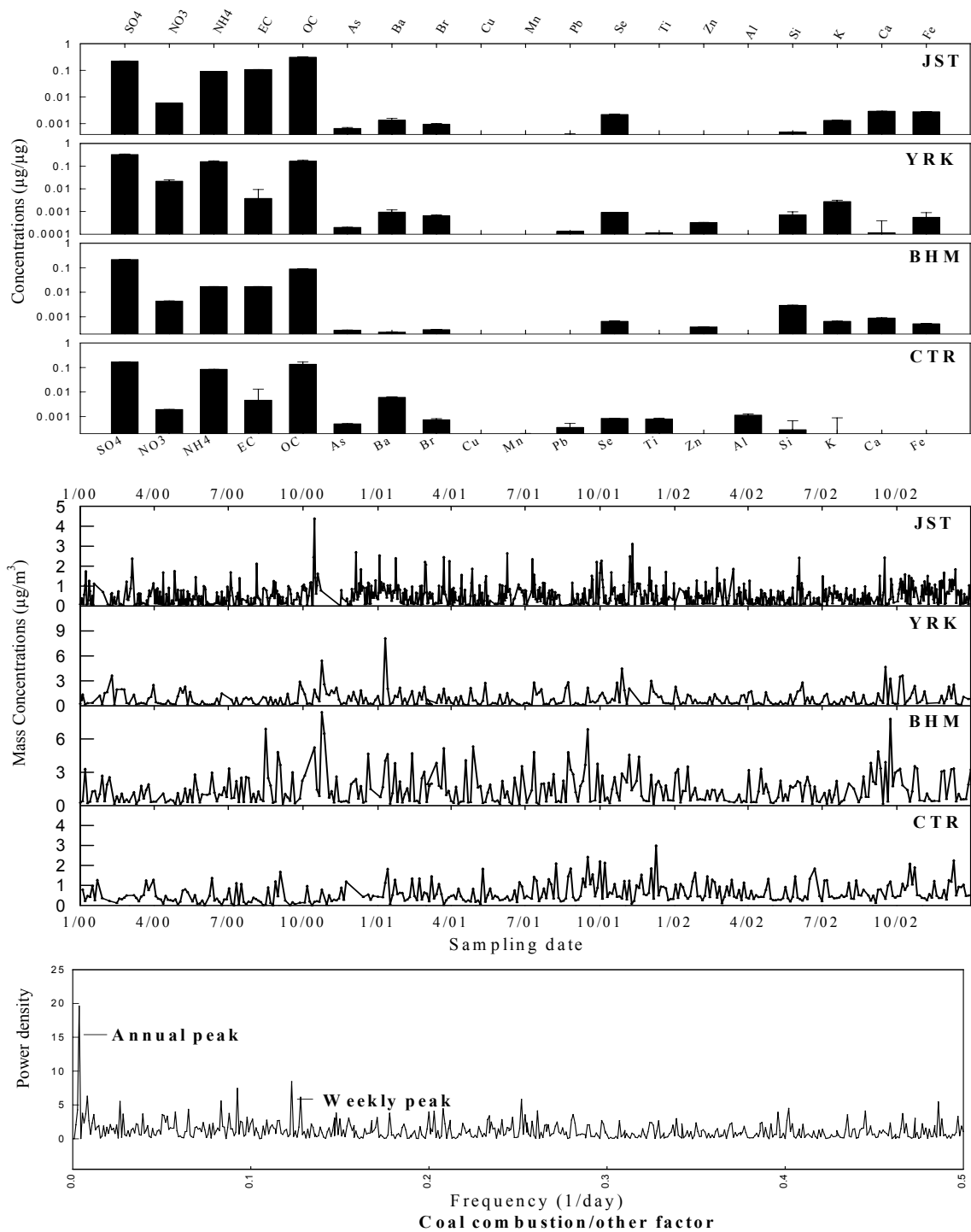


Figure 3

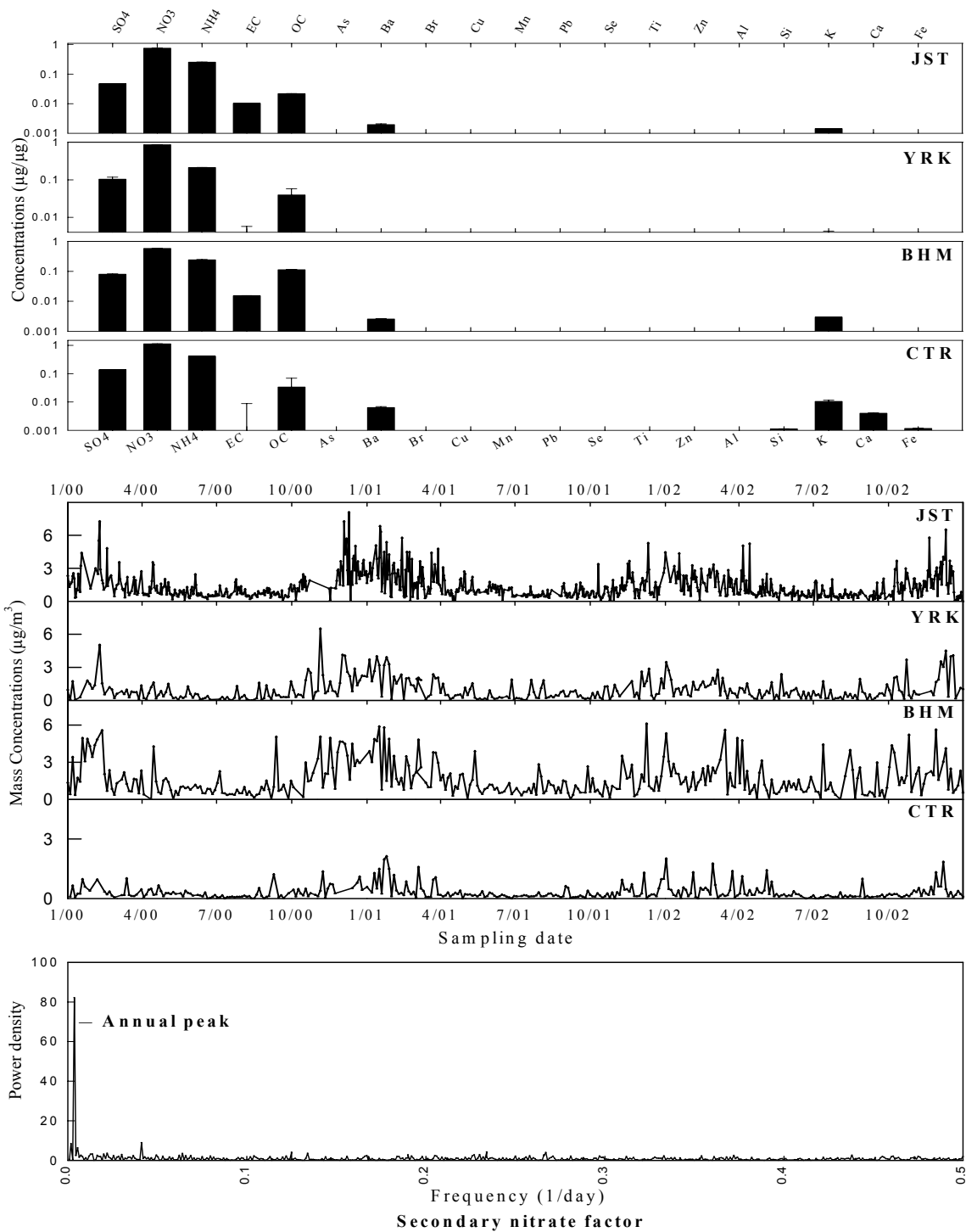


Figure 4

