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Supplement of

$PM_{2.5}$ water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies

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Table S1. Sampling schedule of Hi-Vol filters collected from June 2012 to September 2013.

Month Year	Season	Sampling site	Trailer site
June-July 2012	Summer	JST	YRK
July-August 2012	Summer	JST	GT
September-October 2012	Fall	JST	RS
November 2012	-	JST	JST
December 2012	Winter	JST	YRK
January-February 2013	Winter	JST	RS
March 2013	Winter	JST	GT
June-July 2013	Summer	CTR	BHM
August 2013	Summer	ESL	-
September-October 2013	Fall	GT	RS

JST - Southeastern Aerosol Research and Characterization Study (SEARCH) Jefferson Street, GA; YRK - SEARCH Yorkville, GA; GT - Georgia Tech, GA; RS - Roadside (on Georgia Tech Campus); BHM - SEARCH Birmingham, AL; CTR - SEARCH Centerville, AL; ESL - East St. Louis, IL.

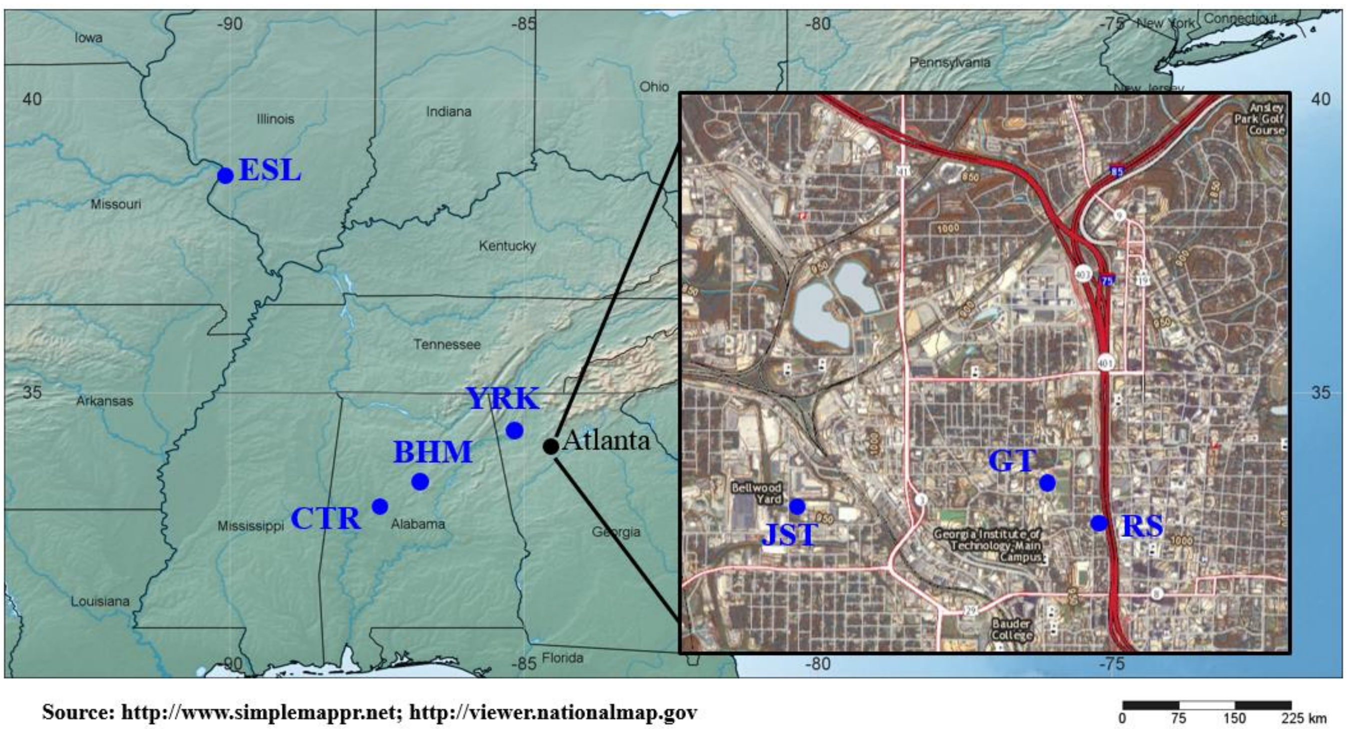


Figure S1. Map of sampling sites including three urban site: Jefferson Street, GA (JST); Birmingham, AL (BHM); East St. Louis, IL, two rural sites: Yorkville, GA (YRK); Centerville, AL (CTR), a near-road site - GT, and a road-side site – RS.

