

# Enhanced source identification of southeast aerosols using temperature-resolved carbon fractions and gas phase components

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## Abstract

Four gas components (CO, SO<sub>2</sub>, HNO<sub>3</sub> and NO<sub>y</sub>) and PM<sub>2.5</sub> (particulate matter  $\leq 2.5 \mu\text{m}$  in aerodynamic diameter) composition data including eight individual carbon fractions collected at four sites in Georgia and Alabama were analyzed with the positive matrix factorization (PMF) method. Multiple linear regression (MLR) was applied to regress the total PM mass against the estimated source contributions. The regression coefficients were used to scale the factor profiles. Nine factors were resolved at two urban sites (Atlanta, GA (JST) and Birmingham, AL (BHM)) and one rural site (Centerville, AL (CTR)). Eight factors were resolved at the other rural site (Yorkville, GA (YRK)). Six factors we refer to as soil, coal combustion/other, diesel emission, secondary sulfate, secondary nitrate, and wood smoke are common among the four sites. Two industry-related factors are similar at the two sites in the same state, but differ between states. Contrary to previous results using only PM<sub>2.5</sub> data with non-speciated EC and OC data, diesel and gasoline emission factors were resolved at the two urban sites instead of only one single motor vehicle factor; diesel and gasoline factors were also resolved at the CTR site and a diesel factor was found at YRK instead of no motor vehicle factors at the two rural sites. The inclusion of gas components also improved the identification of the coal combustion/other factor among the four sites. This study shows that inclusion of gas phase data and temperature-resolved fractional carbon data can enhance the resolving power of source apportionment studies, especially for the factors we refer to as gas, diesel, and coal combustion/other.

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## 1. Introduction

Particulate matter (PM) is a complex mixture of suspended, condensed (liquid, solid, or mixed) phase particles. Particles vary widely in size, shape and chemical composition, and may contain inorganic ions, metallic compounds, elemental carbon (EC), organic compounds, and compounds from the

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earth's crust. PM is a public health concern because it can be inhaled into the upper airways and lungs, with the amount inhaled directly related to size and shape (Vedal, 1997; Rudell et al., 1999; Dockery et al., 1993; Schwartz et al., 1993; Lipfert and Wyzga, 1995; Gilliland et al., 2001; Peters et al., 2001; Pope et al., 2002).

PM may be either directly emitted into the atmosphere (primary particles) or formed by chemical reactions of gases (secondary particles) from natural or man-made (anthropogenic) sources such as SO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub> and certain organic compounds. SO<sub>2</sub> emissions are mainly from power plants and other industrial related oil or coal-burning sources. Motor vehicles are the predominant sources of NO<sub>x</sub>, NO<sub>y</sub>, and CO (<http://www.epa.gov/ttn/chief/trends/>).

Particulate-phase pollutants emitted by motor vehicles (especially diesel vehicles) consist mostly of carbonaceous aerosol, with its two components, EC (also referred to as black carbon) and organic carbon (OC) (Funasaka et al., 1998). The temperature resolved OC/EC fractions source profiles of diesel and gasoline emissions have been measured in dynamometer studies (Watson et al., 1994; Cao et al., 2006).

Identification of source contributions to air quality impacts is an important step in the development of regional air quality control strategies. Receptor modeling, using measurements of pollutant concentrations at one or more sample sites, is one way of estimating those contributions. Regional and local source contributions to PM<sub>2.5</sub> have been explored by applying PMF analysis in the Northeast (Song et al., 2001, Poirot et al., 2001) and the Southeast (Liu et al., 2005). Improved source identification has been found at JST by using carbon fractions (Kim et al., 2004a, b), as operationally defined by the Desert Research Institute thermal optical reflectance method (Chow et al., 1993). Including gaseous species as additional constraints has been suggested previously (Zhou et al., 2005; Kim et al., 2005). The combination of gas phase components, fine and coarse PM mass (without PM components), and temperature in a receptor model analysis also has been reported (Paterson et al., 1999).

In this study, PMF is applied to PM<sub>2.5</sub> compositional data including eight individual carbon fractions, and with four gas components collected during a 3-year period at four sites in Georgia and Alabama. We show that the inclusion of gas and

carbon fraction measurements in receptor model analysis improves the resolution of factor profiles and contributions.

## 2. Data collection

PM<sub>2.5</sub> and gas compositional data analyzed in this study consisted of the measurements taken at four sites: 2 urban-rural pairs in two states: Alabama (North Birmingham [BHM] and Centre-ville [CTR]), and Georgia (Atlanta [JST] and Yorkville [YRK]). The detailed description of the receptor sites has been given elsewhere (Hansen et al., 2003; Liu et al., 2005).

Twenty-four hour integrated PM<sub>2.5</sub> samples were collected daily at the JST site. PM<sub>2.5</sub> samples were collected every third day at the other sites. PM<sub>2.5</sub> 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 5 m above ground level. A thermal optical reflectance/Interagency Monitoring of Protected Visual Environments (TOR/IMPROVE) protocol (Chow et al., 1993) was used to determine the eight temperature-resolved carbon fractions (Desert Research Institute, Reno, NV). Details can be found elsewhere (Kim et al., 2003). Hourly averaged gaseous component data from the same time period were also collected at the four sites (Hansen et al., 2003). The daily concentrations were calculated by averaging the 24 1-h average values.

Compositional data from 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 to December 2002. For each sample, concentrations of 25 particulate components (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, As, Ba, Br, Cu, Mn, Pb, Se, Ti, Zn, Al, Si, K, Ca, Fe, OC1, OC2, OC3, OC4, OP, EC1, EC2, and EC3) and 4 trace gases (CO, SO<sub>2</sub>, HNO<sub>3</sub>, and NO<sub>y</sub>) were usually available for PMF analysis. There are occasional "missing data" (no reported measurement) for one or more species. Total PM<sub>2.5</sub> mass concentration for each sample, and the estimated analytical uncertainty and detection limit for each chemical species were also obtained.

## 3. Method

PMF (Paatero and Tapper, 1994, Paatero, 1997) was used to analyze PM<sub>2.5</sub> and gas phase data at the

four sites in this study. Application of PMF requires that error estimates for the data be judiciously determined to reflect the quality and reliability of each data point. This feature provides one of the important advantages of PMF: an ability to handle missing and below detection limit data by adjusting the corresponding error estimates. In the four data sets used, there were missing and below detection limit values for different chemical species in different samples. The summary of the sample missing values and below detection limit data for PMF analysis is listed in Table 1. Missing data were replaced by the geometric averages of the corresponding elements, which dampens the variability, but should not skew the results, and the errors are assigned to such data are four times the geometric averages (Polissar et al., 1998). Half of the detection

limit was used for values below the detection limit and 5/6 of the detection limit was used for the corresponding error estimates (Polissar et al., 1998). In this study, samples, where PM<sub>2.5</sub> mass concentrations or all eight carbon fractions were not available, were excluded from the analysis. If the percentage of the missing data of a species exceeded 25%, the species was down weighted by doubling the associated uncertainties.

Multiple linear regression (MLR) was performed to regress the mass concentration against the factor scores obtained from PMF. Because of uncertainties introduced by the measurement matrix, a fraction of the measured variations is not captured by PMF. We take into account the unexplained portion by regressing the factor scores only to the explained portion of the mass concentrations. The regression

Table 1  
Fractions of samples with missing and below detection limit values used in the analysis

Species	JST		YRK		BHM		CTR	
	MV <sup>a</sup> (%)	BDL <sup>b</sup> (%)	MV <sup>a</sup> (%)	BDL <sup>b</sup> (%)	MV <sup>a</sup> (%)	BDL <sup>b</sup> (%)	MV <sup>a</sup> (%)	BDL <sup>b</sup> (%)
PM <sub>2.5</sub>	0	0	0	0	0.3	0	0	0
SO <sub>4</sub>	5.4	0	1.2	0	11.9	0	11.8	0
NO <sub>3</sub>	5.5	0.5	2.3	0	11.3	0	11.8	0.6
NH <sub>4</sub>	5.5	0.0	2.9	0	13.4	0	13.0	0
As	0	52.1	0	65.4	0	28.0	0	70.1
Ba	0	0.0	0	0	0	0	0	0
Br	0	4.7	0	6.6	0	5.7	0	9.2
Cu	0	59.0	0	88.8	0	29.5	0	97.6
Mn	0	35.2	0	58.5	0	7.7	0	48.5
Pb	0	50.2	0	77.2	0	15.8	0	79.6
Se	0	40.1	0	54.2	0	44.0	0	69.8
Ti	0	0	0	0	0	0	0	0
Zn	0	0.6	0	3.2	0	0	0	6.5
Al	0	0	0	0	0	0	0	0
Si	0	0.1	0	1.2	0	0	0	0.6
K	0	0	0	0	0	0	0	0
Ca	0	0.9	0	7.2	0	0.3	0	6.5
Fe	0	0	0	2.9	0	0	0	4.7
OC1	3.9	0.5	10.1	8.6	9.5	2.1	19.8	8.9
OC2	3.9	0	10.1	0	9.5	0	19.8	0
OC3	3.9	0	10.1	0	9.5	0	19.8	0
OC4	3.9	1.0	10.1	0.3	9.5	0	19.8	0
OP	3.9	6.7	10.1	0.3	9.5	18.2	19.8	0.3
EC1	3.9	0	10.1	0.3	9.5	0	19.8	0
EC2	3.9	0.1	10.1	0.3	9.5	0	19.8	0
EC3	3.9	0	10.1	0	9.5	0	19.8	0
CO	8.6	0.1	28.5	0	46.1	0	17.8	0
SO <sub>2</sub>	27.6	0.3	19.3	0.9	44.3	0.3	20.1	1.8
HNO <sub>3</sub>	20.4	6.4	32.0	3.2	67.3	8.9	27.5	11.2
NO <sub>y</sub>	16.0	0	29.4	0	45.2	0	23.7	0

<sup>a</sup>MV = % missing values.

<sup>b</sup>BDL = % below detection limit.

coefficients were used to convert the factor profiles and contributions to physically meaningful units — in this case,  $\mu\text{g m}^{-3}$ .

