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Characterization of organic nitrogen in aerosols at a forest site in the southern Appalachian Mountains

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Table S1. List of quantified target compounds by GCMS with surrogate compound and quantitation ions.

	Quantified as	Characterized ions	Mean Concentration (Range) (ng/m^3)
Isoprene SOA markers			
2-Methylglyceric acid	meso-erythritol	219, 233, 306, 321	1.55(0.20-4.79)
2-Methylthreitol	meso-erythritol	219, 319, 293, 203	10.3(0.61-49.4)
2-Methylerythritol	meso-erythritol	219, 319, 293, 203	48.6(1.00-194)
C-5 alkene triols	meso-erythritol	231, 147, 73	82.0(1.21-367)
Monoterpene tracers			
3-Hydroxyglutaric acid	cis-ketopinic acid	349, 275, 303, 185, 365	14.7(1.99-58.4)
Biomass burning tracers			
Levoglucosan	Levoglucosan	333, 217, 204	18.7(3.62-101)

Table S2. List of quantified Nitrogen aromatics compounds by LCMS with compound formula, surrogate compound, molecular weight (MW), quantitation ion and major product ions.

Nitro-aromatics	Chemical Formula	Quantified as	MW	Quant $[M-H]^-$ ion (m/z)	Major $[M-H]^-$ product ions(m/z)	Mean Concentration (Range) (ng/m^3)
Nitrophenol	$C_6H_5NO_3$	4-nitrophenol	139.1	138.0196	108(-NO), 92(-NO_2)	0.01(ND-0.06)
Nitrocatechol	$C_6H_5NO_4$	4-nitrocatechol	155.1	154.0145	123,124(-NO), 95, 108(-NO_2)	0.08(ND-1.26)
Methyl nitro catechol	$C_7H_7NO_4$	2-methyl-4-nitroresorcinol	169.1	168.0301	138(-NO), 122(-NO_2) 109	0.02(ND-0.44)
Methyl nitro phenol	$C_7H_7NO_3$	2-methyl-4-nitrophenol	153.1	152.0353	122(-NO), 106(-NO_2)	0.00(ND-0.02)
Dimethyl nitro catechol	$C_8H_9NO_4$	2-methyl-4-nitroresorcinol	183.2	182.0459	123, 152(-NO)	0.01(ND-0.12)

Table S3. List of quantified Organosulfates compounds by LCMS with compound formula, surrogate compound, molecular weight (MW), quantitation ion and major product ions.

Organosulfates	Chemical Formula	Quantified as	MW	Quant $[M-H]^-$ ion (m/z)	Major $[M-H]^-$ product ions(m/z)	Mean Concentration (Range) (ng/m^3)
Isoprene SOA	$C_2H_4O_5S$	Camphor sulfonic acid	140.1	138.9707	97,80	0.51(0.06-1.41)
	$C_3H_6O_5S$	Camphor sulfonic acid	154.1	152.9863	97,80	3.02(0.30-9.75)
	$C_2H_4O_6S$	Camphor sulfonic acid	156.1	154.9656	97,80	7.24(0.11-28.4)
	$C_5H_{10}O_6S$	Camphor sulfonic acid	198.2	197.0125	97,80	0.81(0.06-3.89)
	$C_3H_6O_6S$	Camphor sulfonic acid	170.1	168.9812	97,80	0.85(0.01-3.67)
	$C_4H_8O_7S$	Camphor sulfonic acid	200.2	198.9918	119,97,80	3.62(ND-18.6)
	$C_5H_{12}O_7S$	Camphor sulfonic acid	216.2	215.0231	97,80	50.7(1.84-167)
	$C_5H_8O_7S$	Camphor sulfonic acid	212.2	210.9918	97,80	6.17(0.19-20.2)
	$C_5H_{10}O_7S$	Camphor sulfonic acid	214.2	213.0074	97,80	5.50(0.19-22.0)
	$C_5H_{11}NO_9S$	Camphor sulfonic acid	261.0	260.0082	197(-HNO_3), 97,80	5.95(0.31-28.8)
Monoterpene SOA	$C_{10}H_{18}O_5S$	Camphor sulfonic acid	250.3	249.0802	97,80	0.59(0.03-1.86)
	$C_{10}H_{16}O_7S$	Camphor sulfonic acid	280.3	279.0543	235(-CO_2), 97,80	2.07(0.33-7.92)
	$C_7H_{12}O_7S$	Camphor sulfonic acid	240.0	239.0231	97,159	2.55(0.49-7.69)
	$C_{10}H_{18}O_7S$	Camphor sulfonic acid	282.1	281.0700	97,80	1.30(0.02-6.35)
	$C_{10}H_{17}NO_7S$	Camphor sulfonic acid	295.3	294.0653	96,80, 220, 231(-HNO_3), 247(-HONO)	1.51(0.11-14.6)
	$C_{10}H_{17}NO_8S$	Camphor sulfonic acid	311.1	310.0602	247(-HNO_3), 263(-HONO), 97,80	0.74(0.04-5.41)
	$C_{10}H_{17}NO_9S$	Camphor sulfonic acid	327.1	326.0551	279(-HONO), 263(-HNO_3), 97,80	0.48(0.02-4.30)
	$C_{10}H_{15}NO_9S$	Camphor sulfonic acid	325.0	324.0395	97,80,277(-HONO),165,119	0.14(ND-0.72)
	$C_{10}H_{17}NO_{10}S$	Camphor sulfonic acid	343.1	342.0500	97,80,279(-HNO_3),261,201,199	1.86(0.13-10.4)
Other SOA	$C_5H_{10}O_8S$	Camphor sulfonic acid	230.2	229.0024	149,97,80	1.42(ND-5.40)