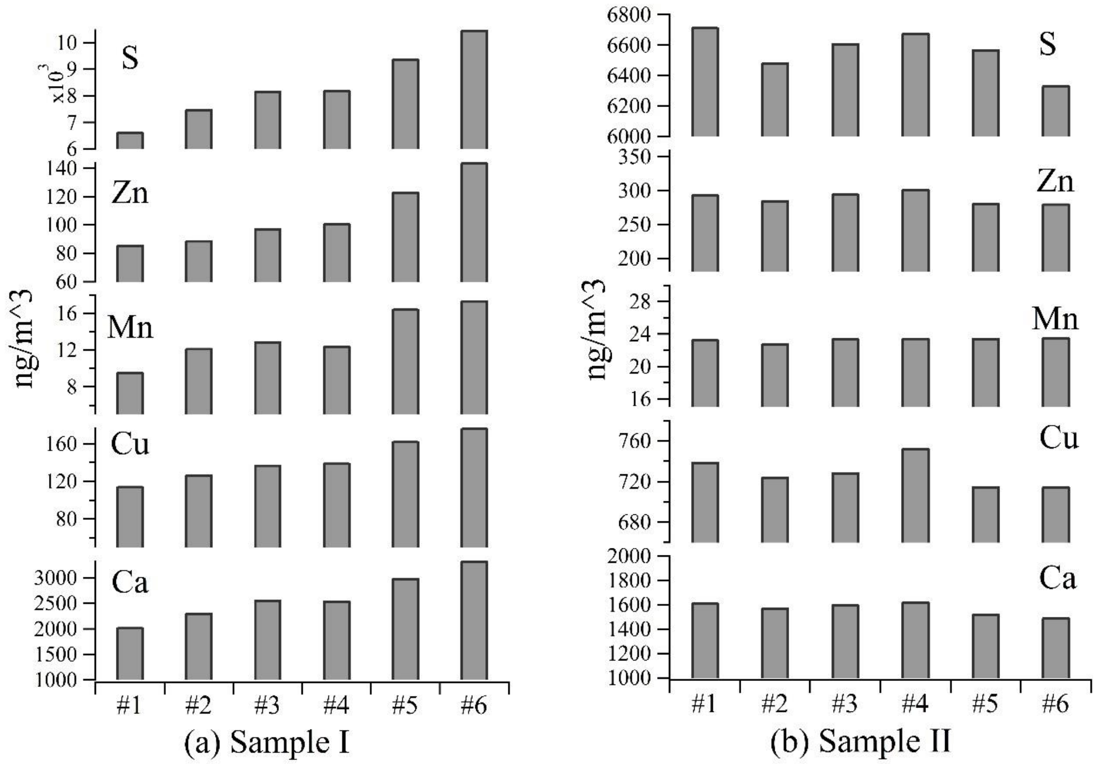


Figure S2. Results on selected elements concentration measured by DIONEX-nebulizer-neutralizer-XRF from 6 duplicates from two filter extracts before (a) and after (b) inserting deionized water with 2% HNO_3 between samples. It illustrates that inserting DI water with 2% HNO_3 is an effect solution to eliminate carry-over issue in the system.

Table S2. Coefficient of divergence (COD) and Pearson's r

Paired sites	JST/GT				JST/YRK				JST/RS				GT/RS	
Seasons	Summer		Winter		Summer		Winter		Fall		Winter		Fall	
COD/r	COD	r	COD	r	COD	r	COD	r	COD	r	COD	r	COD	r
S	**0.10**	**0.98**	**0.06**	**0.97**	**0.18**	**0.79**	**0.18**	**0.98**	0.39	0.53	0.26	0.50	0.31	**0.77**
K	**0.15**	0.63	**0.07**	**0.95**	**0.18**	0.69	0.29	**0.68**	**0.18**	0.69	0.28	0.51	**0.16**	**0.79**
Ca	**0.09**	**0.97**	0.36	**0.84**	0.30	0.61	0.28	**0.78**	0.21	**0.77**	0.44	0.37	0.46	0.40
Fe	0.22	**0.90**	0.30	**0.82**	0.46	0.53	0.54	0.42	0.40	0.25	0.29	0.52	0.34	0.53
Zn	0.32	0.69	**0.19**	**0.71**	0.29	0.61	0.38	0.68	0.35	-0.19	0.36	0.15	0.39	0.03
Cu	0.52	0.68	0.35	-0.06	0.41	0.05	0.61	0.21	0.45	-0.21	0.59	-0.13	0.34	0.02
Ba	**0.18**	**0.90**	0.24	**0.85**	0.52	0.27	0.46	0.54	0.61	-0.43	0.53	0.31	0.55	0.36
Mn	**0.14**	**0.94**	**0.13**	**0.84**	0.23	0.64	0.37	**0.76**	0.46	0.04	0.34	0.41	0.33	0.39
Br	**0.18**	0.67	0.26	**0.91**	0.32	0.68	0.43	0.68	0.43	0.30	0.35	**0.72**	0.41	0.65
Sr	**0.13**	**0.89**	0.30	**0.86**	0.46	0.50	0.52	0.34	0.51	-0.11	0.62	0.13	0.51	0.67
Pb	0.28	**0.78**	**0.16**	**0.85**	0.24	0.62	0.34	0.68	0.49	0.53	0.40	0.07	0.40	0.42
As	0.30	0.62	0.21	**0.72**	0.34	0.13	0.42	0.40	0.53	0.25	0.44	0.02	0.41	0.65
Ti	0.38	0.48	0.36	0.51	0.43	0.54	0.46	0.38	0.57	-0.31	0.46	0.17	0.54	0.37
Se	**0.14**	**0.98**	**0.11**	**0.91**	0.28	0.48	0.30	**0.93**	0.28	**0.76**	0.31	**0.71**	0.39	0.62
WSOC	0.30	0.22	0.38	0.49	**0.18**	**0.87**	0.23	**0.79**	**0.19**	0.52	0.48	0.04	0.41	-0.14

