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Revising the use of potassium (K) in the source apportionment of PM_{2.5}

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ABSTRACT

Elemental potassium has been extensively used as an indicator of biomass burning in the source apportionment of PM_{2.5}. We present a method to estimate the fraction of potassium associated with biomass burning (K_b) based on a linear regression with iron that can be applied at any site where PM_{2.5} chemical speciation is available. The estimated fraction has a significantly greater correlation with levoglucosan ($R^2=0.63$), an organic tracer of biomass burning, than total potassium ($R^2=0.39$). We explore temporal and spatial variability of K_b over a period of six years in the Atlanta area. K_b is larger in spring when biomass burning activity is more prevalent and during weekends due to the use of fireplaces in winter and outdoor charcoal cooking in summer. K_b is the predominate form of potassium for the rural site in this study. The use of K_b in a receptor model results in a lower fraction of PM_{2.5} apportioned to biomass burning and a greater fraction to mobile sources when compared to the use of total K. Results suggest that K_b is a good indicator of biomass burning.

Keywords: PM_{2.5}, potassium, levoglucosan, PMF, factor analysis, biomass burning



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1. Introduction

Receptor models solve the mass balance equation with or without the use of source profiles to estimate source impacts at a receptor site. When source profiles are available, specific species are often identified as indicator of sources, alone or in concert with other species. For example, the elemental carbon (EC) to organic carbon (OC) ratio is used to differentiate combustion sources (e.g. gasoline and diesel vehicles, biomass burning) and potassium (K) has been used to further differentiate the impact of biomass burning (Lee et al., 2008; Pio et al., 2008; Watson et al., 2008). When source profiles are not available, the same species can be used to associate factors with emissions sources. Potassium, for example, has been extensively used to apportion PM_{2.5} to biomass burning in EPA–PMF model applications (Kim et al., 2003; Kim et al., 2004; Liu et al., 2005; Marmur et al., 2005; Liu et al., 2006; Marmur et al., 2006; Lee et al., 2009).

One disadvantage of using potassium in source apportionment modeling by factor analysis is that this element has multiple emission sources (e.g., wood smoke, soil dust, sea salt, coal fire, industry and meat cooking) (Andreae, 1983; Watson and Chow, 2001; Watson et al., 2001). Zhang et al. (2010) indicated that soluble potassium (K^+) concentrations do not exhibit the seasonal trends expected if it is dominantly from biomass burning. They also found a low correlation of K^+ with fire counts from satellite data. Several studies have proposed that organic tracers, such as levoglucosan and retene, can be used as a biomass tracer instead of K (Lewis et al., 1988; Simoneit et al., 1999; Jordan et al., 2006; Puxbaum et al., 2007). Levoglucosan was found highly correlated

with satellite fire counts when biomass burning emissions are expected to be mainly from outdoor burning (Zhang et al., 2010) and retene concentrations were found greater in March and December when prescribed fires and residential wood burning are more intense than other months (Li et al., 2009). Unfortunately, measurements of these organic compounds are not as widely available as potassium.

Attempts to estimate the fraction of potassium from biomass burning have used relationships between K and other metals. Andreae (1983) defined excess potassium as the portion not attributable to sea salt or soil dust in aerosol samples collected on a cruise in the Atlantic Ocean. The excess potassium was estimated as $K' = K - 0.75 \times Ca$. The K/Ca ratio of 0.75 was the best fit in the coarse fraction ($D_p > 2 \mu m$). In that study Ca was selected for its abundance in sea salt. The K' fraction showed a similar temporal trend to soot and was attributed to biomass burning emissions from land (fire wood, waste incineration, agricultural burning). Lewis et al. (1988) estimated a soil-corrected potassium as $K' = K - 0.45 \times Fe$. The K/Fe ratio of 0.45 was the average of samples in the coarse fraction taken in a residential area in Albuquerque, NM. The K' fraction had a maximum value at night because of residential wood burning. Miranda et al. (1994) used a similar approach defining non-soil K (NSK) = $K - 0.52 \times Fe$, then applying K/Fe ratio of coarse soil. Using ratios of K/Ca and K/Na, Pio et al. (2008) estimated potassium not associated with sea salt and soil particles as $K_{bb} = K - 0.036 \times Na - 0.12 \times (Ca_{nss} - Ca_{bb})$ and is proposed to be related with biomass combustion. In this expression, Ca_{nss} refers to non sea-salt calcium and Ca_{bb} refers to Ca emitted in biomass burning. The use of Si in the identification of K from biomass burning was

used by Lewis et al. (2003) who defined potassium tracer for wood burning as $K_w = K - 0.15 \times Si$ assuming a potassium soil source contribution equivalent to 0.15 times elemental silicon. The application of K_w in a source apportionment exercise resulted in good agreement between two independent receptor models.