#### 4. Results and discussion

A critical step in PMF analysis is the determination of the number of contributing factors. Normal practice is to experiment and find the optimal number with the most physically meaningful results. The robust mode was used to reduce the influence of extreme values on the PMF solution. A data point was classified as an extreme value if the residual (Paatero and Tapper, 1994) exceeded four times the error estimate. The estimated uncertainties of those extreme values were then increased so that the weights of the extreme values in the solution were decreased. Analysis of the model cost function,  $Q$ , can be used to help determine the optimal number of factors (Yakovleva et al., 1999). Assuming that the measurement errors are reasonably estimated, the value of  $Q$  should be approximately equal to the number of data points. The final  $Q$  value for the four sites are 27450 with 932\*29 data at the JST site, 10329 with 336\*29 data at the BHM site, 10341 with 347\*29 at the YRK site, and 9826 with 338\*29 data at the CTR site. However, the resulting solution also needs to be physically meaningful within the system of interest. Based on evaluation of the resulting factor profiles by trial and error with different numbers of source factors, the PMF solutions shown in this study were chosen. The results reported here mainly focus on the improvements of factor resolution by including fractional carbon and gas measurements and then comparison to the more traditional approach without using these data in factor analysis. Factor profiles with uncertainties of particulate species are shown as the mass fraction,  $\mu\text{g } \mu\text{g}^{-1}$ , open bars are used when the uncertainty is larger than the contribution. We show the explained variations (EVs), which is dimensionless, for the full factor profiles with both particulate and gas components because of the incompatibility of units between gaseous and particulate components. The value of  $EV_{ij}$  is the (mass) fraction of species  $i$  that can be explained by factor  $j$  (Paterson et al., 1999).

##### 4.1. Gasoline and diesel factors

In our previous study (Liu et al., 2005), only a single motor vehicle-dominated factor was resolved

in the two urban sites while no motor vehicle-dominated factor was identified at rural sites. With the inclusion of the eight carbon species, CO, and  $\text{NO}_y$ , gasoline and diesel-dominated factors are resolved and their contributions are quantified (Figs. 1 and 2). Gasoline-fueled vehicles have higher CO emissions, while diesel vehicles tend to have higher NO emissions. A diesel factor is resolved at all four sites while the gasoline factor is resolved at the two urban sites and a gasoline/other factor was found at the rural CTR site but not at YRK.

The PMF factor profiles show that diesel and gasoline factors have abundant OC2 fractions. The EC2 fraction in the diesel factor is significantly higher than in gasoline. In comparison, the OC3 fraction in the gasoline factor is more abundant than in diesel. There is very little EC3 in either the diesel or gasoline factor. Some Fe, Si, and other dust elements are also included in the factor profiles (Figs. 1 and 2) possibly because gasoline/diesel emissions are mixed with soil dust constituents during transport or these may represent the elements in fuel additives (Schauer et al., 2002). Compared to the results from a previous study at JST (Kim et al., 2004a, b), the gasoline vehicle factor has a smaller amount of OC4 and a larger amount of OC2. The diesel factor contains less EC1 and more EC2.

PMF analysis constructs the factor profiles by analyzing the data covariance structure. The resulting factor profiles represent those of the emissions only, assuming that atmospheric processes do not significantly alter the later, which is the assumption of the chemical mass balance analysis. CMB has been successfully applied only to primary emissions because of this assumption. It is therefore instructive to compare the PMF factor profiles with available diesel and gasoline emission profiles. Several previous studies (Chow et al., 1993, Watson et al., 1994, Cao et al., 2006) have applied thermal/optical reflectance (TOR) carbon analysis to diesel or gasoline emissions obtained in dynamometer tests. These measured elemental and OC fraction profiles are also shown in Fig. 3.

The PMF diesel and gasoline factor profiles are in qualitative agreement with the emission profiles by Cao et al. (2006), particularly with respect to the key fractions (i.e., OC2 and EC2 for diesel, and OC2 and OC3 for gasoline). The OC1 abundances in both diesel and gasoline profiles are very different between Cao et al. (2006) and Watson et al. (1994). PMF resolved profiles are in better agreement with

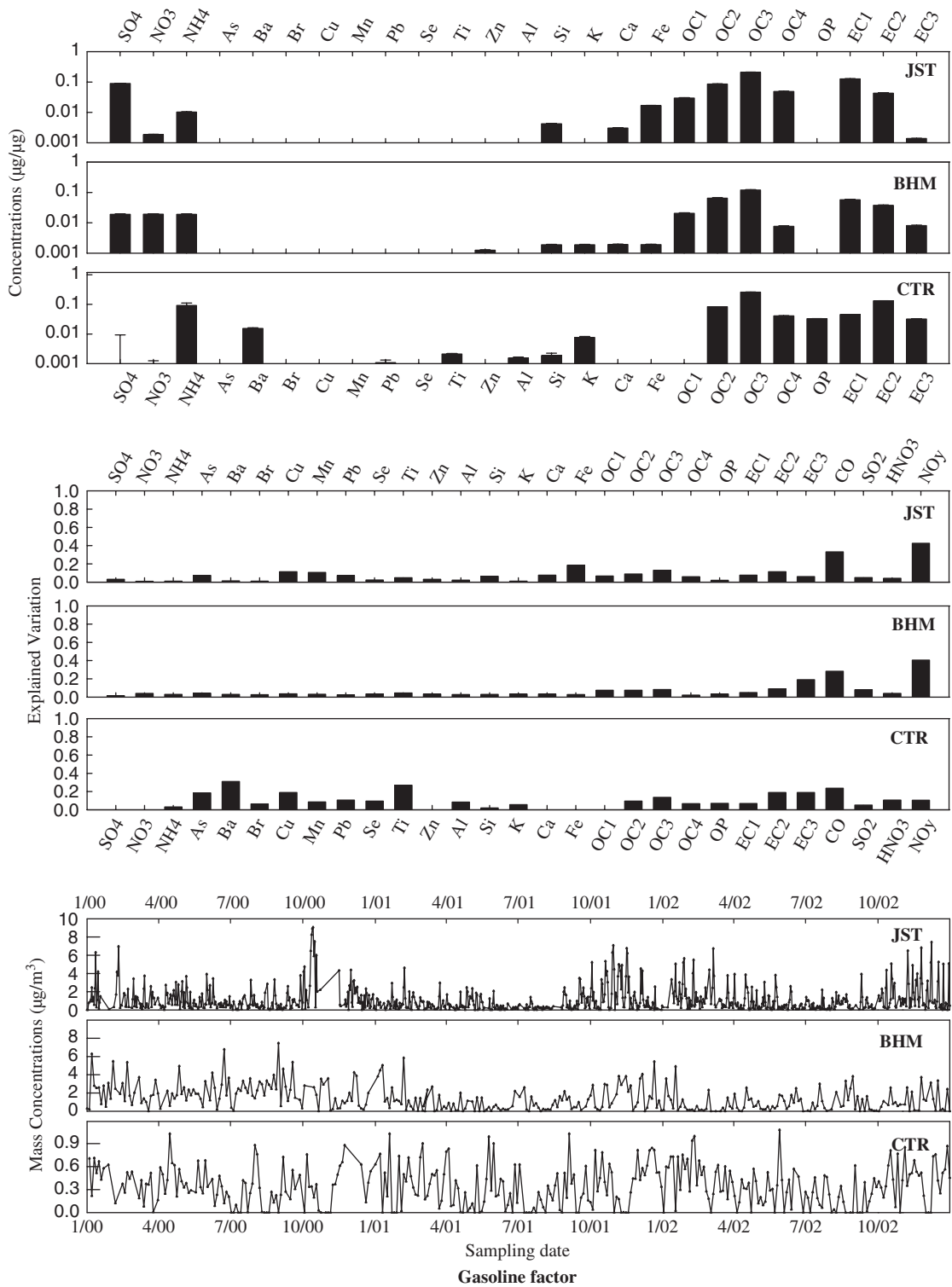


Fig. 1. Factor profiles and factor contributions of the gasoline factor resolved by PMF at the three sites. The top panel shows the factor profiles in  $\mu\text{g m}^{-3}$  unit without the gas components and the middle panel shows the factor profiles as explained variation.

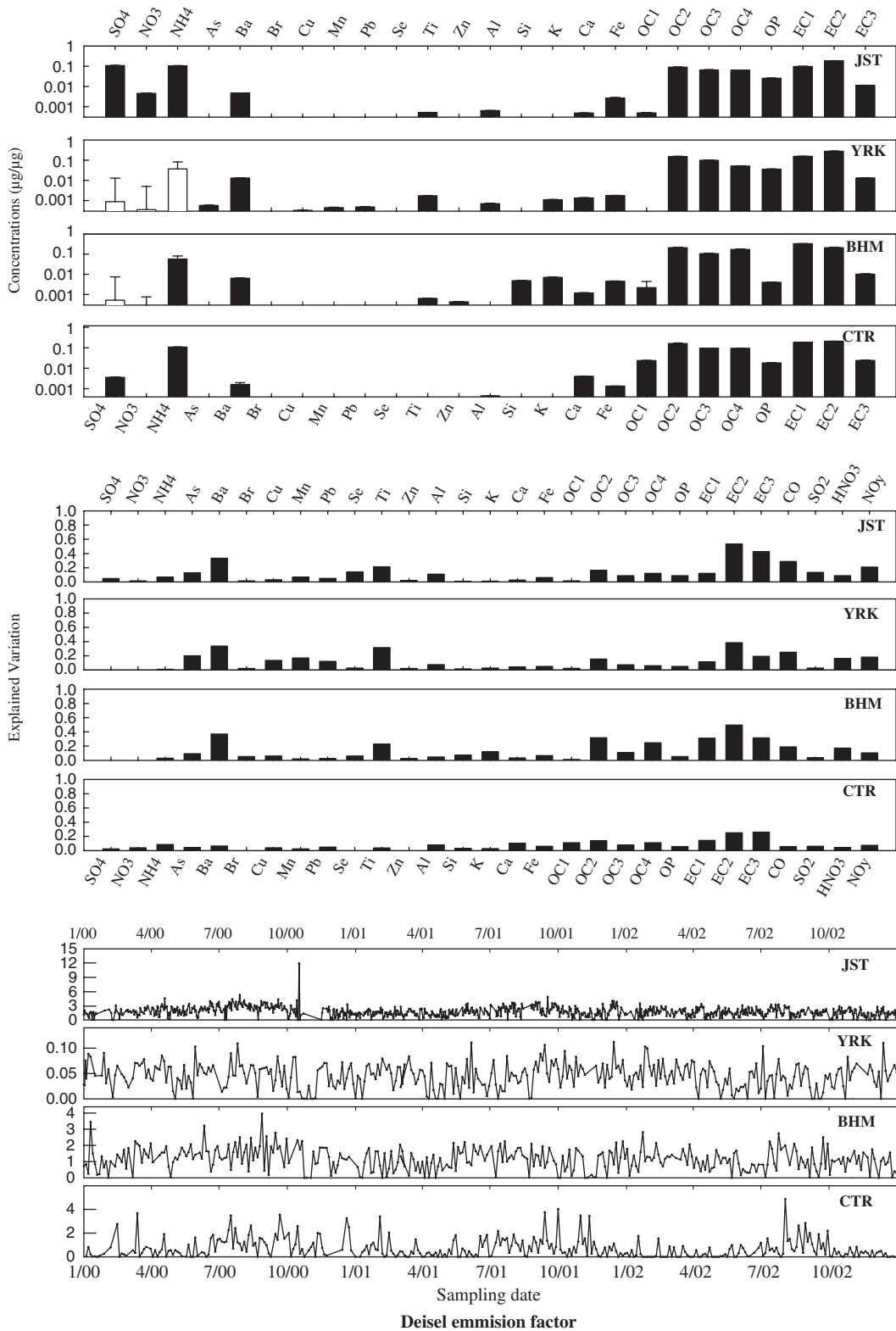


Fig. 2. Same as Fig. 1 but for the diesel factor resolved by PMF at the four sites.