Note: COD≤0.2 and r≥0.7 are bolded in blue and red, respectively

The CODs were calculated as follows:

$$COD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\frac{c_{ij} - c_{ik}}{c_{ij} + c_{ik}}\right]^2} \qquad (S1)$$

where c_{ij} and c_{ik} are the water-soluble elements (ng/m^3) measured at paired sites j and k, respectively, and N is the sample size. A COD close to 0 represents a homogenous distribution and near 1 indicates heterogeneity, opposite to correlation coefficients (r). Both are summarized in Table S2.

Table S3. Correlations (Pearson's r) between water-soluble Cu, Fe, Zn, Mn and other elements

Season. Year	Sites		S	K	Ca	Ti	Mn	Fe	Cu	Zn	As	Se	Br	Sr	Ba	Pb
Summer 2012	JST	**Mn**	0.61	0.64	0.29	0.62	1	0.66	0.43	0.67	0.03	0.66	**0.80**	**0.80**	0.61	0.52
		Fe	**0.71**	0.48	0.30	**0.81**	0.66	1	0.63	**0.73**	0.41	**0.71**	0.64	0.52	**0.73**	0.67
		Cu	0.51	0.19	0.44	**0.70**	0.43	0.63	1	0.68	0.45	0.59	0.35	0.27	0.68	0.66
		Zn	0.47	0.41	0.32	**0.70**	0.67	**0.73**	0.68	1	0.38	0.59	0.51	0.43	0.64	**0.74**
	YRK	**Mn**	0.65	0.47	**0.91**	0.21	1	0.44	-0.12	0.53	-0.04	0.53	0.48	**0.82**	0.54	0.37
		Fe	**0.76**	0.60	0.56	0.55	0.44	1	-0.01	0.58	0.02	0.52	**0.73**	0.56	0.33	**0.84**
		Cu	0.09	0.07	-0.05	-0.05	-0.12	-0.01	1	0.20	0.08	0.07	0.13	-0.15	-0.15	0.14
		Zn	0.68	0.54	0.60	0.20	0.53	0.58	0.20	1	-0.02	0.60	0.52	0.51	0.44	0.67
	GT	**Mn**	0.31	0.61	0.15	0.16	1	0.55	0.17	**0.70**	-0.03	0.27	0.22	**0.79**	0.25	-0.21
		Fe	**0.73**	0.67	0.07	0.52	0.55	1	0.64	0.66	0.51	0.59	0.58	0.35	0.59	0.11
		Cu	0.66	0.25	0.00	0.39	0.17	0.64	1	0.26	0.51	0.54	0.40	0.05	0.44	0.04
		Zn	0.42	0.51	0.22	0.43	**0.70**	0.66	0.26	1	0.35	0.35	0.47	0.57	0.51	0.10
Fall 2012	JST	**Mn**	0.37	0.30	-0.22	0.30	1	0.61	0.69	0.58	-0.02	0.30	**0.70**	**0.75**	0.36	0.30
		Fe	**0.76**	0.43	0.18	**0.75**	0.61	1	**0.74**	0.65	0.27	0.62	**0.79**	0.56	0.67	0.61
		Cu	0.57	0.55	0.03	**0.73**	0.69	**0.74**	1	0.64	0.59	0.63	0.68	0.24	0.69	**0.75**
		Zn	0.35	0.36	-0.12	0.51	0.58	0.65	0.64	1	0.32	0.38	0.57	0.33	0.47	0.65
	RS	**Mn**	0.06	**0.76**	0.58	0.30	1	0.18	0.00	0.41	0.09	0.30	0.39	**0.74**	0.46	0.13
		Fe	0.62	0.35	0.38	0.62	0.18	1	0.37	0.60	0.14	0.50	0.62	0.46	0.42	0.34