Though these methods have been successfully employed to estimate K in biomass burning emissions, they have not directly compared the use of K and the fraction of K from biomass burning in the source apportionment of $PM_{2.5}$ in urban regions where biomass burning can greatly impact air quality. In the Atlanta area, for example, biomass burning was estimated to contribute between 1.72 and 3.68 $\mu\text{g}/\text{m}^3$ to $PM_{2.5}$ (6–22% of total $PM_{2.5}$ mass) (Kim et al., 2003; Kim et al., 2004; Liu et al., 2005; Liu et al., 2006; Lee et al., 2008). Biomass burning also emits carbonaceous material (EC and OC) that can be difficult to apportion in heavily traffic impacted areas without the use of accurate source profiles. The OC/EC ratio has been used to confirm the profiles of biomass burning and mobile sources, since biomass burning usually has higher OC/EC ratios (7–15) (Lee et al., 2005; Pio et al., 2008) than gasoline (3.0–4.0) or diesel vehicles (<1.0) (Lee and Russell, 2007; Zheng et al., 2007).

The objective of this study is to estimate the fraction of potassium associated with biomass burning (here called K_b) in the $PM_{2.5}$, using a relationship between K and a species (M) that shares similar sources with K except biomass burning. From previous studies, Fe or Ca can be used for M. We examine temporal and spatial variability of K_b and compare K_b concentrations with levoglucosan concentrations. Finally, we assess the changes in source apportionment of $PM_{2.5}$ when PMF is implemented with K_b instead of total K.

2. Methods

This work follows six steps to estimate the K_b fraction as an indicator of biomass burning activity: (i) site description and air quality data collection, (ii) estimation of the K_b fraction, (iii) assessment of temporal and spatial variability of the K_b fraction, (iv) evaluation of the relationship between K_b and organic tracer levoglucosan, (v) assessment of changes in source apportionment and (vi) comparison with similar studies.

2.1. Site description and air quality data collection

$PM_{2.5}$ speciation data was obtained at the Jefferson Street (JST) site in downtown Atlanta from 1999–2007. JST is part of the SEARCH project and description of the network is found elsewhere (Hansen et al., 2003; Edgerton et al., 2005). Data treatment of missing data and values below method detection limits (MDL) was performed as suggested by Hansen et al. (2003). Briefly, for data below MDL, the concentrations were replaced with the value MDL/2 and the uncertainty was set as (5/6)×MDL. For missing data, concentrations were replaced by the geometric mean and the respective uncertainty was set at four times that of this mean concentrations. The $PM_{2.5}$ species considered in the analysis are: NO_3^- , SO_4^{2-} , EC, OC, Al, Si, K, Fe, Ca, Br, Se and Zn. For NO_3^- , SO_4^{2-} , EC and OC, no values were below MDL; for Si, K, Fe and Zn the values below MDL were less than 1%, for Ca (5%), Br (8%), Al (8%) and Se (40%). A total of 2 586 samples were available with concentrations above MDL in the period 1999–2007. Water soluble ions (SO_4^{2-} , NO_3^-) were measured using ion chromatography (IC) using a Dionex ion chromatography system (DX-500). Carbonaceous species (EC and OC) are measured on 24-hr $PM_{2.5}$ samples using quartz filters from a particle composition monitor (PCM) and analyzed by the thermal-optical reflectance (TOR) method at the Desert Research Institute (DRI) following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol (Chow et al., 1993). Trace elements were measured via X-ray fluorescence (Al, Si, K, Fe, Ca, Br, Se, Zn).

Two additional monitoring sites in the area are considered in this study: South DeKalb (SD) and Yorkville (YKV). SD is part of the Speciation Trends Network (EPA-STN) and is located 15 km southeast from JST. SD is 200 m away from a major interstate with significant heavy-duty traffic. YKV is a site operated by the SEARCH project located 60 km west of JST and classified as a rural site. Air quality sampling at SD was conducted every three days and at YKV was conducted daily from 1999–2003 and every three days from 2004–2007. After applying a similar treatment for missing data and values below MDL, a total of 783 samples were available for SD in the period 1999–2007 and 1 247 samples at YKV.

2.2. Estimation of the K_b fraction in association with an exclusive non-biomass burning source indicator species (M)

Factor analysis is used to examine the variability in $PM_{2.5}$ data and identify species (M) that share similar sources with K but are not emitted by biomass burning. The statistical package R (R Development Core Team, 2011) is used. The number of factors is selected based on the number of eigenvalues greater than one and the overall statistical fit of the analysis. The association of factors with $PM_{2.5}$ emissions sources is conducted based on the analysis of factor loadings (i.e., correlations between factor scores and the original species).

After an associated species (M) is identified, linear regression between total K and M, based on the 2 586 samples, is used to estimate the fraction of potassium from common factors and excess potassium [intercept in Equation (1)]. Daily estimates of K_b can then be obtained using the regression results and total potassium [Equation (2)].

$$K_i = a + b \times M_i \quad (1)$$

$$(K_b)_i = K_i - b \times M_i \quad (2)$$

where the i subscript is used for the i^{th} sample. One condition that this estimate should satisfy is that $(K_b)_i > 0$ in all cases. If $(K_b)_i < 0$ for a particular day, $(K_b)_i$ is set to zero. The error in the K_b variable can be estimated by propagating the errors from Equation (2).

$$\sigma_{K_b}^2 = \sigma_K^2 + b^2 \sigma_M^2 + \sigma_b^2 M^2 \quad (3)$$

where σ_K and σ_M are the measurement uncertainties in the K and M species respectively, and σ_b is the uncertainty in the regression slope. To evaluate σ_b we have implemented a bootstrapping technique in which we evaluate the slopes and intercepts of 10 000 bootstrap samples and compute σ_b as the standard deviation.