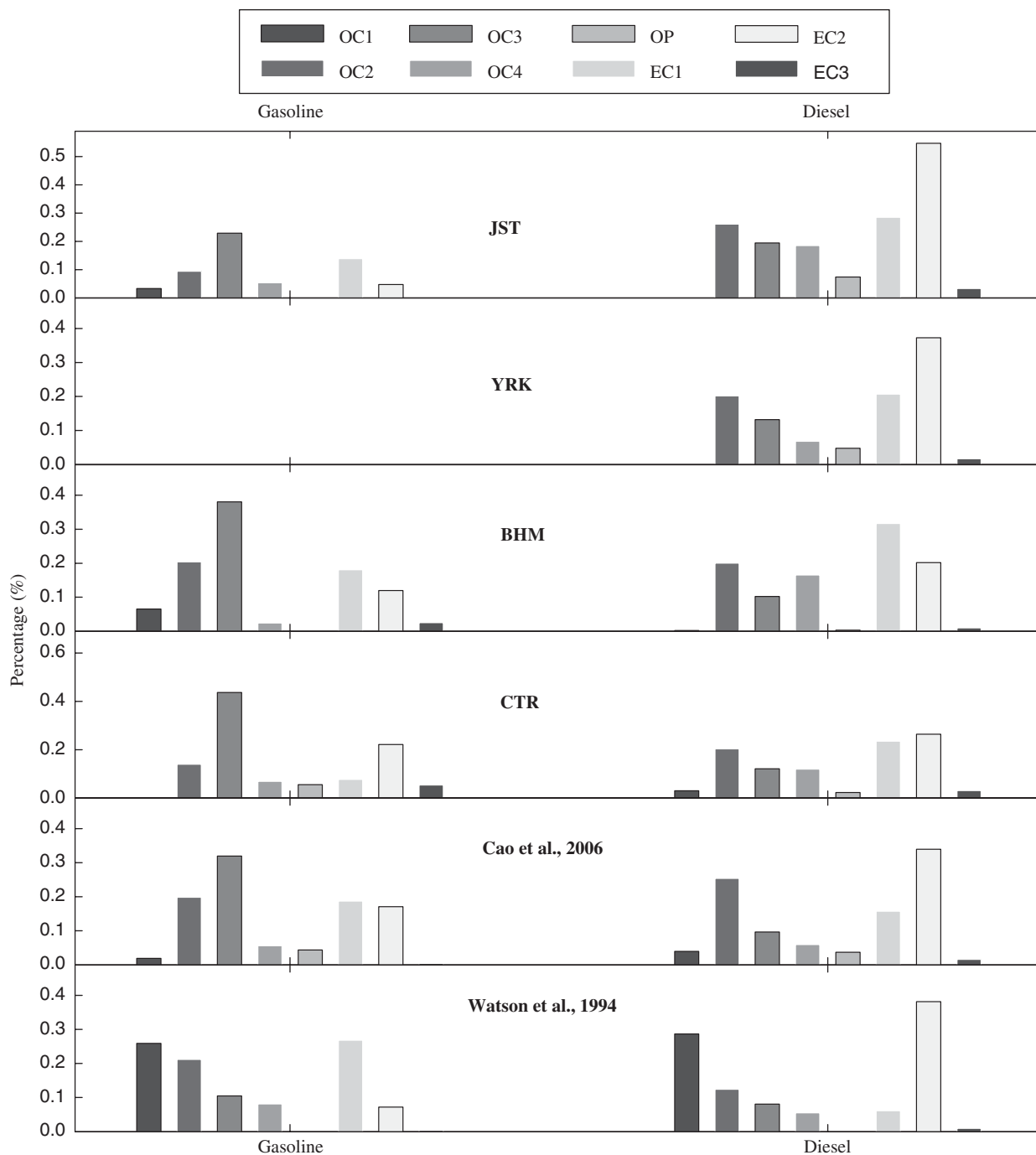


Fig. 3. Comparison of the diesel (top) and gasoline (bottom) carbon thermal fractions extracted by PMF from the measurements at the four sites and those reported by Cao et al. (2006) and Watson et al. (1994).

Cao et al. (2006), showing little OC1 in gasoline and diesel emissions. Results by Cao et al. (2006) may better represent the current engine technology and fuel composition, considering the changes that have taken place in the intervening decade.

OC/EC ratio in fresh exhaust is usually much higher for gasoline engines than for diesel. Cadle et al. (1999) found that the former is typically 2.05 while the latter is only 0.72. The PMF resolved OC/EC ratios for diesel and gasoline factors are

Table 2  
OC/EC ratio of factors resolved by PMF for the four sites

	Gasoline emission factor (OC/EC)	Diesel emissions factor (OC/EC)
JST	2.20	0.90
YRK	N/A	0.82
BHM	2.07	0.90
CTR	2.36	0.98

listed in Table 2. The OC and EC concentrations are computed using the IMPROVE protocol ( $OC = OC1 + OC2 + OC3 + OC4 + OP$  and  $EC = EC1 + EC2 + EC3 - OP$ ). The OC/EC ratios for the resolved gasoline factor range from 2.07 (BHM) to 2.36 (CTR) and those for the diesel factor range from 0.82 (CTR) to 0.98 (CTR). PMF results are in agreement with the ratios determined by Cadle et al. (1999).

#### 4.2. Coal/other factor

Another major improvement of the PMF results over those by Liu et al. (2005) is largely due to the inclusion of  $SO_2$ , which helps resolve a coal combustion/other factor. Characterized by high concentrations of  $SO_2$  and Se (Fig. 4), this factor represents the fresh emission from coal and residual oil combustion sources (Grahame and Hidy, 2004). Factor contributions at the four sites are lower in summer time (April–September) than in winter time (October–March) reflecting in part the seasonal change of boundary layer height. The factor contribution at the BHM site is much larger than the other three sites. This is probably because BHM site has a much more significant local impact from local industry sources such as coke ovens, steel mill, mineral wool which use coal in various ways.

#### 4.3. Secondary sulfate factor

The resolved sulfate factor includes gas-phase  $HNO_3$  at all four sites (Fig. 5). The high correlation between the secondary sulfate and  $HNO_3$  is likely due to following reasons. First,  $H_2SO_4$  and  $HNO_3$  are secondary photochemical products of co-emitted  $SO_2$  and  $NO_x$  emissions from large elevated point sources. Secondly, this factor tends to be higher during warmer than cooler months, reflecting in part the thermal stability of aerosol  $NH_4NO_3$  in

the cooler months (Russell et al., 1983). Lastly, the more abundant  $H_2SO_4$  production in summer leaves little ammonia for the conversion of  $HNO_3$  to particulate nitrate.

#### 4.4. Wood smoke factor

A wood smoke source is characterized by OC, EC and K (Watson et al., 2001). The factor profiles at the four sites show large amounts of OC (OC1–OC4), K and EC1, except that some EC2 is mixed in this factor at the BHM and YRK sites (Fig. 6). The seasonal variability of this factor is similar to that observed in the previous study (Liu et al., 2005). For the two urban sites, this factor has seasonally high values in winter and occasional spikes in spring and summer. The seasonal peaks at the rural sites are in spring. Wood combustion for heating and reduced ventilation account for the urban winter peaks, while prescribed burning in the Southeast contributes largely to the spring peak.

#### 4.5. Soil factor

The soil factor has high concentrations of Si, Fe, Al, K, Ca, and Ti resolved for the four sites (Fig. 7). The soil factor has high source contribution peaks during April 2001, June and July 2001, and June and July 2002. The April event likely reflects the intercontinental dust transport from Asia and the two June/July events likely reflect dust transport from Saharan Africa (Liu et al., 2005).

#### 4.6. Secondary nitrate factor

Another common factor, secondary nitrate, is also resolved (Fig. 8). Compared to this factor from the previous study (Liu et al., 2005), which did not consider the gases, some contributions by CO,  $SO_2$  and  $NO_y$  now appear in this factor, particularly at the two rural sites, likely reflecting the effects of nitrate transport from major urban regions. Nitrate and the gases are mixed during transport and their concentrations are higher in winter due in part to a shallow boundary layer. OC is present in the form of higher temperature OC fractions (OC3–OP) as shown in Fig. 8. The temporal variation of the factor contributions is quite similar to the previous study, with higher concentrations during winter and lower concentrations during summer.