		Cu	0.27	0.30	0.06	0.39	0.00	0.37	1	0.38	0.00	0.11	0.39	0.43	**0.70**	0.18
		Zn	0.66	0.40	0.42	0.51	0.41	0.60	0.38	1	0.32	0.53	0.63	0.52	0.52	0.28
Winter 2012	JST	**Mn**	0.24	0.39	0.62	0.35	1	0.38	0.21	0.62	0.30	0.31	0.30	0.68	0.66	0.35
		Fe	0.53	0.56	0.07	0.48	0.38	1	0.63	**0.70**	0.45	0.48	0.51	0.18	0.38	0.62
		Cu	0.25	0.48	-0.11	0.44	0.21	0.63	1	0.51	0.47	0.29	0.19	0.19	0.38	0.52
		Zn	0.29	0.55	0.24	0.48	0.62	**0.70**	0.51	1	0.57	0.46	0.37	0.35	0.50	0.67
	YRK	**Mn**	0.05	**0.86**	**0.86**	0.19	1	0.53	-0.04	**0.89**	0.18	0.62	0.67	**0.79**	0.63	0.28
		Fe	0.54	0.43	0.23	0.23	0.53	1	0.32	0.50	0.25	**0.83**	0.52	0.11	0.36	**0.76**
		Cu	0.63	0.01	-0.16	0.11	-0.04	0.32	1	0.16	0.08	0.28	-0.04	-0.09	-0.10	0.44
		Zn	0.15	**0.87**	**0.75**	0.38	**0.89**	0.50	0.16	1	0.31	0.62	0.58	**0.73**	0.66	0.42
	GT	**Mn**	0.15	**0.83**	0.54	0.12	1	0.50	0.63	0.61	0.63	**0.78**	**0.77**	0.52	0.65	0.13
		Fe	0.47	**0.78**	-0.21	0.38	0.50	1	**0.74**	0.59	**0.70**	0.68	**0.72**	0.23	0.52	0.68
		Cu	0.30	0.68	-0.11	0.28	0.63	**0.74**	1	**0.77**	0.44	0.53	0.58	0.06	0.63	0.50
		Zn	0.44	0.46	0.19	0.50	0.61	0.59	**0.77**	1	0.50	0.53	0.39	0.27	**0.81**	0.57
	RS	**Mn**	0.18	**0.76**	**0.83**	0.55	1	0.56	0.37	0.54	0.49	0.27	0.56	0.35	0.63	0.16
		Fe	0.36	**0.73**	0.16	0.43	0.56	1	0.60	0.48	0.61	0.56	**0.73**	0.34	0.39	0.40
		Cu	0.28	0.59	0.14	**0.73**	0.37	0.60	1	0.42	0.62	0.31	0.46	**0.76**	**0.78**	0.49
		Zn	0.17	0.53	0.20	0.28	0.54	0.48	0.42	1	0.69	0.32	0.44	0.21	0.36	0.49
Fall 2013	GT	**Mn**	0.57	0.46	0.59	0.47	1	0.57	0.63	0.69	0.35	0.52	0.49	0.36	0.48	0.49
		Fe	0.55	**0.73**	**0.70**	**0.72**	0.57	1	0.63	0.51	0.64	0.46	**0.82**	0.54	0.69	0.62
		Cu	0.35	0.46	0.39	0.54	0.63	0.63	1	0.53	0.58	0.20	0.62	0.35	0.67	0.51
		Zn	0.33	0.28	0.23	0.39	0.69	0.51	0.53	1	0.58	0.31	0.51	0.23	0.62	0.59
	RS	**Mn**	**0.78**	**0.84**	**0.93**	0.51	1	**0.76**	0.55	**0.85**	0.38	0.64	**0.76**	0.26	0.65	0.31
		Fe	**0.74**	0.67	0.62	**0.71**	**0.76**	1	0.55	0.62	0.62	0.56	**0.82**	0.20	**0.75**	0.47
		Cu	0.30	0.63	0.36	**0.80**	0.55	0.55	1	0.58	0.62	0.21	0.57	0.59	**0.84**	0.37
		Zn	0.64	**0.74**	0.69	0.51	**0.85**	0.62	0.58	1	0.51	0.58	0.62	0.22	0.66	0.57

Note: r≥0.7 are bold and in red.