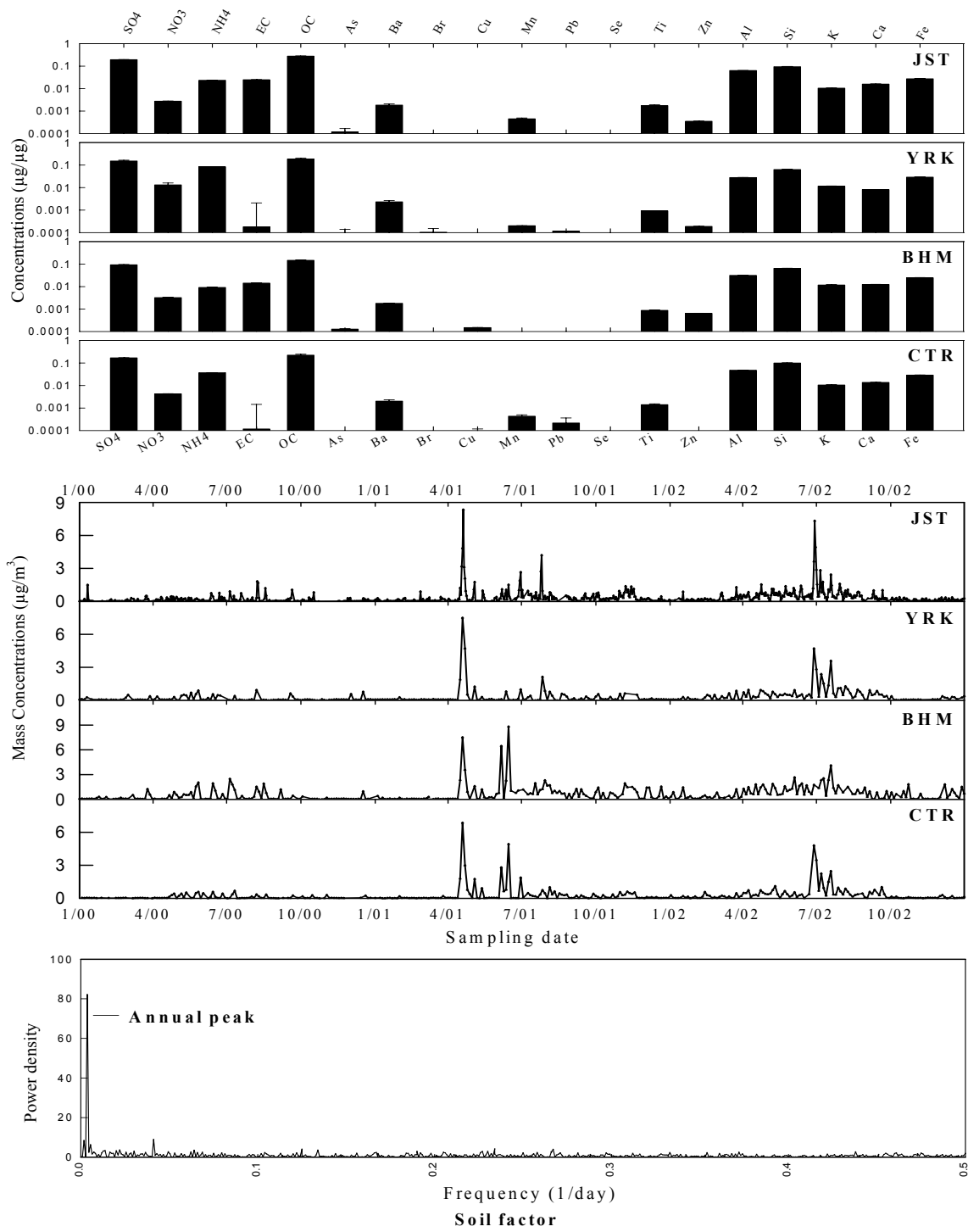


Figure 5

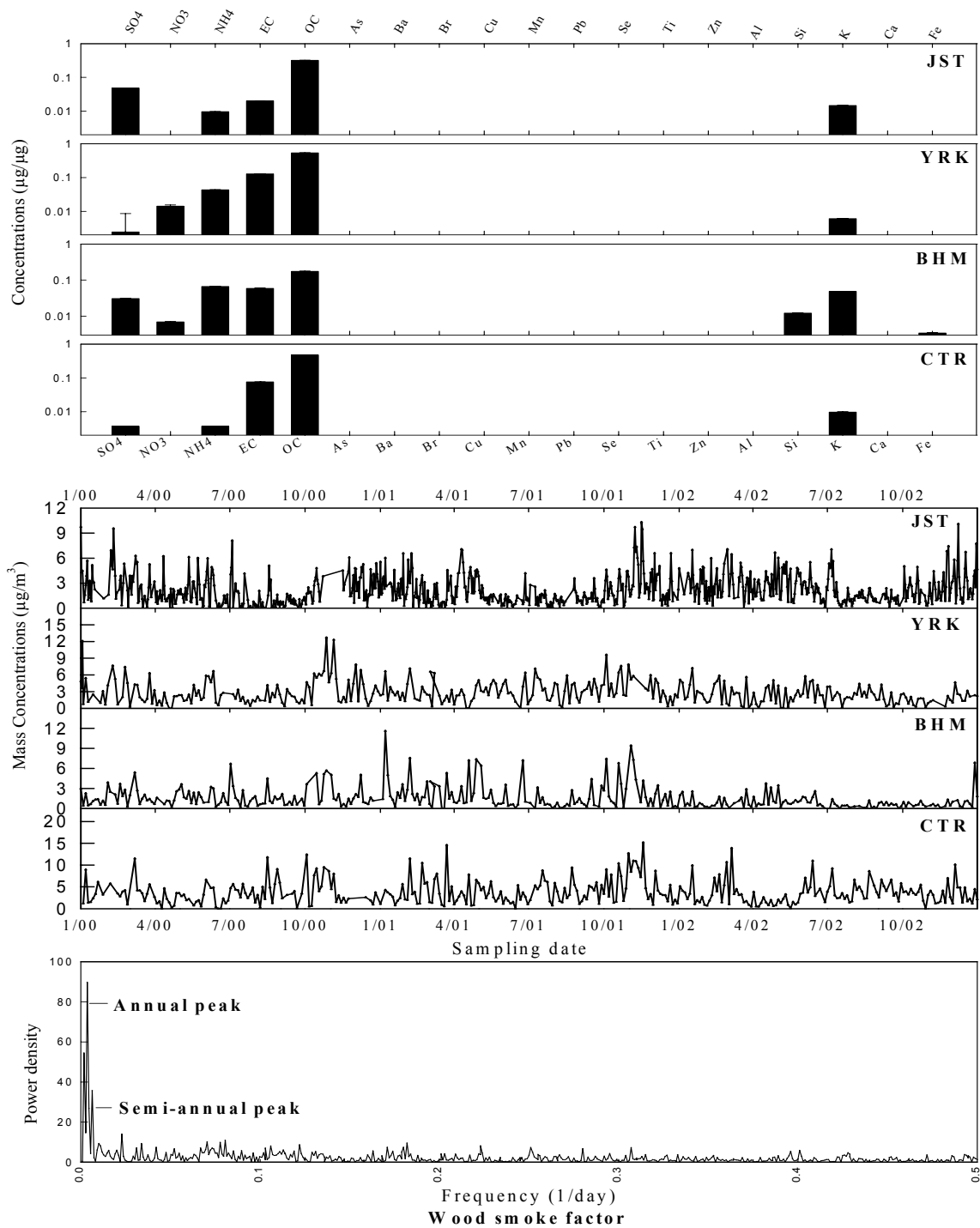


Figure 6

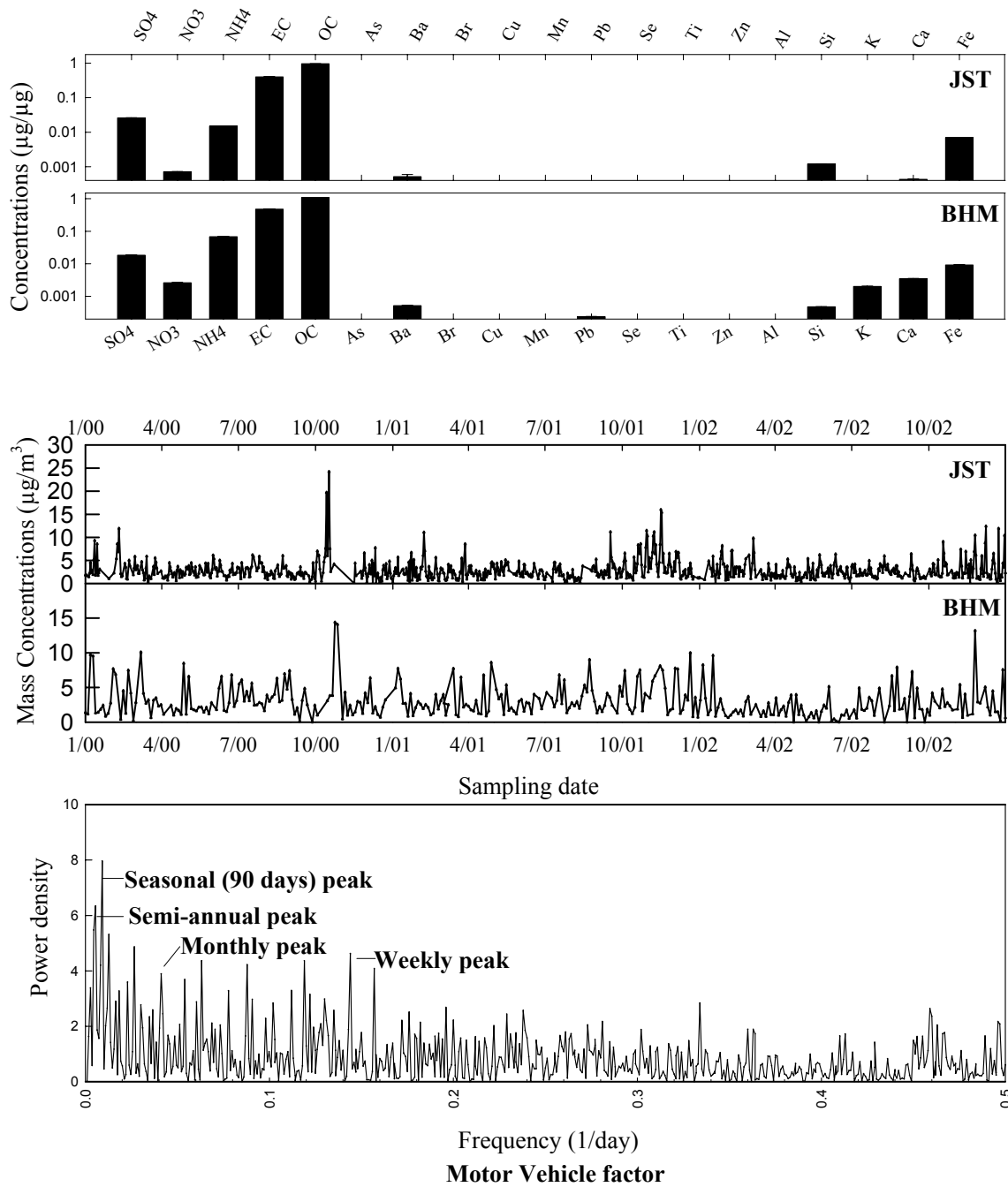