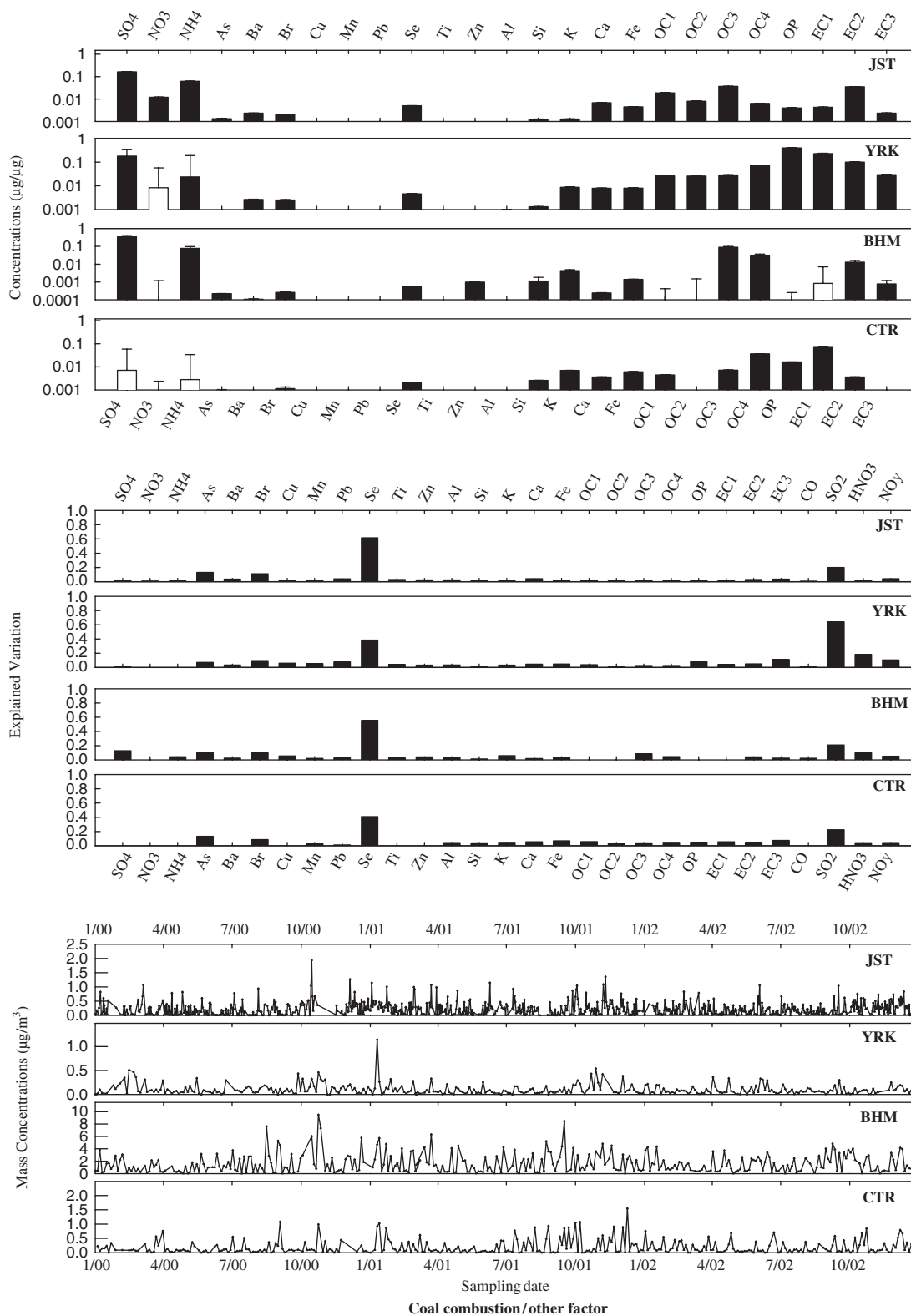


Fig. 4. Same as Fig. 1 but for the coal combustion/other factor resolved by PMF at the four sites.

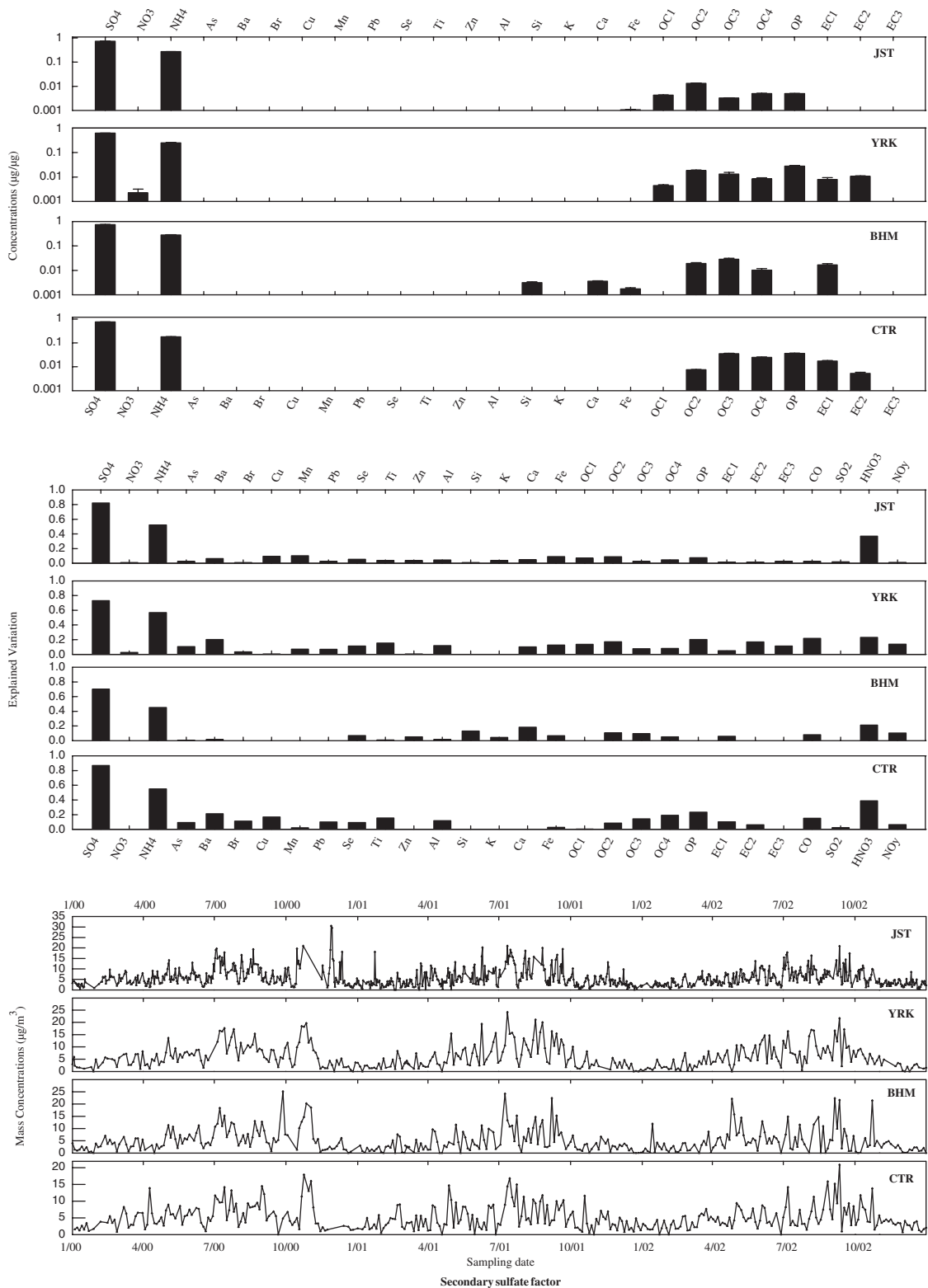


Fig. 5. Same as Fig. 1 but for the secondary sulfate factor resolved by PMF at the four sites.

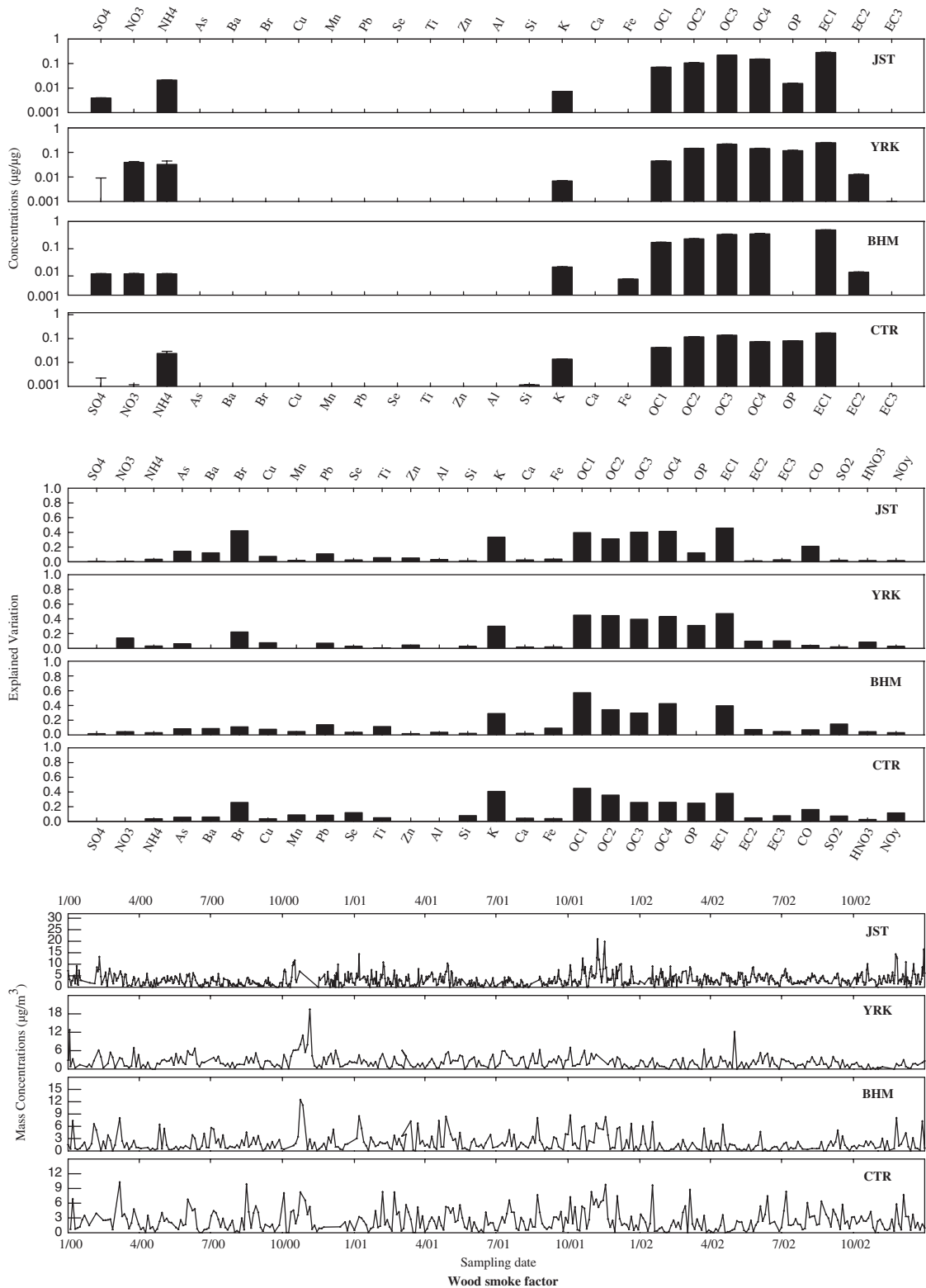


Fig. 6. Same as Fig. 1 but for the wood smoke factor resolved by PMF at the four sites.