Table S4. List of quantified organic acids compounds by LCMS with compound formula, surrogate compound, molecular weight (MW), quantitation ion and major product ions.

Terpenoic acids	Chemical Formula	Quantified as	MW	Quant $[M-H]^-$ ion (m/z)	Major $[M-H]^-$ product ions(m/z)	Mean Concentration (Range) (ng/m^3)
	$C_8H_{12}O_5$	Suberic acid	188.1	187.0617	125(-[H_2O+CO_2]) 143(-CO_2)	54.4(5.54-154)
	$C_7H_{10}O_5$	Suberic acid	174.1	173.0455	129(-CO_2) 111(-[H_2O+CO_2])	26.7(4.03-65.7)
	$C_8H_{12}O_6$	Suberic acid	204.1	203.0561	141(-[H_2O+CO_2]) 185(-H_2O)	22.3(2.27-60.4)
	$C_9H_{12}O_6$	Suberic acid	216.1	215.0573	171(-CO_2) 153(-[H_2O+CO_2])	2.82(0.02-12.4)
	$C_8H_{14}O_5$	Suberic acid	190.1	189.0768	145(-CO_2) 127(-[H_2O+CO_2])	4.58(ND-15.1)
	$C_8H_{10}O_5$	Suberic acid	186.1	185.0465	141(-CO_2) 125(-CH_3COOH)	6.59(1.52-18.2)
	$C_8H_{12}O_4$	Suberic acid	172.1	171.0663	127(-CO_2)	7.03(1.04-19.4)
	$C_7H_{10}O_6$	Suberic acid	190.1	189.0405	145(-CO_2) 127(-[H_2O+CO_2])	8.78(0.98-22.9)
	$C_5H_8O_4$	Suberic acid	132	131.035	87(-CO_2)	2.88(0.54-9.05)
	$C_7H_{12}O_5$	Suberic acid	176.1	175.0612	113(-[H_2O+CO_2])	2.04(ND-6.95)
	$C_9H_{14}O_4$	Suberic acid	186.1	185.0819	141(-CO_2) 123(-[H_2O+CO_2])	2.82(0.02-9.21)
	$C_7H_{10}O_4$	Suberic acid	158.1	157.0506	113(-CO_2)	5.01(0.68-17.7)
	$C_6H_8O_4$	Suberic acid	144	143.035	99(-CO_2) 83(-CH_3COOH)	1.67(ND-5.30)
	$C_{10}H_{16}O_5$	cis-Pinonic acid	216.1	215.0925	171(-CO_2) 153(-[H_2O+CO_2])	45.3(10.5-163.4)
	$C_{10}H_{16}O_6$	cis-Pinonic acid	232.1	231.0874	169(-[H_2O+CO_2])	13.5(3.32-35.8)
	$C_{12}H_{18}O_5$	Dodecanedioic acid	242.1	241.1084	197(-CO_2)	1.88(ND-6.32)
	$C_{13}H_{20}O_5$	Dodecanedioic acid	256.1	255.1247	211(-CO_2) 193(-[H_2O+CO_2])	4.51(0.59-13.68)
	$C_{10}H_{14}O_5$	cis-Pinonic acid	214.1	213.0768	169(-CO_2)	63.9(15.0-216.4)

Table S5. Recoveries of standard/surrogate compounds used in HPLC-ESI(-)-QTOF-MS and GCMS analysis.

Standard Compound	Recovery (%)
4-Nitrophenol	97.0±0.7
4-Nitrocatechol	75.2±5.6
2-Methyl-4-nitroresorcinol	102.0±3.3
2-Methyl-4-nitrophenol	98.3±2.2
Camphor sulfonic acid	89.2±1.4
Suberic acid	117.2±5.9
cis-Pinonic acid	129.4±4.2
Dodecanedioic acid	117.0±4.9
meso-Erythritol	88.5±3.2
cis-Ketopinic acid	95.3±1.7
Levoglucosan	98.6±1.4

Table S6. Correlation coefficients among nitro-aromatics and levoglucosan.