2.3. Assessment of temporal and spatial variability of K_b

Daily and seasonal trends of K and K_b are examined at the JST site. Air quality data from SD and YKV were included for the assessment of spatial variability. To explore the variability in combustion source impacts between sites, we apply factor analysis again, but this time including only the following species: EC, OC, K and Fe, measured at JST, YKV and SD. K_b at YKV and SD was also estimated similarly to K_b at JST [Equations (1) and (2)], but using site-specific values of the slope “b”. K_b was also included in the inter-site variability analysis. In addition, correlation between K and K_b for each pair of sites is assessed as part of the spatial variability analysis.

2.4. Evaluation of the relationship between K_b and organic tracer levoglucosan

Levoglucosan is often used as a tracer for biomass burning. Levoglucosan concentrations were available during 2007 from $PM_{2.5}$ filters collected from the EPA-STN monitoring sites in the Southeastern US (Zhang et al., 2010). Because JST is not an EPA-

STN site, surrogate data from the SD site was used. Similar emission sources at JST and SD and the relatively short distance between sites supports the use of SD levoglucosan as a surrogate for JST levoglucosan. These concentrations were compared with the estimated K_b fraction at JST. Ratios between levoglucosan and potassium (K and K_b) are estimated and compared with ratios from biomass burning samples.

2.5. Assessment of changes in source apportionment using K_b

Changes in source apportionment of $PM_{2.5}$ are assessed when K_b is used instead of K in EPA-PMF v.3.0 (Norris and Vedantham, 2008). SO_4^{2-} , NO_3^- , NH_4^+ , EC, temperature-resolved OC1 through OC4, Al, Si, Ca, Br, Mn, and Zn were selected as strong species, while Cu, Pb, and Se were selected as weak species. Two cases were compared: the first included K as a strong species, while the second considered K_b as a strong species. Since K constitutes less than 1% of the $PM_{2.5}$ mass, it is expected that changes in the $PM_{2.5}$ if any are a result of the redistribution of major species associated with combustion. PMF was run from 1999–2004 only to better compare PMF results with local studies conducted mainly from 1998 to 2002.

2.6. Comparison with similar studies

Comparing source apportionment results from PMF with previous studies is challenging. First, differences in source impacts from different time periods may be influenced by the implementation of controls or economic considerations. Secondly, data treatment (e.g. methods by which the missing days and samples below the detection limit are treated and uncertainty is estimated) vary considerably, resulting in different factor impacts in PMF. Third, the association of factors in PMF with emission sources is subjective; thus, species used as indicators of a particular source may change with time. Reff et al. (2007) offers a more complete review of methodological details in PMF. Here, local studies with similar conditions were compared to our PMF results using K (PMF-K) and K_b (PMF- K_b) to examine whether using K_b can improve source apportionment results.

3. Results

3.1. Development of a method to estimate K from biomass burning

The application of factor analysis to the JST data resolved four factors with eigenvalues greater than one leading to a good statistical fit (p -value<0.01), explaining 67% of the total variance. The interpretation of the factors was conducted based on the most significant species in each factor (highlighted in bold in Table 1a, base case): soil dust factor (F1) has high correlations with Al and Si, traffic factor (F2) with EC and OC, biomass burning factor (F3) with K and Br, and secondary sulfate factor (F4) with SO_4^{2-} . It is worth to note that these factors are a combination of various different sources and should not be interpreted as the actual emission sources. Nevertheless, K has the strongest correlation with F3, but significant correlations with F1 and F2 as well, suggesting multiple sources of potassium.

Fe and Ca have significant loadings on F1, since they are crustal elements. In addition, these elements are also observed in F2, likely due to the presence of Fe and Ca in mobile source emissions (e.g. from brake dust, tire wear, road dust and engine oil) (Majestic et al., 2009). The correlations between Fe and Ca with F3, however, are poor, suggesting that Fe and Ca are not significant constituents of biomass burning emissions. This result is consistent with the chemical composition of $PM_{2.5}$ from prescribed burning emissions, where Ca and Fe are typically found in low percentages in the $PM_{2.5}$ mass (<0.1%) compared to K (0.57%) (Lee et al., 2005). Based on this result, Fe or Ca can be used to identify the fraction of potassium largely associated with traffic and soil dust rather than biomass burning [i.e., Fe or Ca serves as the M species in the linear regression in Equation (1)]. These results support the use of Fe and Ca in $PM_{2.5}$ for source attribution to improve the use of K as biomass burning tracer as previously proposed in the coarse fraction by several studies (Andreae, 1983; Lewis et al., 1988). However, in coastal areas, Ca should be included to subtract the influence of sea-salt as shown by Pio et al. (2008).