Figure 7

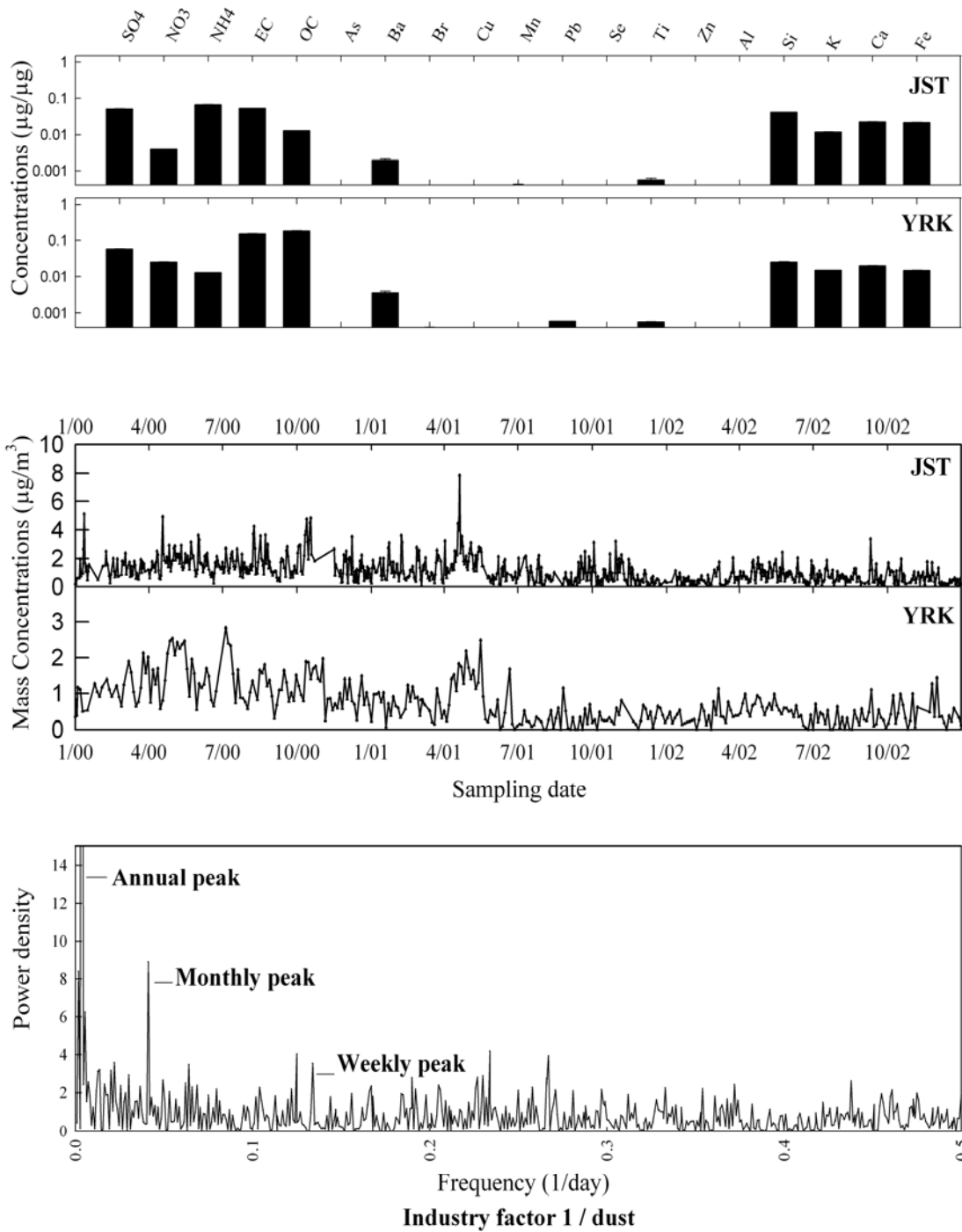


Figure 8

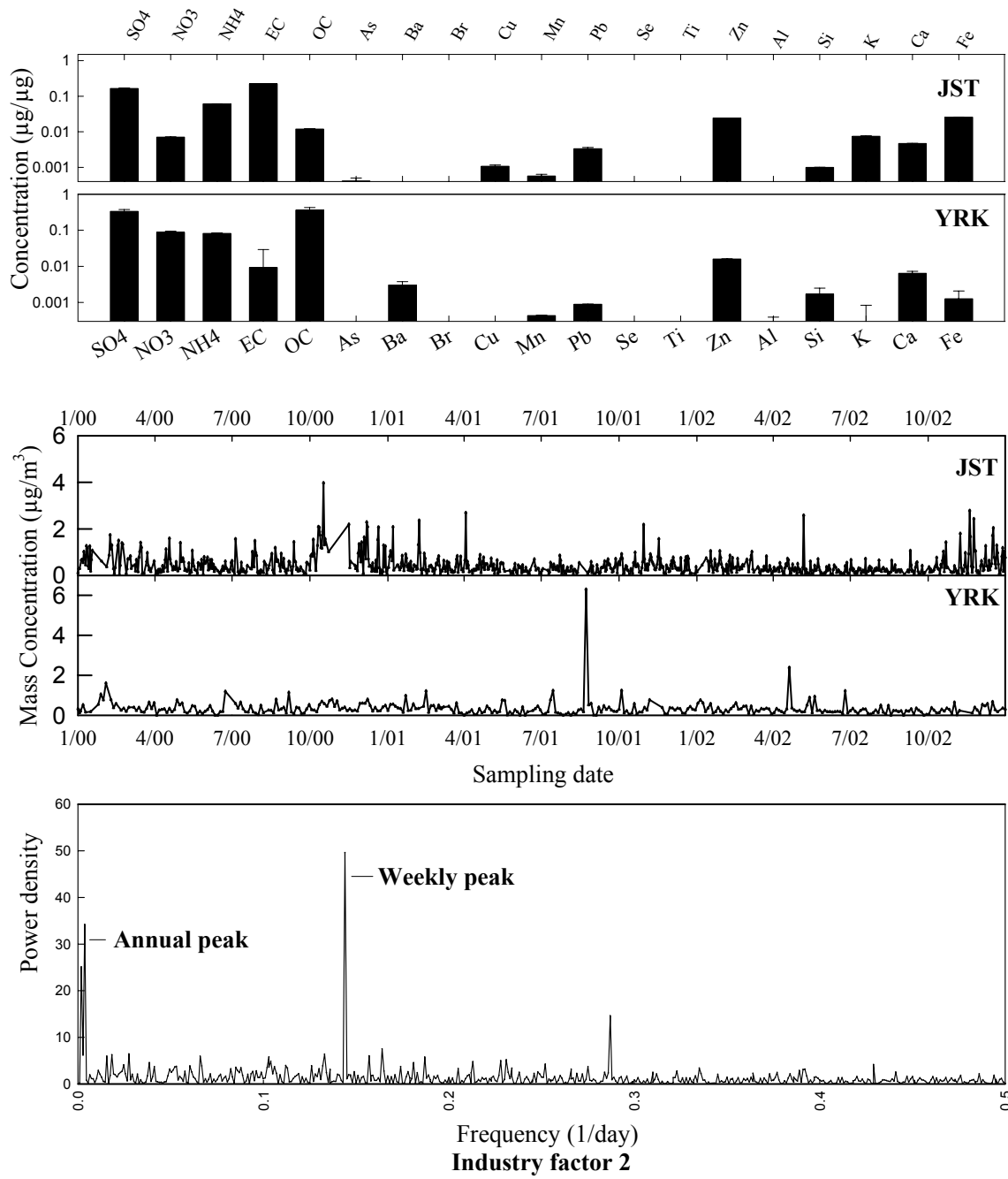