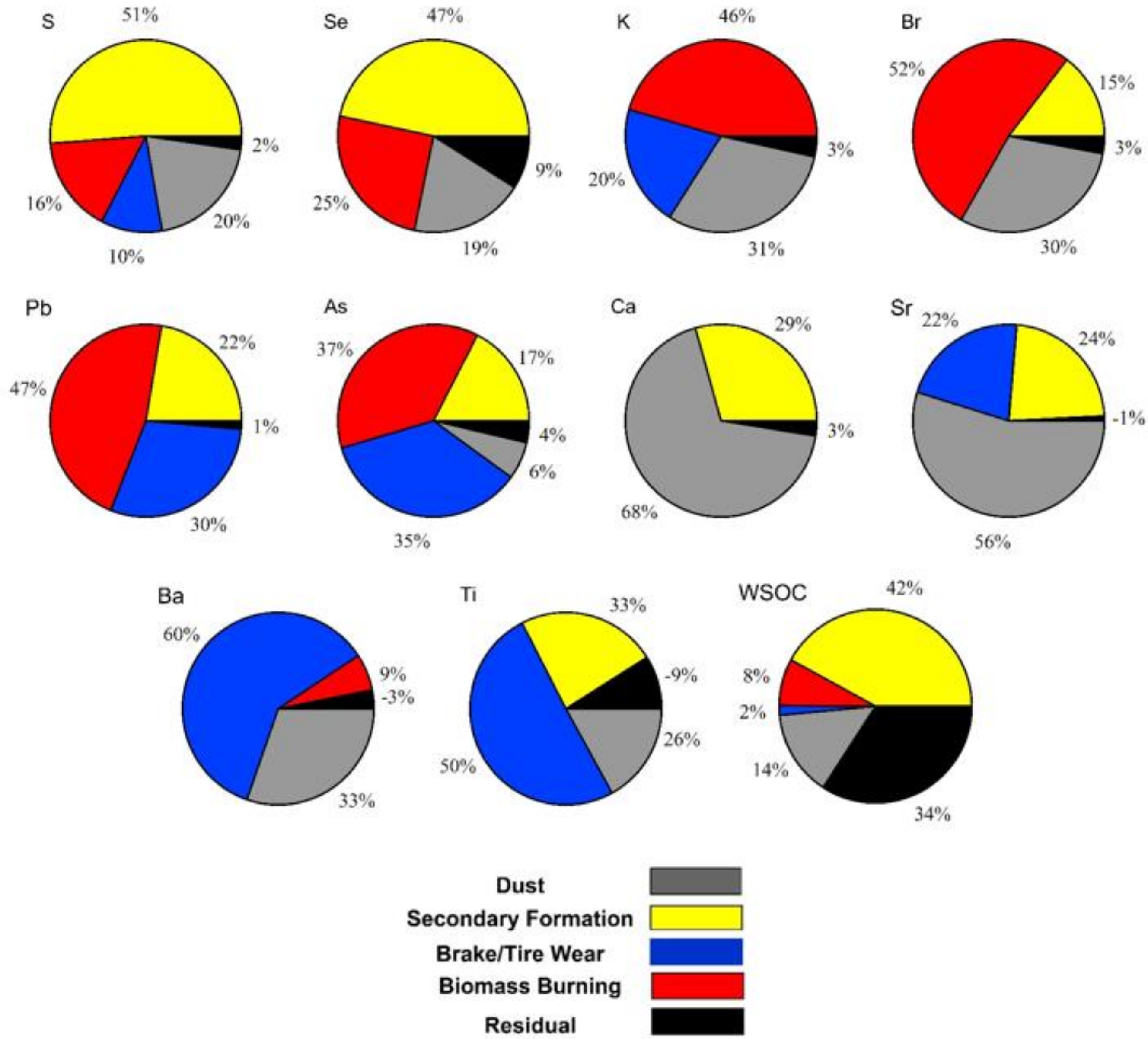


Figure S3. Factor contributions for the various water-soluble elements in $PM_{2.5}$ based on the PMF analyses.

Table S4. Correlations (Pearson's r) between PM2.5 and various water-soluble elements

Sites	*Season (Month)*	*S*	*K*	*Ca*	*Ti*	*Mn*	*Fe*	*Cu*	*Zn*	*As*	*Se*	*Br*	*Sr*	*Ba*	*Pb*
JST	Summer (June)	0.66	0.69	0.53	0.67	0.58	0.64	0.54	0.53	0.15	0.65	0.65	0.41	0.48	0.67
	Summer (Aug.)	**0.82**	0.28	0.05	0.45	0.51	**0.80**	0.66	0.58	0.32	0.62	**0.71**	0.39	0.42	0.62
	Fall (Sept.)	**0.83**	**0.80**	0.13	0.69	0.27	**0.80**	0.59	0.69	0.67	**0.78**	0.67	0.52	0.47	**0.77**
	Winter (Dec.)	0.52	0.64	0.23	0.46	0.41	**0.80**	0.54	**0.71**	0.57	**0.73**	0.69	0.17	0.39	0.65
	Winter (Feb.)	**0.78**	0.57	0.06	0.16	0.29	0.68	0.49	0.35	0.24	**0.79**	**0.79**	0.10	0.05	**0.78**
	Winter (March)	0.35	**0.81**	0.27	0.48	0.52	**0.75**	0.30	**0.76**	**0.70**	**0.80**	0.61	0.51	0.41	0.58
YRK	Summer (June)	**0.89**	0.61	0.66	0.57	0.50	**0.73**	0.07	0.53	0.15	**0.70**	**0.83**	0.66	0.41	**0.70**
	Winter (Dec.)	**0.78**	0.48	-0.01	0.07	0.37	0.69	0.56	0.46	0.33	**0.82**	0.57	-0.06	0.21	**0.81**
GT	Summer (Aug.)	**0.86**	0.61	0.33	0.48	0.38	**0.79**	0.60	0.56	0.59	**0.80**	**0.78**	0.38	0.56	0.28
	Winter (March)	0.26	**0.89**	0.11	**0.47**	**0.84**	**0.76**	0.64	0.61	**0.76**	**0.81**	**0.80**	0.31	0.66	0.30
	Fall 2013 (Sept.)	**0.73**	0.24	0.31	0.50	0.33	0.53	0.22	0.08	0.08	0.42	0.58	0.03	0.03	0.08
RS	Fall (Sept.)	0.54	0.65	0.18	0.56	0.45	0.55	0.46	0.57	0.19	0.54	**0.79**	0.50	0.60	0.53
	Winter (Feb.)	0.23	**0.86**	0.53	0.58	**0.76**	**0.74**	0.65	0.51	0.65	0.40	**0.74**	0.40	0.62	0.33
	Fall 2013 (Sept.)	0.65	0.19	0.54	0.18	0.51	0.65	-0.06	0.42	0.32	0.43	0.54	-0.06	0.23	0.11
BHM	Summer 2013 (June)	**0.82**	0.15	0.58	0.41	0.35	**0.77**	0.04	0.20	0.41	0.65	**0.81**	0.17	0.00	0.27
CTR	Summer 2013 (June)	**0.75**	0.57	0.63	0.37	0.55	0.30	-0.18	0.48	0.50	0.64	0.67	0.34	0.39	0.39
ESL	Summer 2013 (Aug.)	0.68	0.67	0.55	0.12	0.04	0.33	0.53	0.11	0.35	0.37	0.34	0.47	0.28	0.49