Table 1. Factor loadings using K and K_b (factors denoted with prime) for the 4-factor solution at JST. Most influential species are highlighted in bold

Species	(a) Factors using regular K (Base Case) ^a				(b) Factors using K_b ^a			
	F1	F2	F3	F4	F1'	F2'	F3'	F4'
NO ₃	-0.16	0.08	0.45	-0.09	-0.16	0.18	0.36	-0.11
SO ₄	0.08	0.08	-0.08	0.99	0.08	0.08	-0.05	0.99
EC	0.10	0.88	0.26	0.17	0.10	0.90	0.13	0.16
OC	0.12	0.71	0.46	0.24	0.12	0.78	0.35	0.22
Al	0.95	-0.03	-0.05	0.04	0.95	-0.03	-0.04	0.04
Si	0.99	0.09	-0.02	0.01	0.99	0.08	-0.02	0.01
Fe	0.67	0.65	0.11	0.13	0.66	0.69	-0.05	0.11
Ca	0.58	0.43	0.01	0.09	0.58	0.43	-0.07	0.09
K	0.41	0.35	0.67	0.13				
K_b					0.02	0.07	0.87	0.05
Br	0.01	0.27	0.60	0.14	0.00	0.40	0.46	0.11
Se	0.02	0.16	0.10	0.39	0.01	0.19	0.04	0.38
Zn	0.07	0.54	0.30	0.11	0.06	0.59	0.19	0.10
Variance	0.24	0.20	0.12	0.11	0.23	0.22	0.11	0.10
Cumulative	0.24	0.44	0.56	0.67	0.23	0.45	0.56	0.66

^a F1 and F1' represent soil dust; F2 and F2' represent mobile sources; F3 and F3' represent biomass burning; F4 and F4' represent secondary sulfate.

The linear regression of K with Fe and Ca for all data (1999–2007) gives the following results:

$$K = 30.2 (\pm 0.98) + 0.37 (\pm 0.01) \times \text{Fe} \quad R^2=0.35 \quad (4)$$

$$K = 40.6 (\pm 1.69) + 0.41 (\pm 0.04) \times \text{Ca} \quad R^2=0.15 \quad (5)$$

where K, Fe and Ca are expressed in ng/m^3 and the uncertainties are the standard deviation of the slope and the intercept calculated over 10 000 bootstrapped samples. A more significant correlation (lower standard error of the regression coefficients and higher R^2) with K is observed for Fe rather than Ca. Furthermore, the use of Ca to estimate K_b resulted in more cases of $K_b < 0$ (23% of the days vs. 4% using Fe). For this reason, our analysis was based on the separation of K with Fe as $K_b = K - 0.37 \times \text{Fe}$ with a $R^2 = 0.35$ (p -value < 0.01). The apparently low strength of the correlation is explained given that a large fraction of the K comes from other sources that do not emit Fe and is used in this work to separate potassium from different sources. The goodness of fit of the model in Equation (4) was evaluated using a Chi-squared test. The results were $\chi^2 = 6.914$ with 2 584 degrees of freedom and a p -value < 0.01 , which demonstrate a good statistical fit. The intercept of Equation (4) ($30.2 \text{ ng}/\text{m}^3$) represents the average amount of potassium from factors other than traffic and soil dust, e.g. biomass burning. The slope (K/Fe) of 0.37, exclusive for this site, is slightly lower than those reported in previous studies (0.45–0.52) in the coarse fraction (Lewis et al., 1988; Miranda et al., 1994) which is explained by lower potassium concentrations in the $\text{PM}_{2.5}$ fraction or differences in soil composition.

The estimated K_b is used instead of K in a new application of factor analysis. The number of factors and their association with emissions sources is similar to the base case (F1'–soil dust, F2'–traffic, F3'–biomass burning, F4'–secondary sulfate in Table 1b), but some important changes are highlighted. The correlation of K_b with F3' ($R^2 = 0.87$) is larger than the corresponding correlation of K with F3 ($R^2 = 0.67$), denoting a better separation of the biomass burning factor. K_b is not correlated with F1' or F2' which suggests little to no influence of soil and traffic dust on K_b . The total variance (approximately 67%) explained by the four factors is maintained in both cases.

3.2. Assessment of temporal variability of K and K_b

Daily estimates of K_b at JST in Atlanta were obtained from 1999 through 2007. Approximately half of the $\text{PM}_{2.5}$ potassium loading is from biomass burning (Table 2) which implies that the other half is associated with soil and traffic dust. These results are in agreement with local source profiles where potassium is associated with multiple sources (Marmur et al., 2007).

K concentrations are similar during weekdays and weekends, whereas K_b concentrations are larger during weekends, possibly due to the use of fireplaces during winter and more intense yard waste and charcoal cooking during summer. K is largest in fall and winter, while K_b is largest in winter and spring. During spring, and particularly in March and April, prescribed burning activities around Georgia are more intense (Li et al., 2009). In summer, biomass burning is expected to be less pronounced (Tian et al., 2008; Zhang et al., 2010) and K_b is lowest during this season. The spring/summer ratio is higher for K_b than K, which is more consistent with observed biomass burning activity.