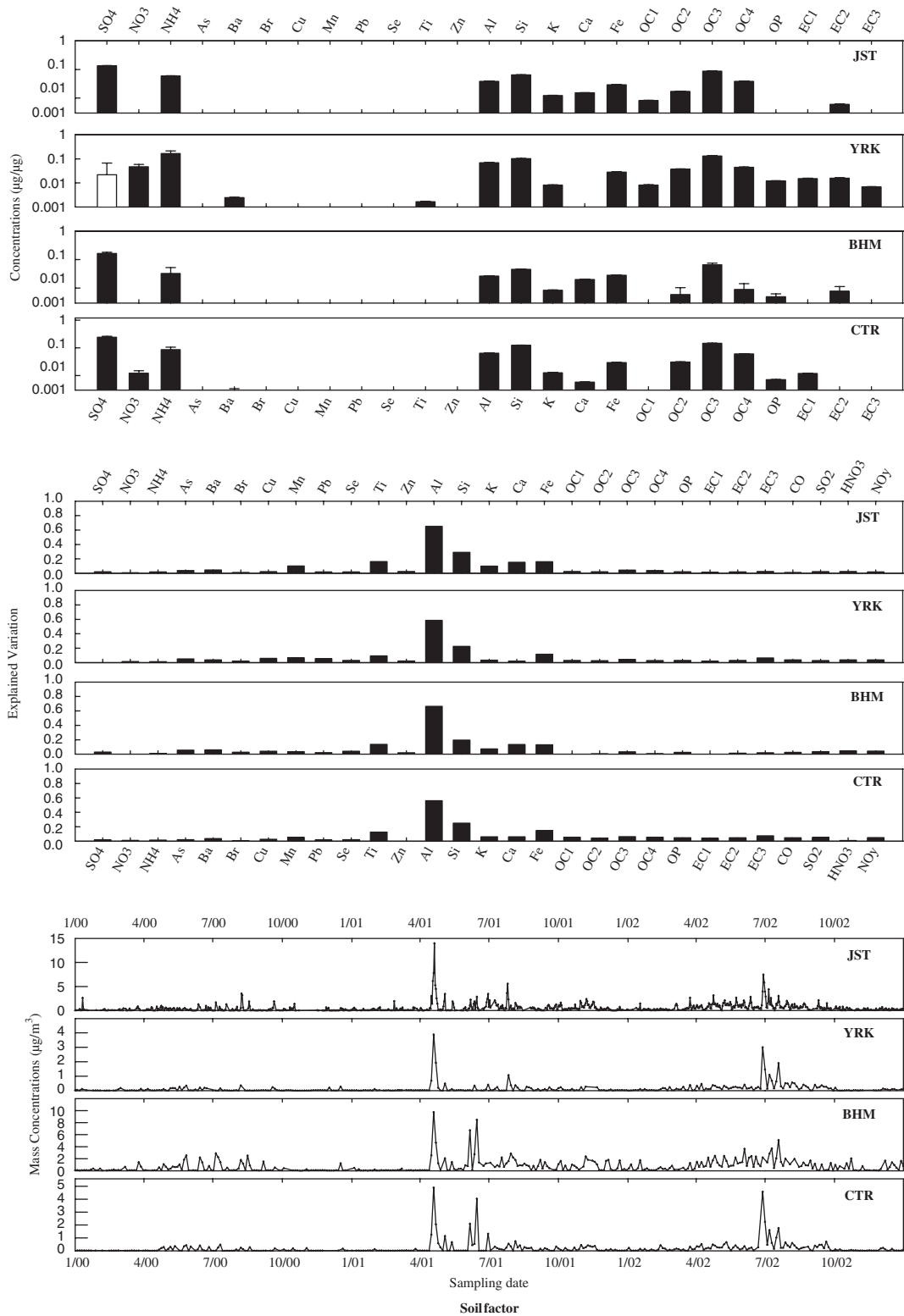


Fig. 7. Same as Fig. 1 but for the soil factor resolved by PMF at the four sites.

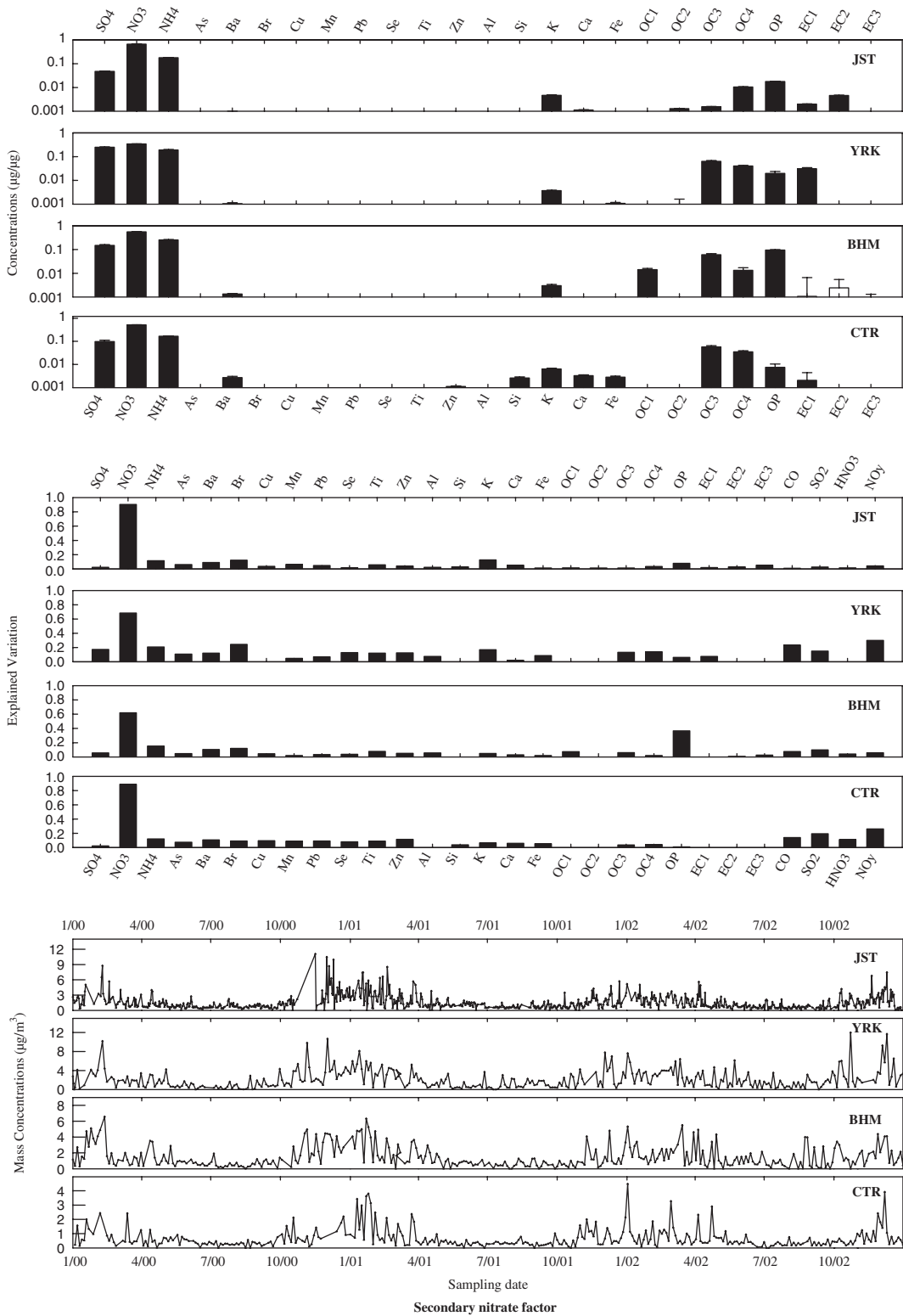


Fig. 8. Same as Fig. 1 but for the secondary nitrate factor resolved by PMF at the four sites.

4.7. Industry factor

Two similar industry factors are resolved for the JST and YRK sites and another two similar industry factors are resolved for the BHM and CTR sites (Figs. 9–12). The factor profiles and the temporal variation of factor contributions for these

industry factors are in good agreement with the previous study (Liu et al., 2005). The “industry factor 1/dust” at the JST and YRK sites is probably a combination of the cement plant source (Kim et al., 2004a, b) and local dust sources. With high concentrations of Zn, the industry factor 2 (JST and YRK sites) and industry factor 3 (BHM and CTR