Figure 9

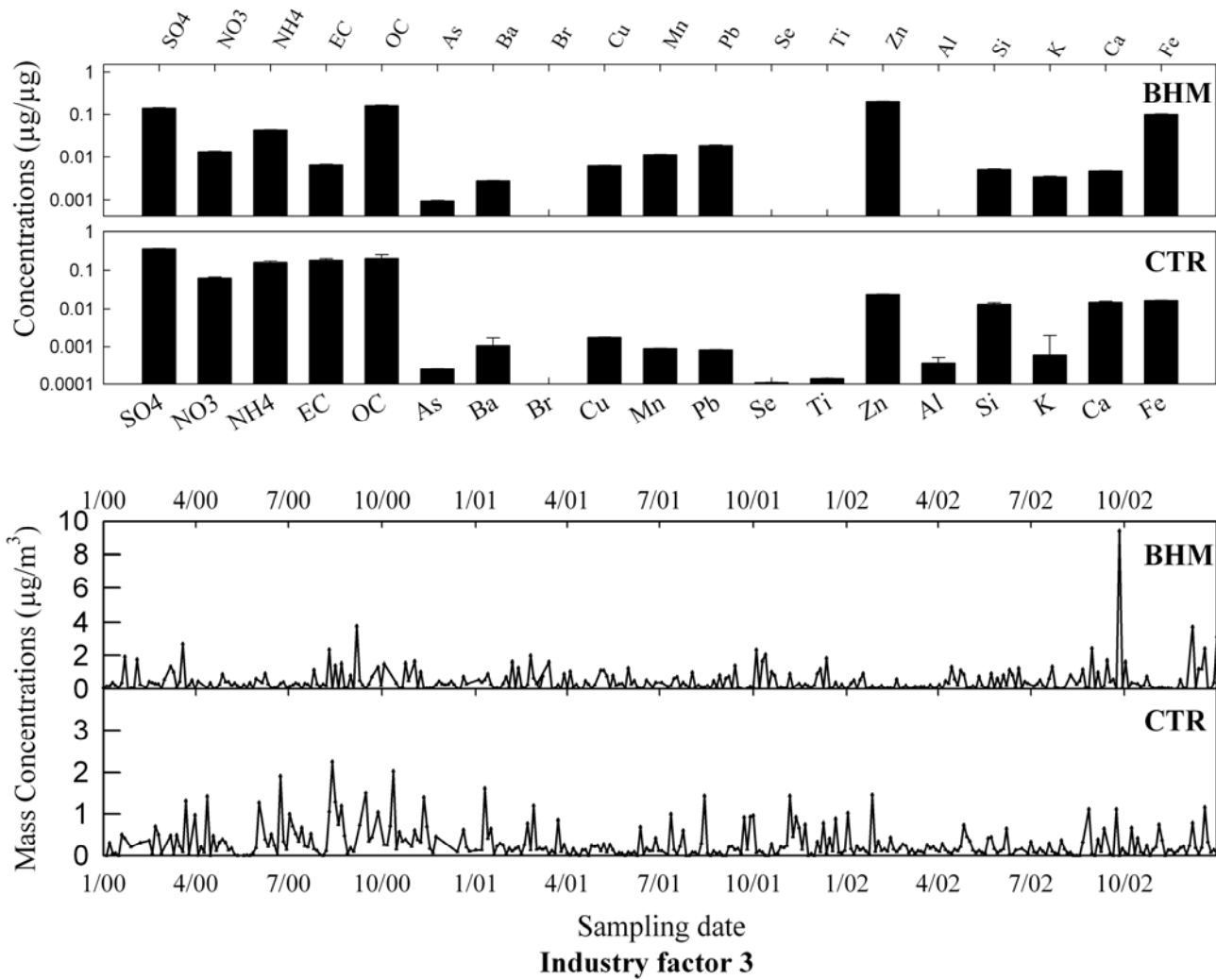


Figure 10

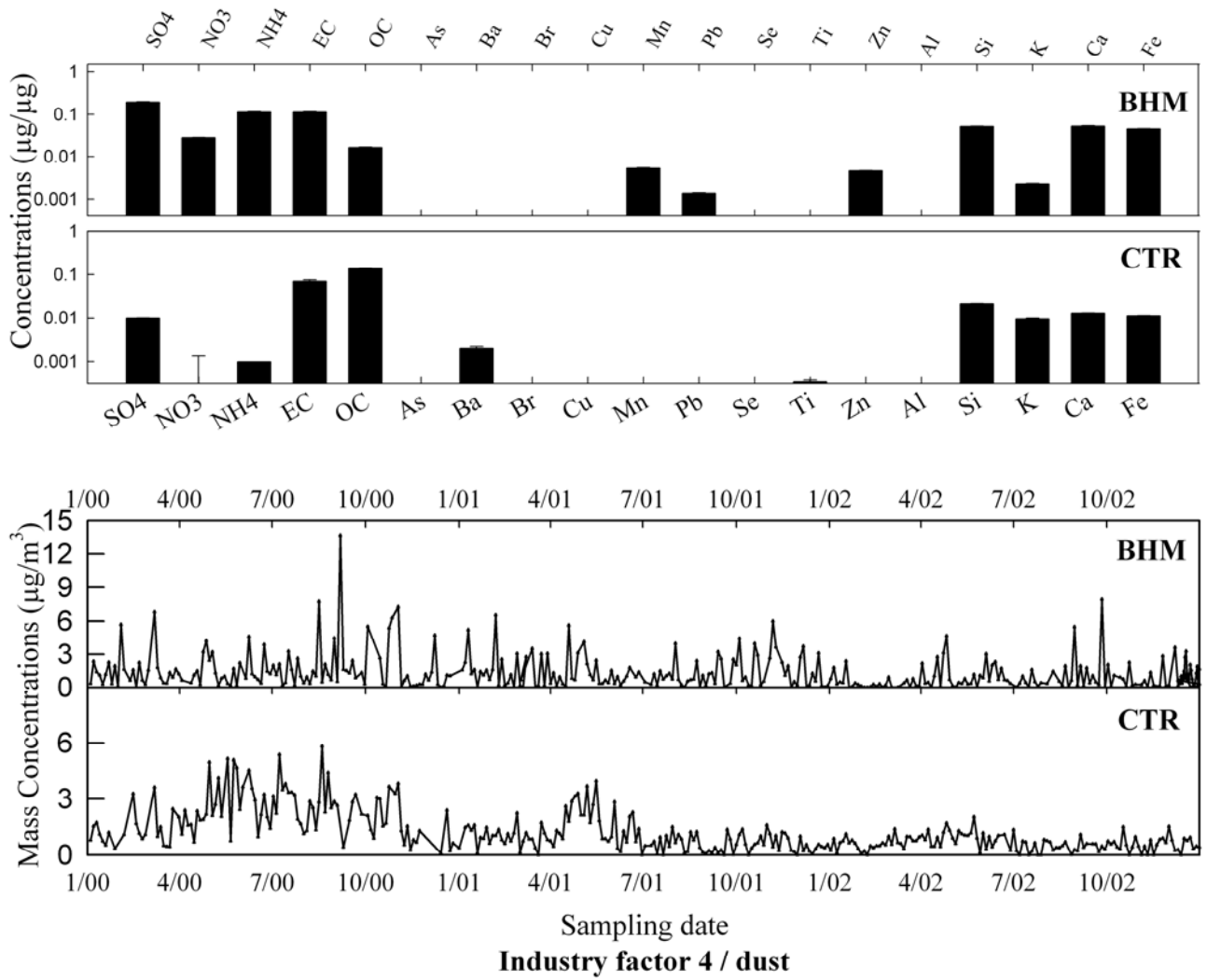