Table 2. Temporal trends of K and K_b at JST

	K	K_b
Average 1999–2007 (ng/m^3)	57.6	30.4
Standard deviation (ng/m^3)	33.2	26.7
Weekend/weekday ratio	0.97	1.23
Seasonal averages (ng/m^3)		
Winter (December–February)	62.4	35.8
Spring (March–May)	58.6	32.3
Summer (July–September)	45.5	18.4
Fall (October–December)	64.0	29.9
Spring/Summer ratio	1.3	1.8

3.3. Assessment of spatial variability of K and K_b

The regression of K with Fe for the JST site is compared to results for the SD and YKV sites (Table 3). The correlation between K and Fe is significantly lower at YKV, yet statistically significant ($R^2 = 0.18$, p -value < 0.01) compared to JST and SD, and suggests that only 18% of the variability of K is explained by common sources with Fe. Although the K/Fe ratio is location-specific, the slope is approximately the same for JST and SD and larger for YKV due to relatively large concentrations of K with respect to Fe at this rural site.

The fraction of K_b to K is the largest at YKV, confirming that a significant amount of potassium is associated with biomass burning at this rural site. This fraction explains the low correlation coefficient between K and Fe, the latter species more associated with soil and traffic dust. At the three sites, K_b/K ratios are greater in winter than summer in concordance with more intense biomass burning in winter. The 82% of the K being estimated as K_b for YKV suggests that separation of potassium at rural sites is not as critical as in urban sites.

The application of factor analysis using only EC, OC, Fe and K species at the three sites resulted in four factors explaining a variance between 75% and 78% when K_b or K were considered respectively (Table 4). This cumulative variance is larger than applying factor analysis with all species at three sites with a total variance of 57% when four factors are considered (Table S1 in the Supporting Material, SM). Although the interpretation of the results with 36 variables is more complicated and vary with respect to application with four species, results were comparable to Table 4. Analyses of inter-site variability suggest that carbonaceous species (EC, OC) are more similar between JST and SD (higher loadings in F1) than YKV and is explained by a significant influence of traffic at the urban sites, while EC and OC at YKV have an independent source (higher loadings in F3) attributed to biomass burning. F2 explains the shared variability between K at the three sites with similar correlations that denotes a low spatial variability of total potassium.

When K_b is included in the analysis instead of K, a similar interpretation of F1' and F3' factors is observed, this is, F1' explains the variability of traffic impacts at JST and SD, whereas F3' explains the influence of biomass burning impacts at YKV. However, K_b has a higher correlation with F2' at JST than YKV and SD, denoting a greater spatial variability of K_b compared to K. K_b has a stronger association between JST and YKV ($R^2 = 0.60$) while correlations of K_b between JST–SD ($R^2 = 0.45$) and YKV–SD ($R^2 = 0.36$) are lower.

Table 3. Results of regression $K = a + b \times \text{Fe}$ for the three sites

	Slope "b" \pm std error	Intercept "a" \pm std error (ng/m^3)	R^2	K (ng/m^3)	K_b/K (summer - winter)
JST	0.37 \pm 0.01	30.2 \pm 0.98	0.35	57.6	0.46 – 0.58
YKV	0.45 \pm 0.04	33.3 \pm 1.17	0.18	45.0	0.61 – 0.79
SD	0.32 \pm 0.02	31.8 \pm 1.78	0.32	59.0	0.34 – 0.49

Table 4. Factor loadings using K and K_b (factors denoted with prime) for three sites in the Atlanta area. Most influential species are highlighted in bold

		(a) Factors using regular K^a				(b) Factors using K_b^a			
		F1	F2	F3	F4	F1'	F2'	F3'	F4'
JST	EC	0.89	0.14	0.21	0.00	0.95	0.03	0.22	-0.04
	OC	0.75	0.32	0.37	-0.02	0.77	0.24	0.35	0.09
	Fe	0.71	0.17	0.08	0.56	0.72	-0.12	0.12	0.49
	K	0.45	0.78	0.19	0.18				
	K_b					0.14	0.91	0.11	0.09
YKV	EC	0.19	0.14	0.62	-0.02	0.23	0.14	0.63	-0.03
	OC	0.21	0.22	0.93	0.18	0.23	0.19	0.92	0.24
	Fe	-0.01	0.27	0.05	0.81	0.06	-0.03	0.08	0.69
	K	0.12	0.79	0.28	0.31				
	K_b					0.26	0.77	0.25	0.03
SD	EC	0.74	0.24	0.16	0.16	0.76	0.12	0.14	0.25
	OC	0.59	0.41	0.45	0.03	0.60	0.34	0.42	0.22
	Fe	0.60	0.29	0.10	0.62	0.62	0.01	0.07	0.78
	K	0.29	0.79	0.16	0.22				
	K_b					-0.09	0.76	0.09	-0.17
Variance		0.29	0.21	0.15	0.13	0.29	0.19	0.14	0.13
Cumulative		0.29	0.50	0.65	0.78	0.29	0.48	0.62	0.75

^a F1 and F1' represent mobile sources at JST and SD; F2 and F2' represent biomass burning at the three sites; F3 and F3' represent combustion sources at YKV; F4 and F4' represent a source associated with Fe.