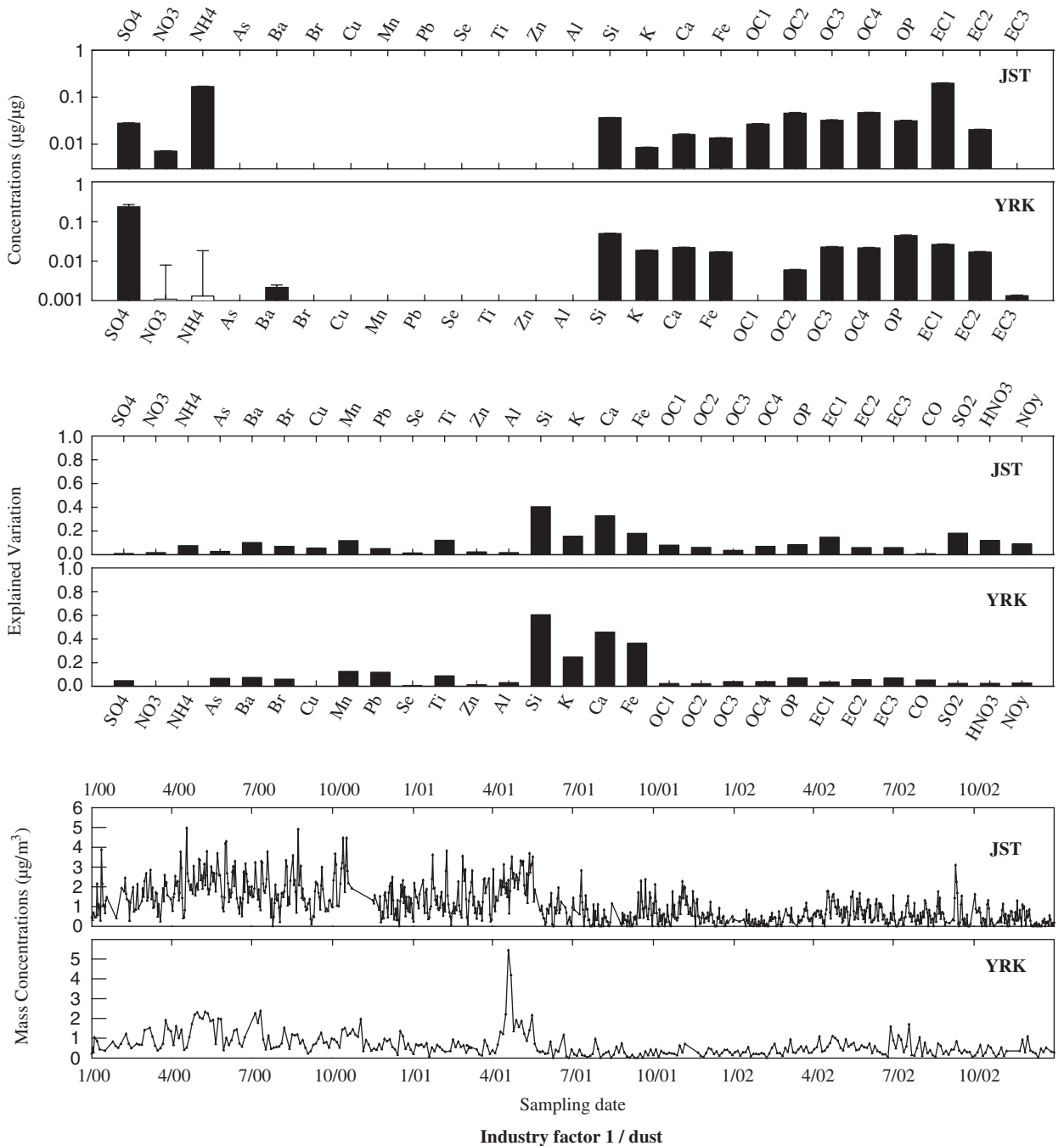


Fig. 9. Same as Fig. 1 but for the industry 1/dust factor resolved by PMF at the four sites.

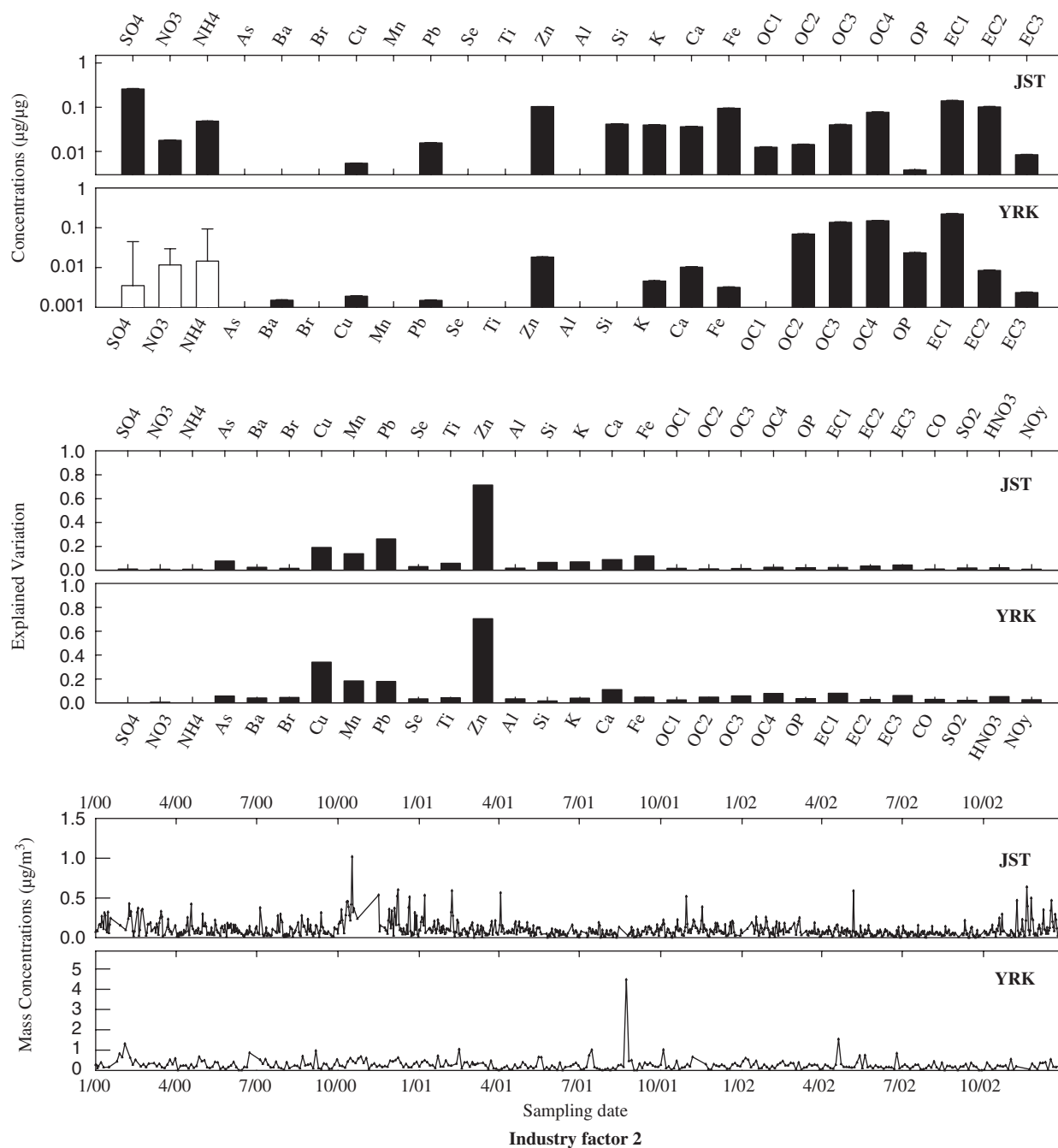


Fig. 10. Same as Fig. 1 but for the industry factor 2 resolved by PMF at JST and YRK sites.

sites) represent the general urban industry sources, which show a decrease from urban to rural sites (Figs. 10 and 11). Industry factor 4/dust at the BHM and CTR sites probably comes from the coke plant near the BHM site mixed with local dust sources.

#### 4.8. Factor correlations

We computed the day to day correlation coefficients ( $r^2$ ) between factor contributions from this study and the previous one (Liu et al., 2005) (Table 3). There is a general agreement between the

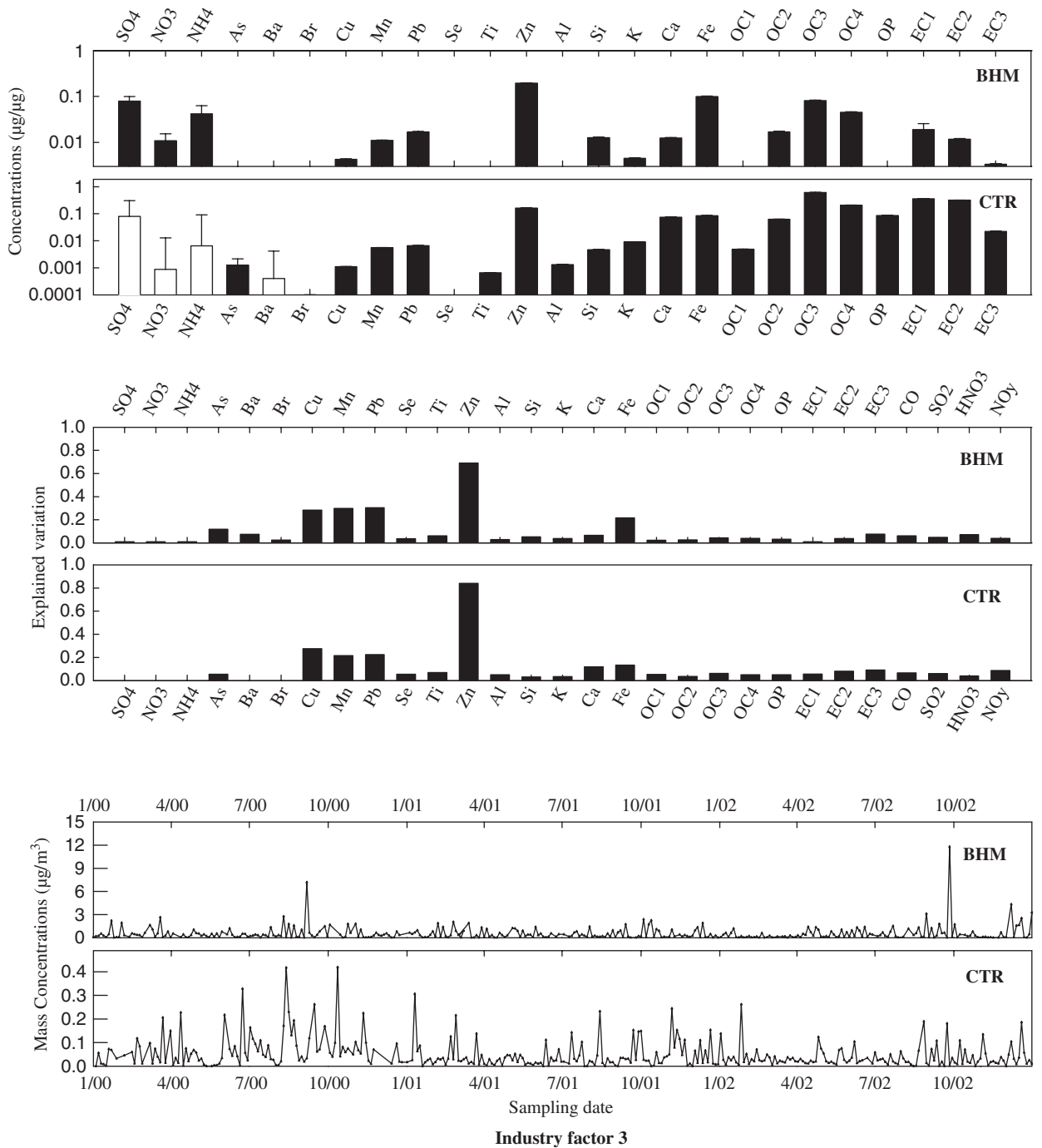


Fig. 11. Same as Fig. 1 but for the industry factor 3 resolved by PMF at BHM and CTR sites.