Note: r≥0.7 are bold and in red.

$PM_{2.5}$ mass concentration were measured by a Tapered Element Oscillating Microbalance (TEOM) by Atmospheric Research Analysis (ARA, Inc.) at SEARCH sites (JST, YRK, BHM, and CTR) and ESL. For the RS and GT sites, the PM mass concentrations were estimated from the sum of chemical components analyzed on the same Hi-Vol filters, including elemental carbon (EC; Sunset Laboratory OCEC analyzer), organic mass (OC*1.6; Turpin and Lim, 2001), water-soluble metals, and ammonium sulfate (assuming sulfate and ammonium are all $(NH_4)_2SO_4$ (Zhang et al., 2010), where sulfate was calculated from sulfur from this work.

PMF results

Input

Positive Matrix Factorization (PMF) analysis was applied to the data from JST (summer, fall, winter 2012, spring 2013), GT (fall, winter 2012, fall 2013), and RS (fall 2012, winter 2013) (total N=299). Missing data were replaced by species median. 15 species including S, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Se, Br, Sr, Ba, Pb and WSOC were run in the model.

PMF solutions

1) **Q/Qexp criterion**

Q/Qexp as a function of P (numbers of factors) was used to narrow down the range of factors to 3, 4 and 5 (see Figure S4).

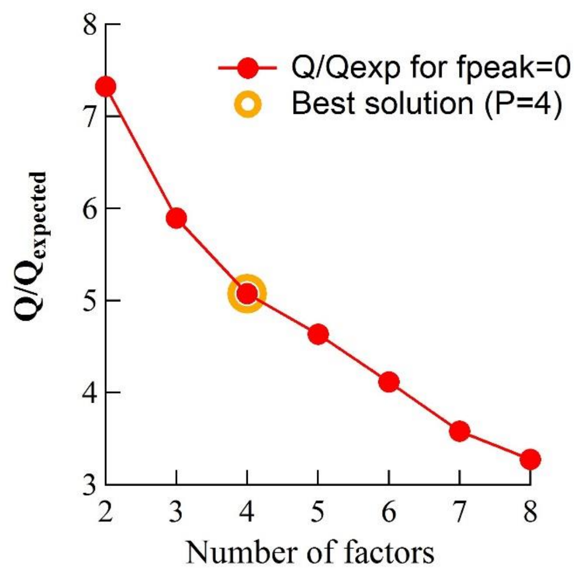


Figure S4. Q/Qexp as a function of the numbers of factors used in the PMF solution.

2) **Determining # of factors**

Best solution P=4 was determined by closer examination of factor spectra, time series and results from bootstrapping for P= 3, 4, and 5.