Figure 11

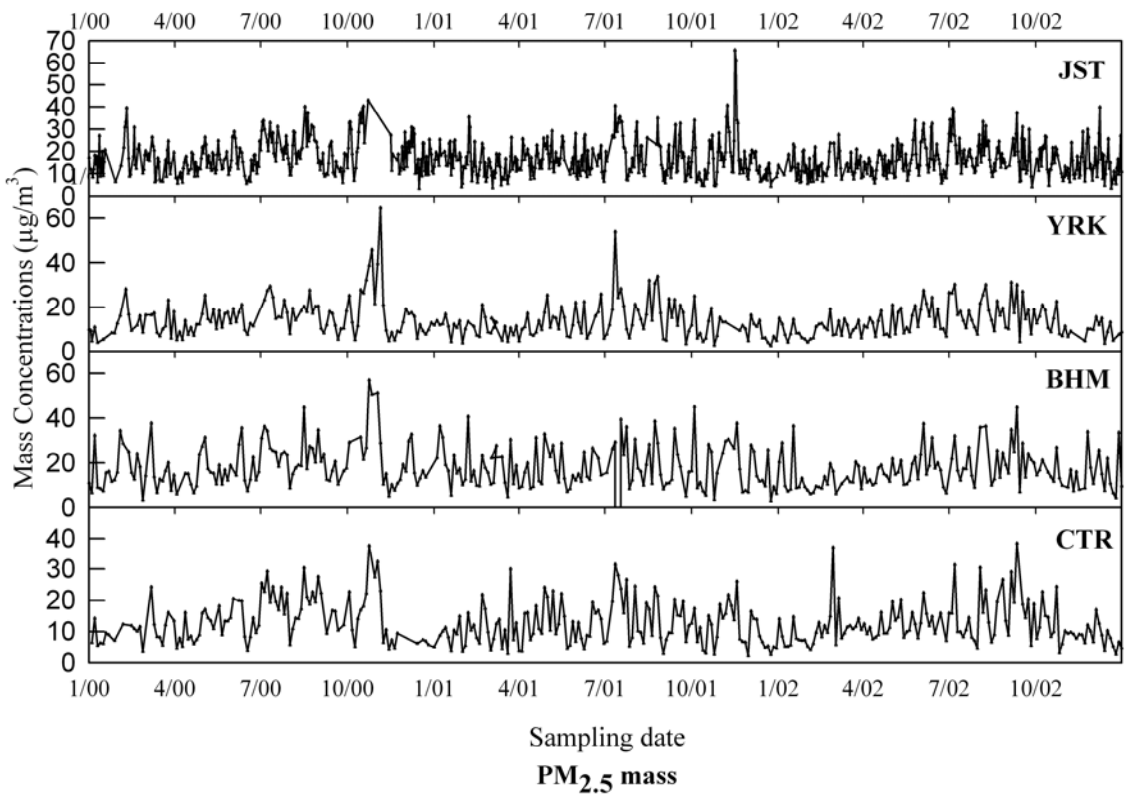


Figure 12

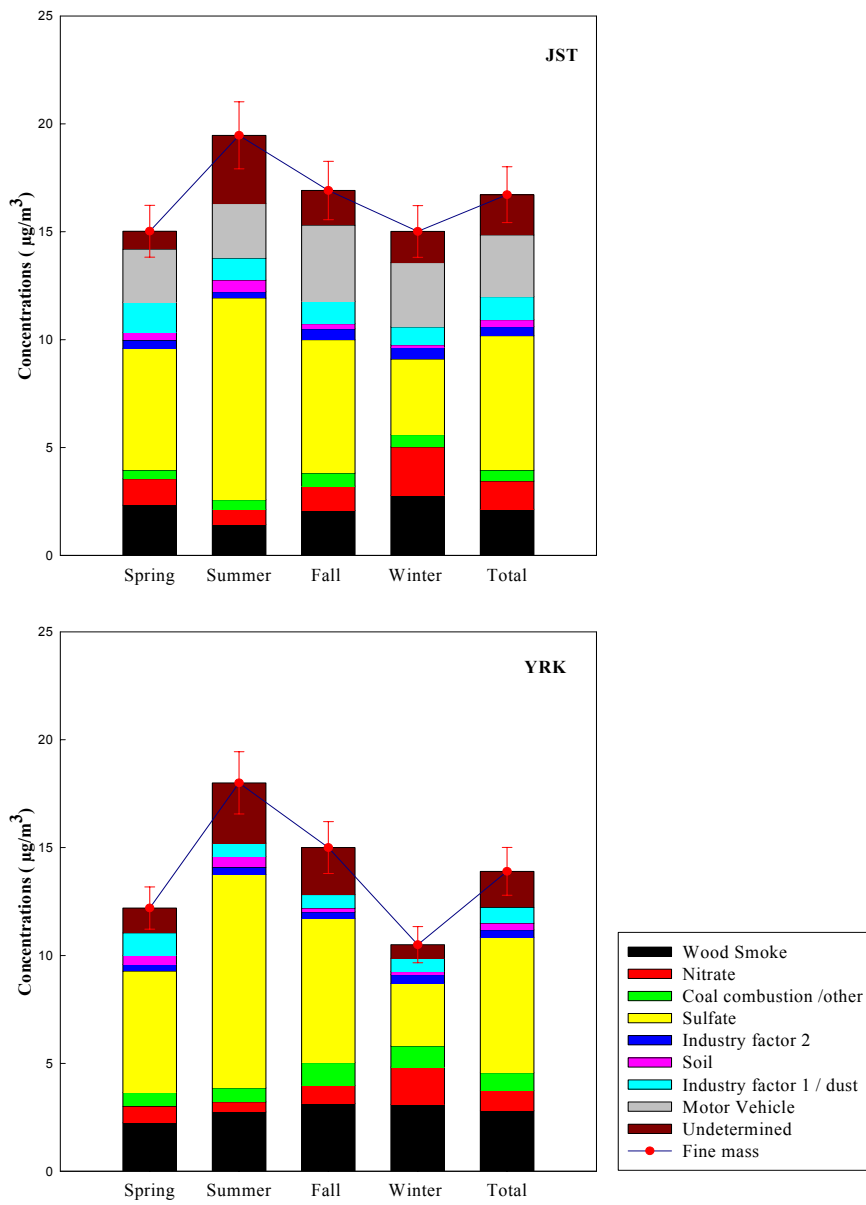


Figure 13