two studies. Diesel, gasoline and diesel+gasoline factor contributions from this study were correlated with the motor vehicle factor from previous study. The correlations between diesel and gasoline factors from this study were also shown. The relative low

correlations for the sulfate and nitrate factors are due in part to missing data (Fig. 13). The correlation of sulfate factor contributions between the two studies is much higher if the missing data are removed. The motor vehicle factor (Liu et al., 2005)



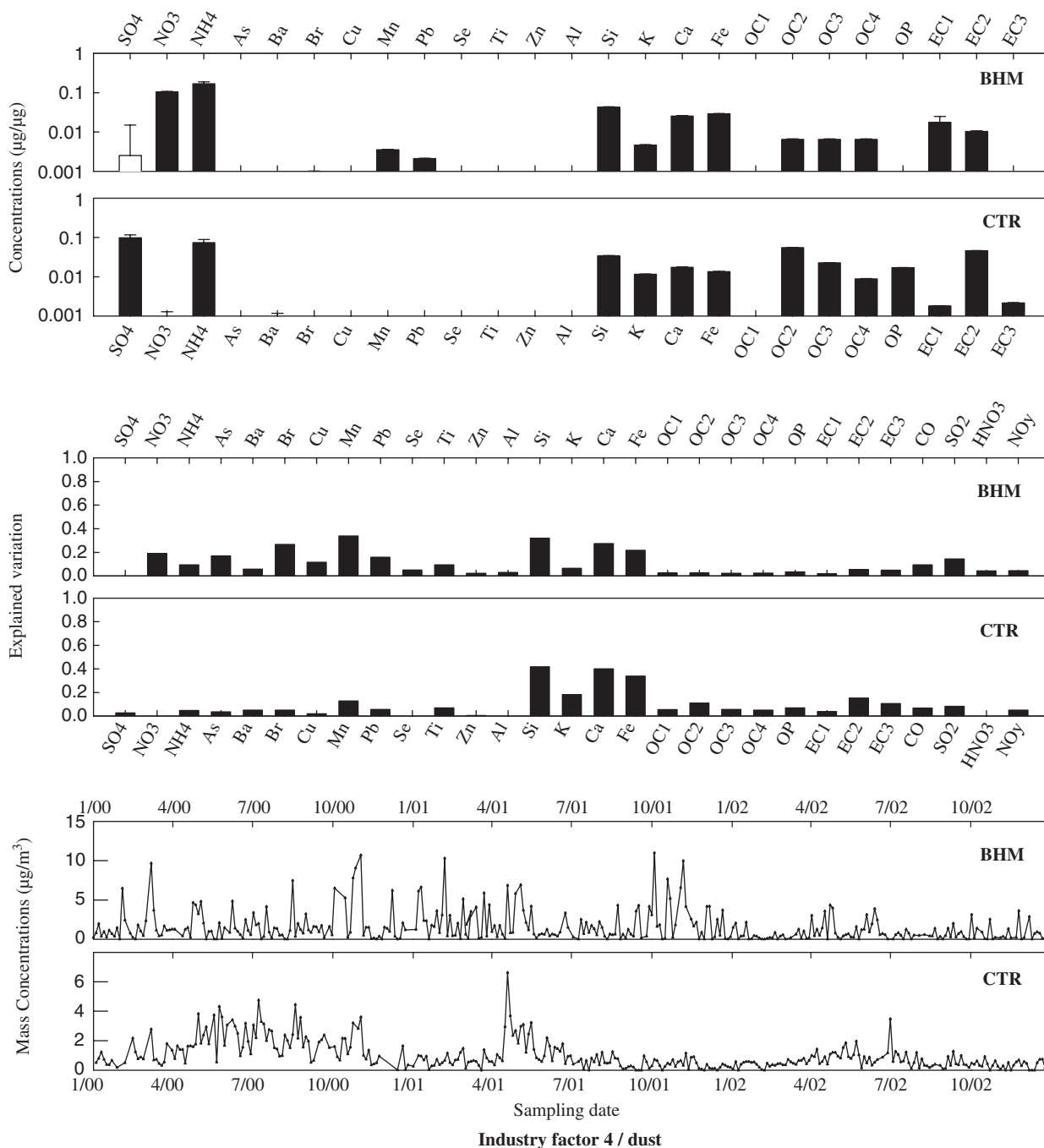


Fig. 12. Same as Fig. 1 but for the industry factor 4/dust resolved by PMF at BHM and CTR sites.

has a higher correlation with the gasoline than diesel factor, suggesting a bias towards gasoline when speciated carbon data are not included in PMF analysis. There is evidence (Shah et al., 2004) that diesel engines emit more OC during stop and go traffic and more EC during cruise. It is possible that

some diesel emissions with high OC contents during stop and go traffic were mixed in our gasoline factor. The poor correlation between the two factors likely reflects the different emission patterns during diurnal and weekend-weekday cycles. It is reflected in the high CO correlations in the gasoline factor in

Table 3

Factor- factor correlation coefficients ( $R^2$ ) between this study and previous study (Liu et al., 2005)

	JST	BHM	YRK	CTR
Sulfate <sup>a</sup>	0.71	0.7	0.89	0.66
Sulfate <sup>b</sup>	0.98	0.97	0.97	0.98
Nitrate <sup>a</sup>	0.73	0.7	0.79	0.79
Soil <sup>a</sup>	0.91	0.98	0.99	0.99
Coal <sup>a</sup>	0.76	0.93	0.49	0.15
Wood smoke <sup>a</sup>	0.55	0.43	0.55	0.78
Industry factor 1/local dust <sup>a</sup>	0.3	N.A.	0.92	N.A.
Industry factor 2 <sup>a</sup>	0.96	N.A.	0.99	N.A.
Industry factor 3 <sup>a</sup>	N.A.	0.97	N.A.	0.99
Industry factor 4/local dust <sup>a</sup>	N.A.	0.59	N.A.	0.94
Current <sup>c</sup> diesel vs. current <sup>c</sup> gasoline	0.08	0.07	N.A.	0.14
Previous <sup>d</sup> motor vehicle vs. current <sup>c</sup> gasoline	0.53	0.38	N.A.	N.A.
Previous <sup>d</sup> motor vehicle vs. current <sup>c</sup> diesel	0.03	0.05	N.A.	N.A.
Previous <sup>d</sup> motor vehicle vs. (current <sup>c</sup> diesel + gasoline)	0.25	0.19	N.A.	N.A.

<sup>a</sup>The correlation coefficient is computed between the factor resolved from this study and that from the previous work by Liu et al. (2005).

<sup>b</sup>The correlation coefficient of sulfate factor contributions between the two studies excluded the missing data.

<sup>c</sup>Current denotes this study.

<sup>d</sup>Previous denotes the study by Liu et al. (2005).

contrast to the low CO correlations in the diesel factor at the two urban sites. The correlation difference does not exist in the CTR site likely reflect the major contribution by regional transport to CO at that location. The lower correlations between the two studies for the coal factor at the CTR site and industry factor /local dust at JST when compared to other industrial factors are due to their sensitivity to the addition of gas and speciated carbon measurements.

Not surprisingly, the coal factor has relatively high correlations with SO<sub>2</sub> among all the sites (Table 4). The gasoline factor has high correlations with CO and NO<sub>y</sub> at the urban sites, but it is not the case in the rural CTR site. The gasoline factor resolved for the CTR site appears to be mixed with industrial trace elements (Fig. 1) implying that this factor is more of a mixed nature in the rural sites. The correlation between the gasoline factor and SO<sub>2</sub> is due in part to the common seasonal cycles of the two factors. The gasoline factor tends to have higher contributions during winter, likely because of cold start emissions and reduced ventilation; SO<sub>2</sub> concentrations tend to be higher during winter because low photochemical oxidation during this period.

#### 4.9. Average factor contributions

Not surprisingly, the secondary sulfate factor is the biggest contributor to the PM<sub>2.5</sub> mass concen-

trations at all four sites (Tables 5 and 6). The diesel factor has a larger contribution than the gasoline factor, which is in agreement with Zheng et al. (2002) and Kim et al. (2004a, b).

We now focus on the difference between the current study and Liu et al. (2005) (Table 6). The changes in factor contributions are due to the inclusion of eight carbon species and four gas components in the data analysis, which add more constraints in the covariance analysis. The uncertainties introduced with these new components also affect the factor contribution results. Compared to the previous study, the coal/other factor contributions are smaller except for the BHM site. The coal combustion/other factors resolved here contain Se and SO<sub>2</sub> instead of only Se. This factor may be truly indicative of primary power plants emissions with the inclusion of SO<sub>2</sub> which likely adds more constraints in the analysis and reduces some rotational uncertainties in the PMF analysis. The wood smoke factor contributions are smaller at the two rural sites. These differences may be due to the resolved diesel and gasoline factors in which the OC and EC associated with the previous wood smoke factor are now split among diesel, gasoline and wood smoke factors. On the other hand, the uncertainties introduced by including the speciated OC, EC and gas components also contribute to the differences in the factor contributions between this and the previous study. A detailed comparison