3.4. Inclusion of K into source apportionment using PMF

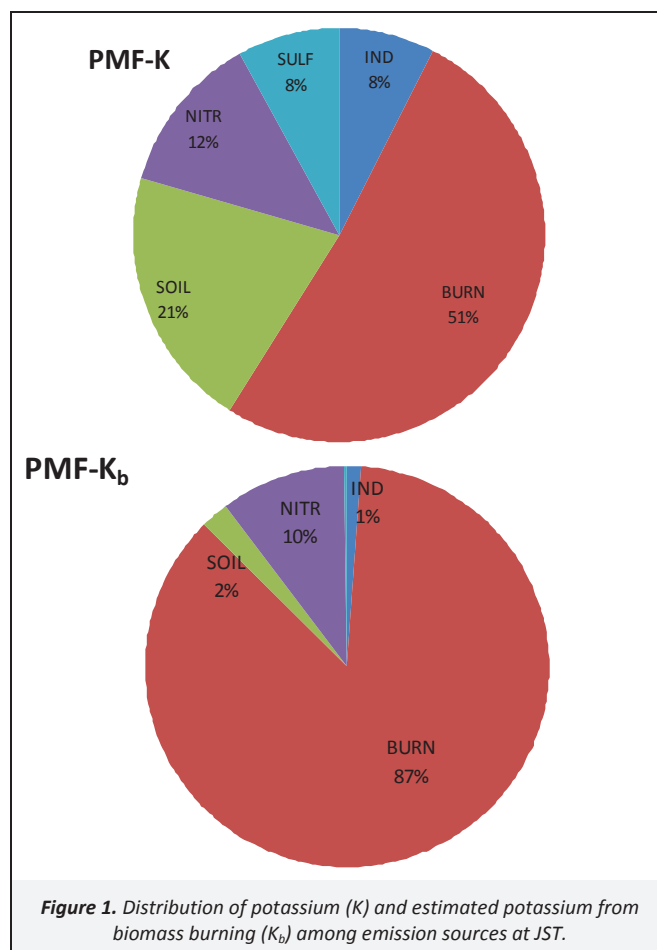
PMF was run using the available species to find seven, eight and nine factors, evaluating at each run the value of the optimization parameters Q_{robust} and Q_{true} , the correlation between predicted and observed species, as well as the different values of factor profile rotation FPEAK parameters (-1.0, -0.5, 0.1, 0.5, 1.0). The seven-factor solution lacked of a secondary ammonium factor and the correlation between predicted and observed NH_4^+ had an $R^2=0.76$. With an eight-factor solution, the secondary ammonium factor was resolved and the correlation between predicted and observed NH_4^+ increased to $R^2=0.97$, similar to that found for nitrate and sulfate. The nine-factor solution created one factor with only OC1 species with no physical interpretation. For the previous reasons, the eight-factor run was selected and secondary sulfate and secondary ammonium were added into one SULF factor for comparison with other studies where sometimes more than one secondary sulfate source is identified.

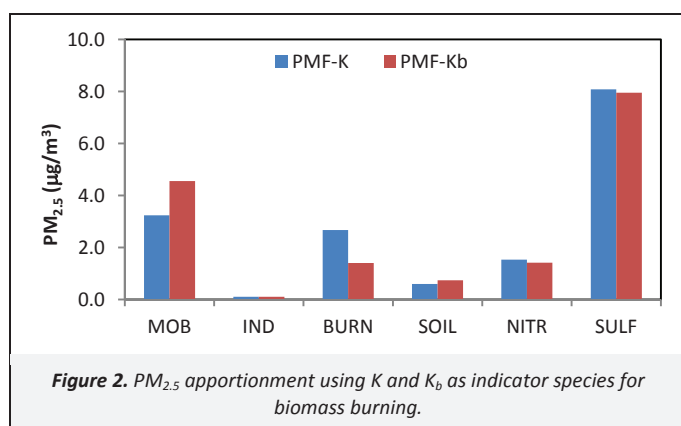
PMF-K and PMF- K_b were run independently at JST solving for eight factors in each case. Resolved factor profiles are included in the SM (Figure S1). In both cases, the correlation between $PM_{2.5}$ estimated and predicted was $R^2=0.88$. Factors were associated with secondary sulfate (SULF), secondary ammonium (add it to the secondary sulfate), secondary nitrate (NITR), soil dust (SOIL), gasoline vehicles (GV), diesel vehicles (DV), biomass burning (BURN) and industrial source (IND). The distinction between GV and DV loadings is conducted based on the following findings: the OC/EC ratio is higher for GV (3.8) than DV (0.90); GV source impacts had a larger correlation with carbon monoxide ($R^2=0.92$) than DV ($R^2=0.59$); GV has larger concentrations of OC2, OC3, and OC4, commonly identified with light duty gasoline vehicles emissions (Kim et al., 2004; Cao et al., 2006).