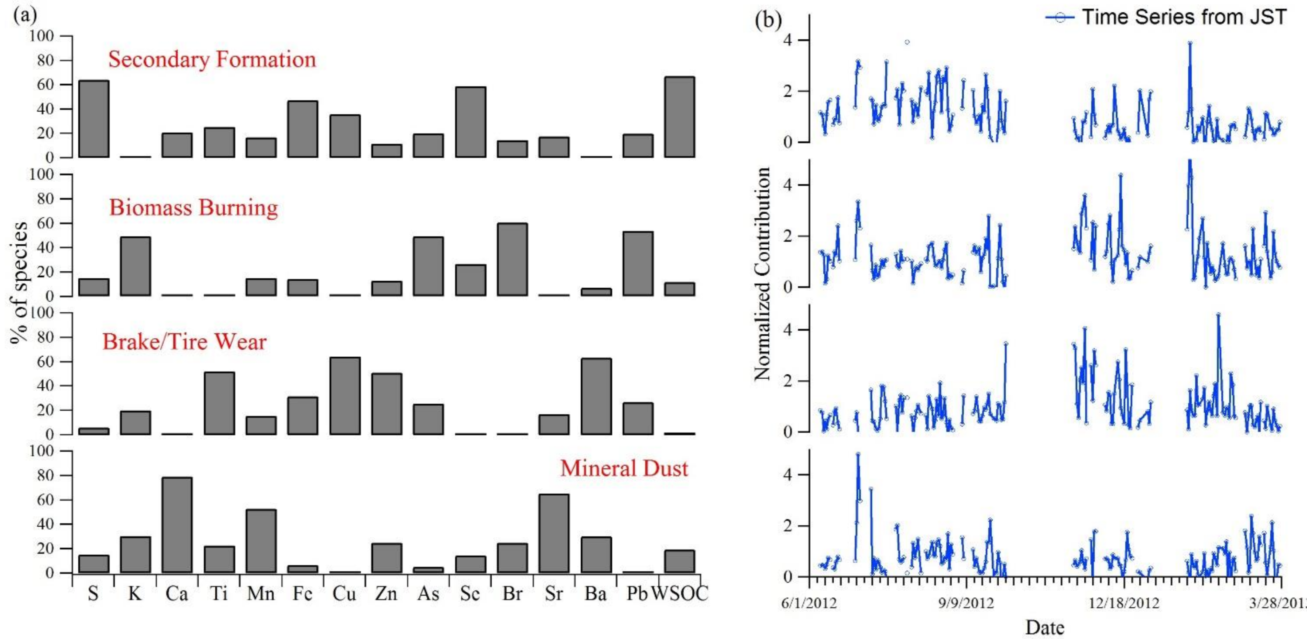
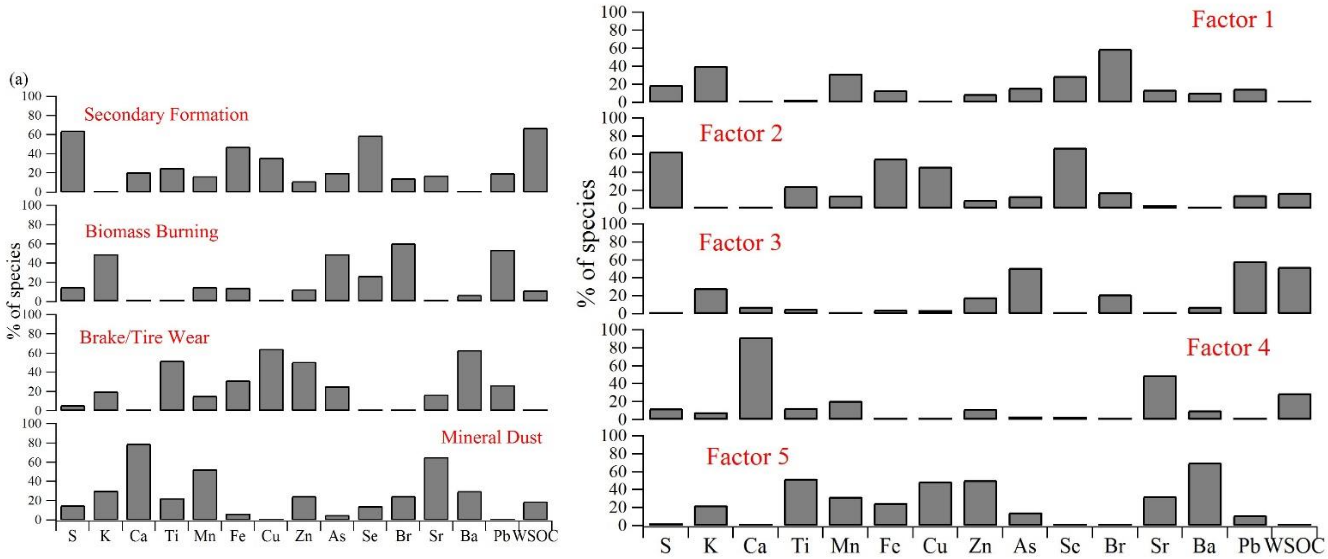


Figure S5. Factor profiles (a) and time series (b) for 4-factor solution

Table S5. Bootstrapping results on 4-factor solution

	Factor 1	Factor 2	Factor 3	Factor 4	Unmapped
Boot Factor 1	100	0	0	0	0
Boot Factor 2	0	100	0	0	0
Boot Factor 3	1	0	99	0	0
Boot Factor 4	0	0	0	100	0



(a) (b)

Figure S6. Factor profiles for 4-factor solution (a) and 5-factor solution (b).

The 5-factor solution resulted in splitting of the “biomass burning” source (Factor 2 in panel a, Fig. S6) into two factors (Factor 1 and 3 in panel b, Fig S6) with no clear identification. Moreover, the bootstrap calculations (Table S6) highlight the bootstrapping factor 5 in 5-facor solution were matched to other factors, indicating less stability of the 5-factor solution.