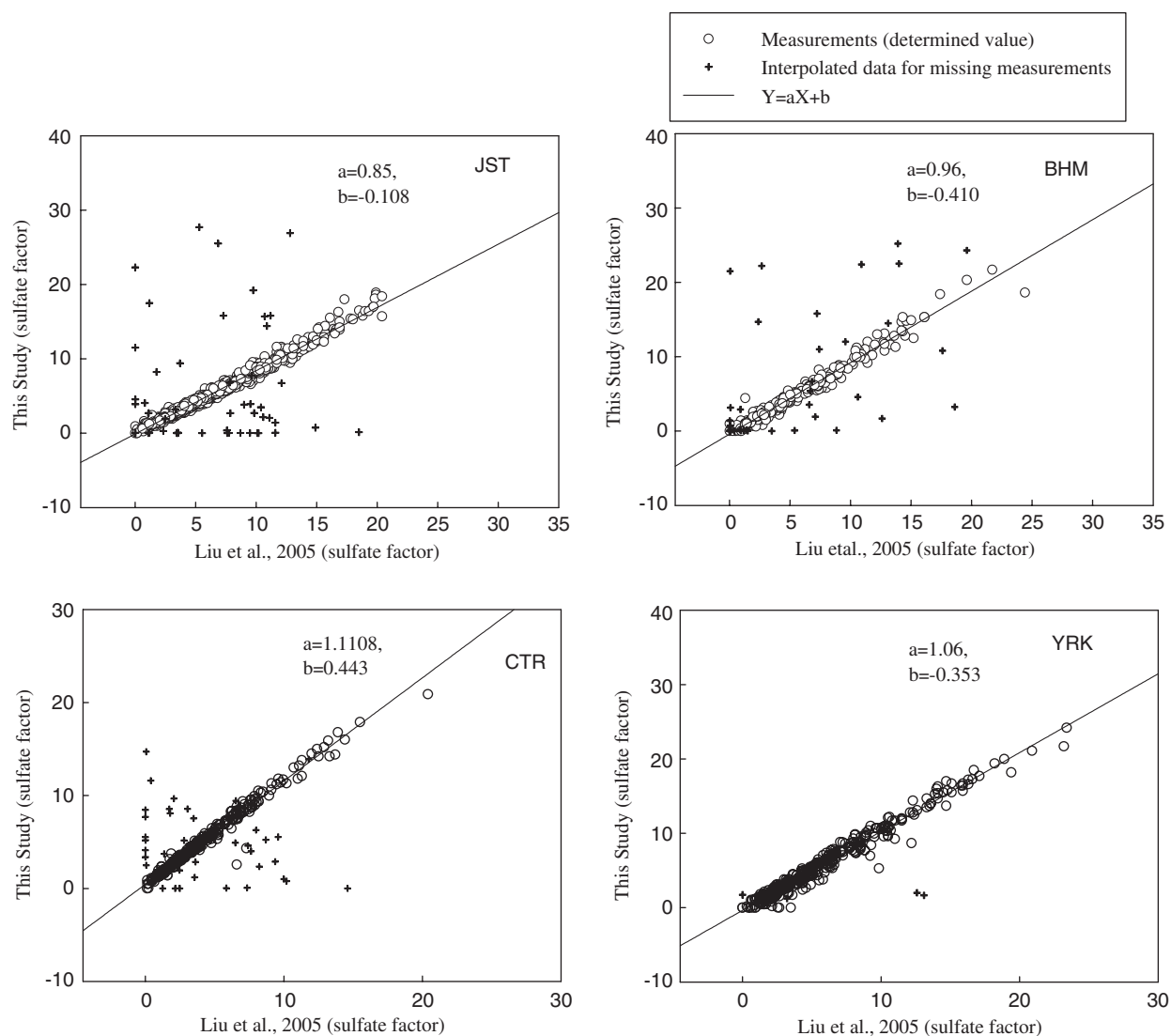


Fig. 13. Comparison of the sulfate factor contributions between this study and the previous one (Liu et al., 2005).

among the four sites yields the following observations:

For the JST site, the sum of diesel and gasoline factor contributions is in agreement with the motor vehicle factor resolved from the previous study (Liu et al., 2005). The contribution of the sulfate factor is lower by 3% of total  $PM_{2.5}$  mass, but the wood smoke factor contribution is higher by 6% of total  $PM_{2.5}$ . The coal combustion/other factor contribution is lower by 2% (from 3% to 1%), as is industry factor 2. Other factor contributions are similar to the previous study.

For the YRK site, the newly resolved diesel factor only contributes 0.3% to the total mass. The nitrate

factor doubled but the coal combustion/other factor dropped from 6 to 1%. The large difference between the secondary nitrate factors at YRK likely results from the inclusion of speciated OC and EC which, in particular, reduced the contribution of nitrate to the coal combustion/other and Industry 2 factors while increasing the contribution of the secondary nitrate factor in this study.

For the BHM site, the sum of the diesel and gasoline factors is smaller than the motor vehicle factor in the previous study. Other factor contributions agree with the results from previous study. The coal combustion/other factor contribution is almost same as in the previous study.

Table 4  
Factor-gas correlation coefficients ( $R^2$ ) for the gasoline, diesel and coal factors in this study

	JST			BHM		
	SO <sub>2</sub>	CO	NO <sub>y</sub>	SO <sub>2</sub>	CO	NO <sub>y</sub>
Gasoline	0.320	0.830	0.860	0.280	0.780	0.920
Diesel	0.044	0.030	0.020	0.190	0.290	0.320
Coal	0.250	0.068	0.070	0.420	0.170	0.120
	CTR			YRK		
	SO <sub>2</sub>	CO	NO <sub>y</sub>	SO <sub>2</sub>	CO	NO <sub>y</sub>
Gasoline	0.045	0.001	0.002	N.A.	N.A.	N.A.
Diesel	0.032	0.034	0.035	0.016	0.001	0.007
Coal	0.380	0.080	0.191	0.940	0.030	0.100

For the CTR site, two new factors, diesel and gasoline, are resolved in the present study. The sum of these factor contributions is around 10%. The wood smoke factor is smaller by 10% of total PM<sub>2.5</sub> (from 29% to 19%), suggesting that the wood smoke factor was overestimated if fractionated carbon measurements were not taken into account. The coal combustion/other factor's contribution to the total mass is smaller by 3% (from 5% to 2%).

Somewhat paradoxically, although inclusion of additional components in the analysis improved its resolving power, the fractional contribution of the undetermined mass was actually greater at all sites in this analysis than in the earlier one. Determining the cause of this difference will require further investigation.

Table 5  
Average factor contributions ( $\mu\text{g m}^{-3}$ ) at the four sites

	JST	YRK	BHM	CTR
Secondary sulfate	4.93±0.55	5.97±0.74	4.9±1.07	5.04±0.69
Secondary nitrate	1.53±0.22	2.12±0.39	1.45±0.40	0.66±0.12
Diesel emissions	1.94±0.10	0.04±0.001	1.15±0.34	0.69±0.31
Gasoline vehicle	0.89±0.19	—	0.96±0.53	0.34±0.13
Wood smoke	3.68±0.05	2.30±0.038	1.91±0.34	2.44±0.38
Coal combustion/other	0.27±0.0.3	0.10±0.02	1.60±0.43	0.19±0.07
Soil	0.52±0.3	0.13±0.03	0.73±0.15	0.20±0.03
Industry factor 1/dust	1.00±0.6	0.65±0.11	—	—
Industry factor 2	0.15±0.0.02	0.27±0.06	—	—
Industry factor 3	—	—	0.55±0.65	0.05±0.01
Industry factor 4/dust	—	—	1.52±0.37	1.00±0.18
Undetermined	1.81	2.30	3.12	1.99

Table 6  
Average percentage factor contributions to PM<sub>2.5</sub> mass concentrations between the previous study with two carbon fractions (Liu et al., 2005) and this study with eight carbon fractions and four gas phase components

	PMF with two carbon fractions				PMF with eight carbon fractions and five gas species			
	JST	YRK	BHM	CTR	JST	YRK	BHM	CTR
Secondary sulfate	37.0±4.9	45.0±4.4	30.0±7.3	36.0±5.2	28.4±3.3	42.9±5.3	27.4±5.9	39.8±5.5
Secondary nitrate	8.0±1.3	7.0±0.9	9.0±2.7	3.0±0.6	8.7±1.3	15.3±2.8	8.1±2.2	5.2±0.9
Motor vehicle	17.0±2.5	—	17.0±2.7	—	—	—	—	—
Diesel emissions	—	—	—	—	10.9±0.6	0.3±0.1	6.4±1.9	5.5±2.5
Gasoline vehicle	—	—	—	—	4.4±1.2	—	5.4±2.9	2.7±1.0
Wood smoke	13.0±2.8	20.0±3.9	9.0±1.5	29.0±4.9	22.2±0.3	16.6±2.7	10.7±1.9	19.2±3.0
Coal combustion	3.0±0.7	6.0±1.6	8.0±2.0	5.0±1.5	1.9±2.0	0.7±0.2	8.9±2.4	1.5±0.5
Soil	2.0±0.3	2.0±0.5	3.0±0.5	2.0±0.4	3.1±1.9	1.0±0.2	4.1±0.8	1.6±0.3
Industry factor 1/dust	6.0±1.4	5.0±1.3	—	—	6.6±3.7	4.7±0.8	—	—
Industry factor 2	3.0±0.4	2.0±0.4	—	—	0.9±0.1	1.9±0.4	—	—
Industry factor 3	—	—	3.0±0.3	2.0±0.4	—	—	3.1±0.36	0.4±0.06
Industry factor 4/dust	—	—	7.0±1.5	9.0±2.6	—	—	8.5±2.1	7.9±1.4
Undetermined	11.0	13.0	14.0	14.0	12.8	16.6	16.4	16.1

## 5. Conclusions

PM<sub>2.5</sub> composition data including eight individual carbon fractions and four gas components collected at four sites in Georgia and Alabama were analyzed using the PMF method. Nine factors were resolved at two urban sites (JST and BHM) and one rural site (CTR). Eight factors were resolved at the rural site (YRK). Soil, coal combustion/other, diesel emission, secondary nitrate, and wood smoke are the six common factors among the four sites. Two industry-related factors are similar at the two sites in the same state, but differ between states.

Unlike results from previous studies using the same compositional data, but with only the non-resolved EC and OC fractions and without the gases (e.g., Liu et al., 2005), diesel and gasoline emission factors were resolved at the two urban sites instead of only one single motor vehicle factor; diesel and gasoline factors were separated at the CTR site and a diesel factor was found at YRK instead of no motor vehicle factor at the two rural sites. The PMF factor profiles show that both diesel and gasoline factors have abundant OC2 fractions. The OC3 fraction in the gasoline factor is more abundant than in diesel while the EC2 fraction in the diesel factor is significantly higher than in gasoline. The diesel and gasoline factor profiles resolved from this study are in good agreement with the emissions profiles obtained by Cao et al. (2006), which are likely more representative of the current engine technology and fuel composition than that by Watson et al. (1994).

With the inclusion of SO<sub>2</sub> in the data analysis, the identification of the coal combustion/other factor was improved, resulting in a significant reduction in its factor contribution. The secondary sulfate factor with high contributions of sulfate, ammonium and gas-phase HNO<sub>3</sub> had the largest contribution to the PM<sub>2.5</sub> mass among the four sites. The diesel factor has a larger contribution to the PM<sub>2.5</sub> mass than the gasoline factor. Uncertainties introduced by including the speciated OC, EC and gas components are also likely contributors to the factor contribution differences between this and the previous study (Liu et al., 2005). This difference is most apparent in the nitrate factor contribution at YRK.

This study shows that the inclusion of gas phase data and temperature resolved fractional carbon data can improve the factor identifications for gasoline, diesel, and coal combustion/other factors. The rotational uncertainties in the PMF analysis are

also reduced. Resulting factor contributions can be significantly altered by including these additional measurements.

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