Gasoline and diesel vehicles were grouped into a mobile factor (MOB) since major species (EC, OC) are present in both GV and DV factor profiles and we found that separation of factor impacts using the thermal fractions of OC is problematic. The lumped mobile factor also facilitates comparison with other studies. K_b is almost exclusively apportioned to the biomass burning factor, compared to K which is apportioned to multiple sources (Figure 1), supporting the use of K_b as a better indicator of biomass burning impacts. The lack of K-contribution from the combined MOB factor can be explained by potassium apportioned to the soil dust factor which can include re-suspended dust from mobile sources. This can be supported by the low amounts of soil-derived elements

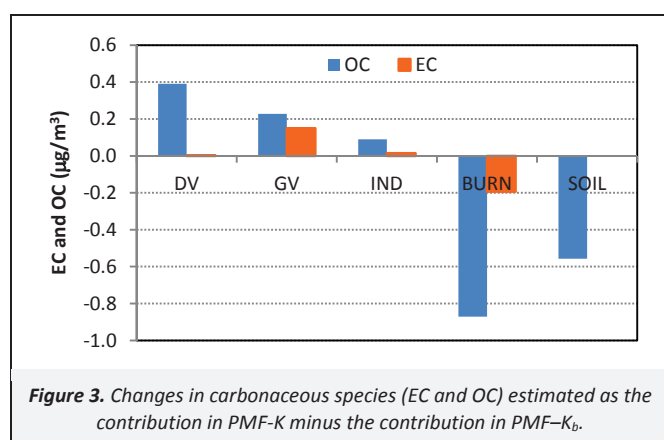
such as Al, Si, Ca, and Fe in the factor profiles of GV and DV (see the SM, Figures S1a and S1b).

The major difference between PMF-K and PMF- K_b is in the apportionment of $PM_{2.5}$ to biomass burning and mobile factors (Figure 2). The biomass burning impact decreases from $2.67 \mu\text{g}/\text{m}^3$ in PMF-K to $1.40 \mu\text{g}/\text{m}^3$ in PMF- K_b (reduction of 47%) while the mobile source impact increases from $3.23 \mu\text{g}/\text{m}^3$ in PMF-K to $4.55 \mu\text{g}/\text{m}^3$ in PMF- K_b (increase of 41%). Soil factor also increases in 23%.





Since K constitutes less than 1% of the PM_{2.5} mass, the changes in the PM_{2.5} apportionment are attributed to the re-distribution of major species in the factors. EC, and especially OC, had the largest changes when PMF is implemented with K_b (Figure 3). EC from BURN is apportioned to GV while OC from BURN and SOIL is redistributed to GV and DV. This re-distribution is explained by the change in correlations between major species used to resolve the factors. The correlation between OC and K ($R^2=0.31$) decreases with K_b ($R^2=0.10$) resulting in a transfer of OC from BURN to MOB where the correlation between OC and EC is higher ($R^2=0.66$). Similar changes in correlations are observed between factor contributions and major species (see the SM, Table S1) supporting the previous analysis. The OC/EC ratio for biomass burning increases from 4.1 in PMF-K to 5.1 in PMF-K_b, more consistent with OC/EC ratios found in biomass burning emissions (Lee et al., 2005).



PMF was also applied to a set of data at SD and YKV to assess the influence of K_b at other locations. At SD, the inclusion of K_b in PMF resulted in an increase of 3% of the PM_{2.5} apportioned to mobile sources. There was little change in PM_{2.5} from biomass burning, but K_b was apportioned almost exclusively (90%) to the biomass burning factor in comparison of the apportionment of K to the same factor (50%). At YKV, the inclusion of K_b resulted in an increase of 4% of the PM_{2.5} mass apportioned to biomass burning, and a decrease in 3% of the PM_{2.5} mass in the mobile factor. Similarly to SD and JST, K_b is apportioned almost exclusively to the biomass burning factor (83%).

3.5. Evaluation of the correlation with levoglucosan

Levoglucosan was more strongly correlated with the estimated K_b fraction ($R^2=0.63$) than the total potassium ($R^2=0.39$) during winter of 2007. The intercept of the regression between levoglucosan and K_b (18.5 ng/m^3) is half of the value of the intercept with K (41.5 ng/m^3). The low intercept suggests that the influence of non-biomass burning sources is greatly reduced. The

regression not passing through zero is consistent with levoglucosan loss processes in the atmosphere and variation in the fraction of levoglucosan in biomass burning emissions. The regression slopes of K and K_b with levoglucosan were both about 0.15. These slopes are similar to the K/levoglucosan ratio of 0.1 found in samples taken during biomass burning campaigns in Georgia (Lee et al., 2005). Puxbaum et al. (2007) report that K/levoglucosan ratios <0.2 are associated with domestic heating with wood in the US. It is expected then both prescribed fires and wood smoke from fireplaces impact the receptor at JST, supporting the greater weekend/weekday ratio for K_b due to the use of fireplaces observed during the winter.