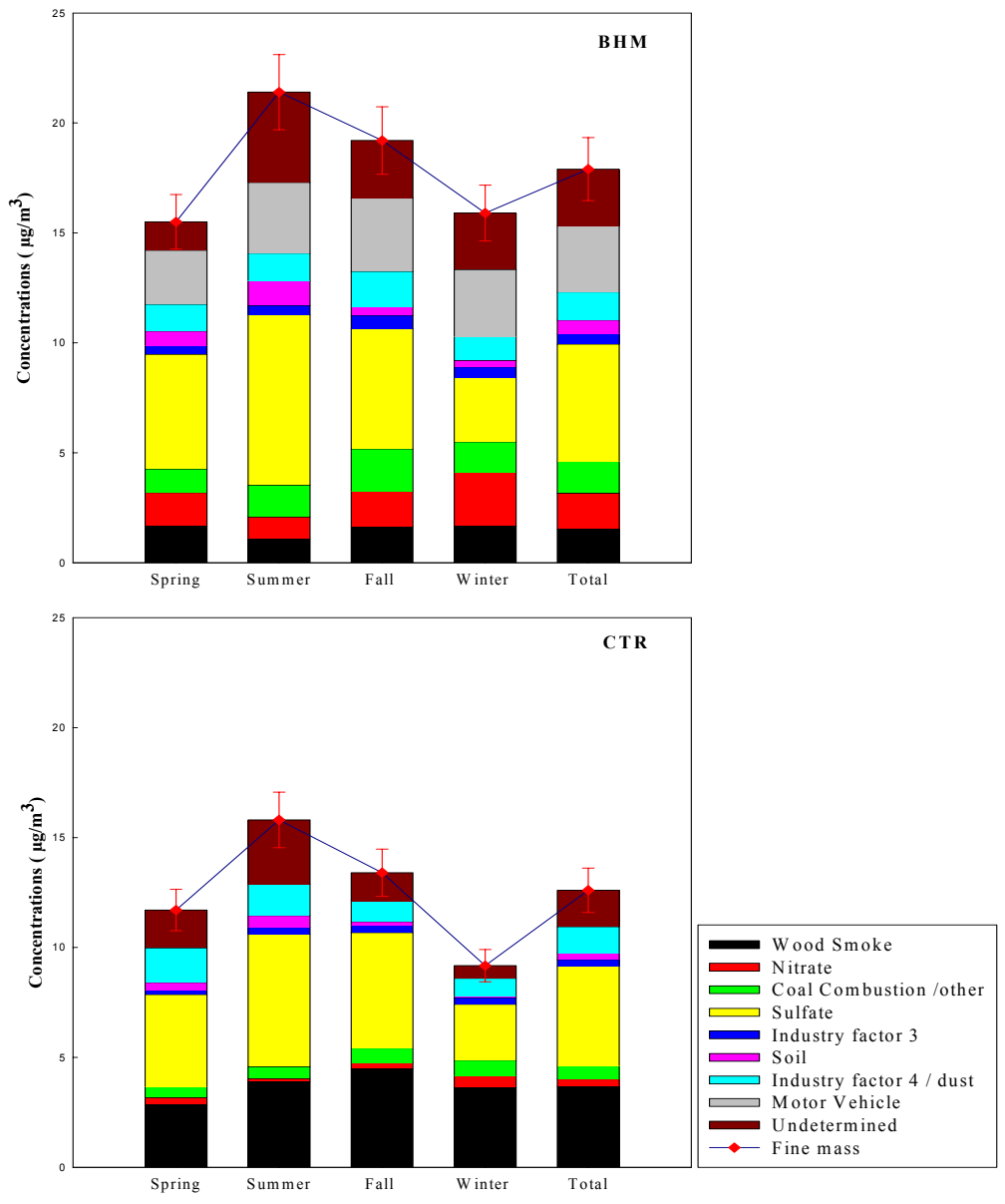
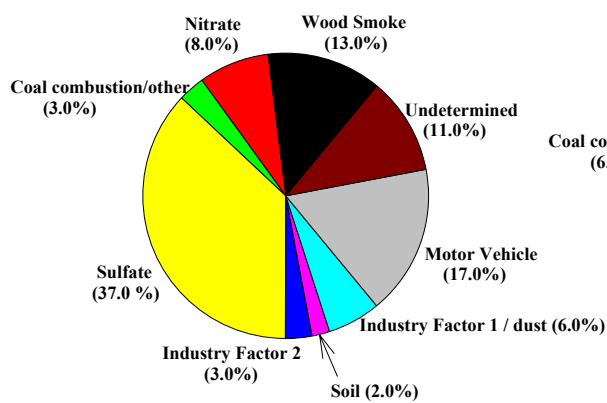
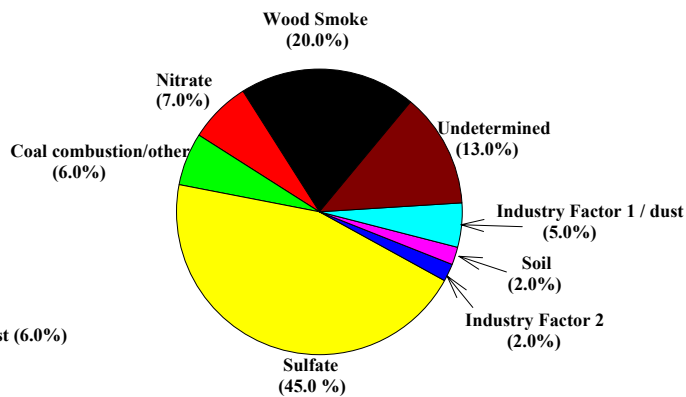