Table S6. Bootstrapping results on 5-factor solution

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Unmapped
Boot Factor 1	83	4	12	0	1	0
Boot Factor 2	0	98	2	0	0	0
Boot Factor 3	0	0	100	0	0	0
Boot Factor 4	0	0	0	99	1	0
Boot Factor 5	0	0	0	0	100	0

In the case of 3 factors, source apportionment leads to factors with no clear physical interpretations (Fig. S8 & Table S7).

Table S7. Bootstrapping results on 3-factor solution

	Factor 1	Factor 2	Factor 3	Unmapped
Boot Factor 1	97	3	0	0
Boot Factor 2	0	99	1	0
Boot Factor 3	3	3	94	0

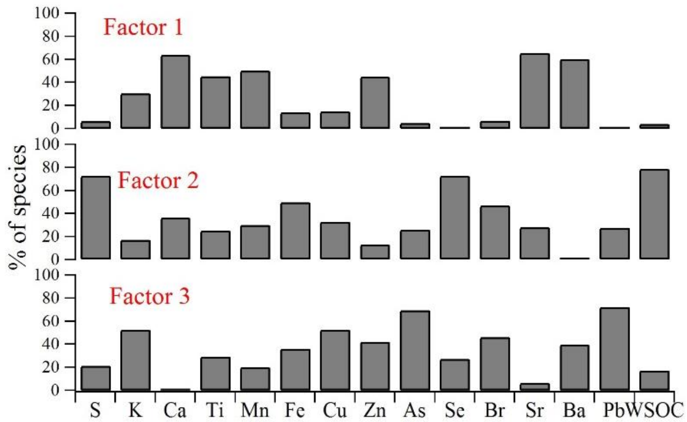


Figure S7. Factor profiles for 3-factor solution

3) Rotational ambiguity: fpeak variation

The rotational ambiguity of the 4-factor PMF solution was explored via the Fpeak parameter in the range ±2 (Fig. S8). The results indicate that Q/Qexp is at a minimum for Fpeak=0, justifying the decision to use Fpeak=0 in the case of the optimal 4-factor solution.

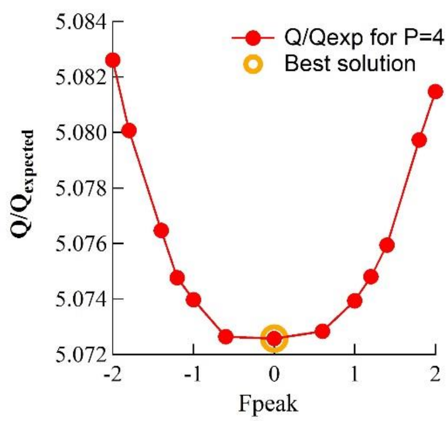


Figure S8. Q/Qexp as function of Fpeak parameter

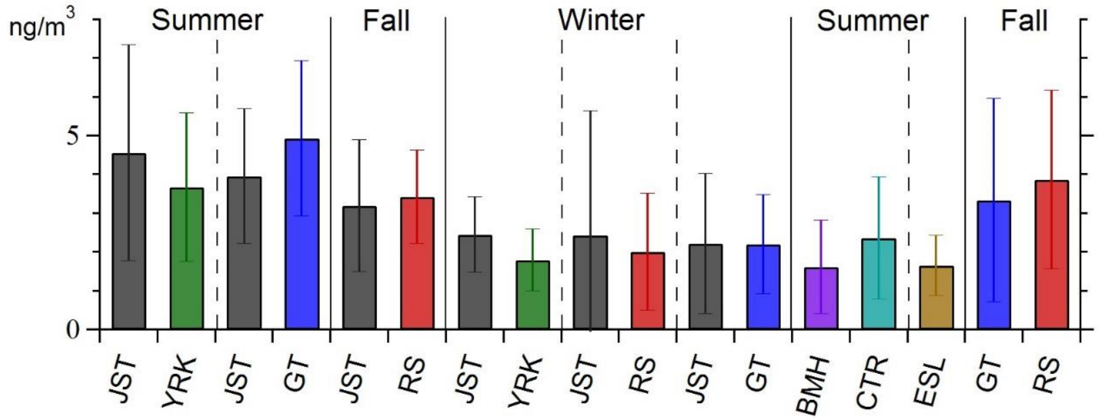


Figure S9. Monthly average of ambient concentration of water-soluble organic carbon (WSOC) at the various sites.

Turpin, B. J. and Lim, H.-J.: Species contributions to PM2:5 mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Tech., 35, 602–610, 2001.

Zhang, X., Hecobian, A., Zheng, M., Frank, N. H., and Weber, R.J.: Biomass burning impact on PM2:5 over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis, Atmos. Chem. Phys., 10, 6839–6853, doi:10.5194/acp-10-6839-2010, 2010.