We also used levoglucosan in a multivariate linear regression between K as independent variable and Fe and levoglucosan as dependent variables, for the days in which levoglucosan and Fe were available at the same time (30 days in 2007). The multilinear regression resulted in a $R^2=0.80$ ($p<0.01$) showing a strong correlation and suggesting that 80% of the variability of K can be explained by factors associated with soil dust, traffic and biomass burning.

3.6. Comparison with similar studies

The use of K_b in PMF at JST resulted in 9% of the PM_{2.5} mass apportioned to biomass burning versus 16% using total K from 1999–2004 at JST (Table 5). Both estimates are within the range found in other studies (7–22%). Our estimate of the mobile source impact (28%) is larger than previous studies (17–22%) which may be more realistic for a source that is ubiquitous in Atlanta. Analysis of emission inventories shows that 92% of EC emissions in the metro area are from mobile sources and approximately 50% of the primary PM_{2.5} is emitted by vehicles (Georgia-DNR., 2007). Such large emissions explain the large impact of vehicles to ambient PM_{2.5}. The application of CMB in Atlanta, using specific source profiles for mobile and biomass burning sources, found that mobile sources contribute approximately 4.0 µg/m^3 (22%) to total PM_{2.5} mass and biomass burning contributed 1.2 µg/m^3 (6.7%) (Lee et al., 2008), similar to here. The same study also points out the overestimation of biomass burning impacts and underestimation of mobile source contributions by PMF.

4. Implications

This study finds that a simple transformation of ambient potassium leads to an indicator that is more strongly associated with biomass burning activities and produces significant changes in the source apportionment of PM_{2.5}. This is a site-specific result, but the K_b fraction can be estimated at any monitoring site where K and Fe concentrations are available, for example, any of the EPA-STN sites throughout the US, not impacted by sea-salt (a simple extension can treat sea salt as well). Future studies of source apportionment may benefit from the use of K_b instead of K. In areas where measurement of levoglucosan and water-soluble potassium are not available, K_b constitutes a good indicator of biomass burning.

Health studies can also benefit from the use of K_b-PM_{2.5} from mobile sources and biomass burning has been associated with cardiovascular diseases (CVD) and EC and OC have been found to have somewhat stronger associations with CVD outcomes than other species (Sarnat et al., 2008; Peng et al., 2009). However, similar characteristics of traffic and vegetative burning sources profiles do not permit precisely delineating between the health impacts of these sources and it is suggested that mobile sources might have influenced the association of biomass burning with CVD (Sarnat et al., 2008). Our results suggest that K_b can help to differentiate the health impact of these sources, since the use of K_b in source apportionment produces a redistribution of EC and OC from biomass burning to mobile sources. The evaluation of PMF-K_b in epidemiological analysis may elucidate whether this is the case.

Table 5. Comparison of factor impacts ($\mu\text{g}/\text{m}^3$) from PMF in similar studies

Study	SULF	NITR	MOB	BURN	IND	SOIL	MIX ^a	UND ^a	Reference
Atlanta (1998-2000)	8.85 (56%)	1.15 (7%)	3.53 (22%)	1.72 (11%)	0.08 (0.5%)	0.18 (1%)	0.36 (2%)		(Kim et al., 2003)
Atlanta (1998-2000)	56%	9%	17%	7%	3%	2%	7%		(Kim et al., 2004)
Atlanta (2000-2002)	37%	8%	17%	13%	9%	2%	3%	11%	(Liu et al., 2005)
Atlanta (2000-2002)	4.93 (30%)	1.53 (9%)	2.83 (17%)	3.68 (22%)	1.0 (6%)	0.52 (3%)	0.42 (2%)	1.81 (11%)	(Liu et al., 2006)
Atlanta (1999-2004)	8.08 (45%)	1.53 (9%)	3.23 (20%)	2.67 (16%)	0.1 (1%)	0.6 (4%)		0.5 (3%)	PMF-K
Atlanta (1999-2004)	7.95 (49%)	1.41 (9%)	4.55 (28%)	1.40 (9%)	0.1 (1%)	0.73 (5%)		0.5 (3%)	PMF-K _b

^a MIX: mixed source, UND: unidentified

5. Conclusions

We apply a method to estimate the fraction of potassium attributable to biomass burning and demonstrated that K_b is a more robust indicator of this source than total potassium for our site. The analysis of temporal variability shows a larger concentration of K_b during spring when biomass burning is more intense and has greater correlation with levoglucosan, an organic compound found to be a good tracer of biomass burning. The examination of spatial variability suggests that K_b is an important fraction in urban areas not impacted by sea-salt where K has multiple sources, but not as important in rural areas where most of the K is from biomass burning. The application of PMF with total potassium appears to overestimate the contribution of biomass burning in urban sites and underestimate the impact of other sources such as traffic. This limitation is avoided when PMF is implemented with K_b , resulting in a modified allocation of $\text{PM}_{2.5}$ mass as a result of the re-distribution of the carbonaceous species within factors.

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Supporting Material Available

Factor profiles for PMF-K (Figure S1a), Factor profiles for PMF- K_b (Figure S1b), Factor loadings using K for three sites in the Atlanta area and using 36 variables (Table S1). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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