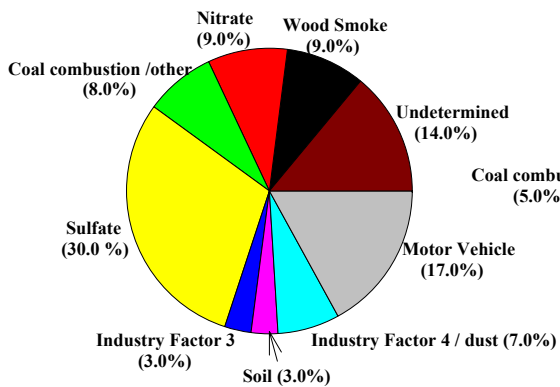
Figure 14



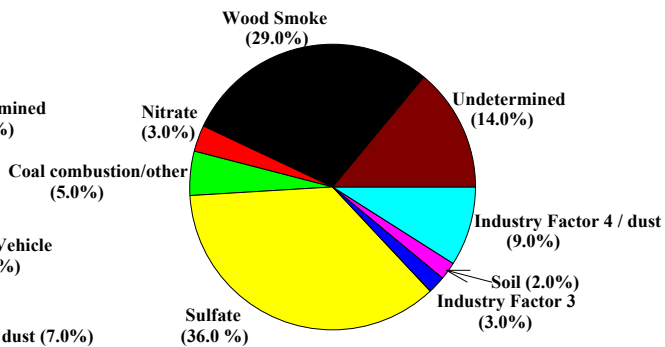
JST Site
(1/1/00 ~ 12/31/02)



YRK Site
(1/1/00 ~ 12/31/02)



BHM Site
(1/1/00 ~ 12/31/02)



CTR Site
(1/1/00 ~ 12/31/02)

Figure 15