	$C_6H_5NO_3$	$C_6H_5NO_4$	$C_7H_7NO_4$	$C_7H_7NO_3$	$C_8H_9NO_4$	Levoglucosan
$C_6H_5NO_3$		**0.860**	**0.429**	**0.778**	**0.359**	**0.538**
$C_6H_5NO_4$			**0.388**	**0.690**	0.289	**0.608**
$C_7H_7NO_4$				**0.488**	**0.674**	**0.545**
$C_7H_7NO_3$					**0.467**	**0.460**
$C_8H_9NO_4$						**0.546**
Levoglucosan						

Values in bold indicate $p<0.01$

Table S7. Correlation coefficients among organosulfates and SOA tracers.

m/z	OS 215	OS 199	OS 197	NOS 260	OS 279	NOS 294	2-MG	C5-alkene triols	2-methyl-threitol	2-methyl-erythritol	HGA
OS 215		**0.696**	**0.861**	**0.829**	**0.484**	-0.217	**0.591**	**0.974**	**0.896**	**0.932**	**0.699**
OS 199			**0.753**	**0.784**	**0.634**	-0.015	**0.686**	**0.759**	**0.715**	**0.721**	**0.700**
OS 197				**0.961**	**0.748**	0.009	**0.690**	**0.881**	**0.848**	**0.871**	**0.769**
NOS 260					**0.800**	-0.057	**0.760**	**0.846**	**0.829**	**0.832**	**0.823**
OS 279						0.320	**0.745**	**0.512**	**0.515**	**0.506**	**0.819**
NOS 294							-0.061	-0.162	-0.195	-0.147	0.029
2-MG								**0.609**	**0.644**	**0.588**	**0.832**
C5-alkene triols									**0.934**	**0.968**	**0.747**
2-methyl-threitol										**0.975**	**0.747**
2-methyl-erythritol											**0.740**
HGA											

Values in bold indicate $p<0.01$; OS-organosulfate, NOS-nitrooxy organosulfate, 2-MG-2-Methylglyceric acid

Table S8. Correlation coefficients among terpenoic acids.

m/z	187 C8	173 C7	203 C8	215 C9	189 C7	185 C8	171 C8	189 C7	131 C5	175 C7	185 C9	157 C7	143 C6	215 C10	231 C10	241 C12	255 C13	213 C10	HGA
187C8		**0.988**	**0.959**	**0.857**	**0.916**	**0.935**	**0.879**	**0.952**	**0.696**	**0.925**	**0.675**	0.259	**0.788**	**0.867**	**0.831**	**0.883**	**0.697**	**0.861**	**0.926**
173C7			**0.972**	**0.847**	**0.913**	**0.955**	**0.882**	**0.968**	**0.743**	**0.918**	**0.676**	0.320	**0.810**	**0.894**	**0.866**	**0.875**	**0.713**	**0.891**	**0.932**
203C8				**0.846**	**0.876**	**0.951**	**0.858**	**0.963**	**0.821**	**0.866**	**0.627**	0.302	**0.755**	**0.899**	**0.886**	**0.884**	**0.804**	**0.900**	**0.944**
215C9					**0.760**	**0.790**	**0.745**	**0.839**	**0.621**	**0.774**	**0.578**	0.151	**0.677**	**0.687**	**0.653**	**0.820**	**0.635**	**0.688**	**0.820**
189C8						**0.887**	**0.929**	**0.857**	**0.597**	**0.973**	**0.846**	**0.463**	**0.811**	**0.919**	**0.751**	**0.868**	**0.648**	**0.899**	**0.851**
185C8							**0.886**	**0.917**	**0.740**	**0.888**	**0.690**	**0.378**	**0.731**	**0.912**	**0.868**	**0.815**	**0.703**	**0.921**	**0.881**
171C8								**0.824**	**0.565**	**0.903**	**0.847**	**0.528**	**0.728**	**0.880**	**0.720**	**0.789**	**0.582**	**0.873**	**0.799**
189C7									**0.796**	**0.876**	**0.619**	0.248	**0.839**	**0.846**	**0.825**	**0.872**	**0.736**	**0.827**	**0.957**
131C5										**0.595**	0.334	0.229	**0.640**	**0.758**	**0.814**	**0.666**	**0.802**	**0.741**	**0.827**
175C7											**0.813**	**0.381**	**0.854**	**0.888**	**0.732**	**0.846**	**0.599**	**0.849**	**0.859**
185C9												**0.565**	**0.700**	**0.743**	**0.450**	**0.729**	**0.435**	**0.705**	**0.592**
157C7													**0.390**	**0.527**	0.266	0.276	0.213	**0.537**	0.233
143C6														**0.745**	**0.597**	**0.778**	**0.568**	**0.695**	**0.807**
215C10															**0.867**	**0.828**	**0.750**	**0.969**	**0.852**
231C10																**0.696**	**0.740**	**0.889**	**0.835**
241C12																	**0.843**	**0.806**	**0.860**
255C13																		**0.752**	**0.760**
213C10																			**0.829**
HGA*																			

*HGA: 3-hydroxyglutaric acid
Values in bold indicate $p<0.01$
Only m/z and carbon number are shown

Figure S1. Satellite image of Coweeta sampling site (red outline represents the Coweeta basin).

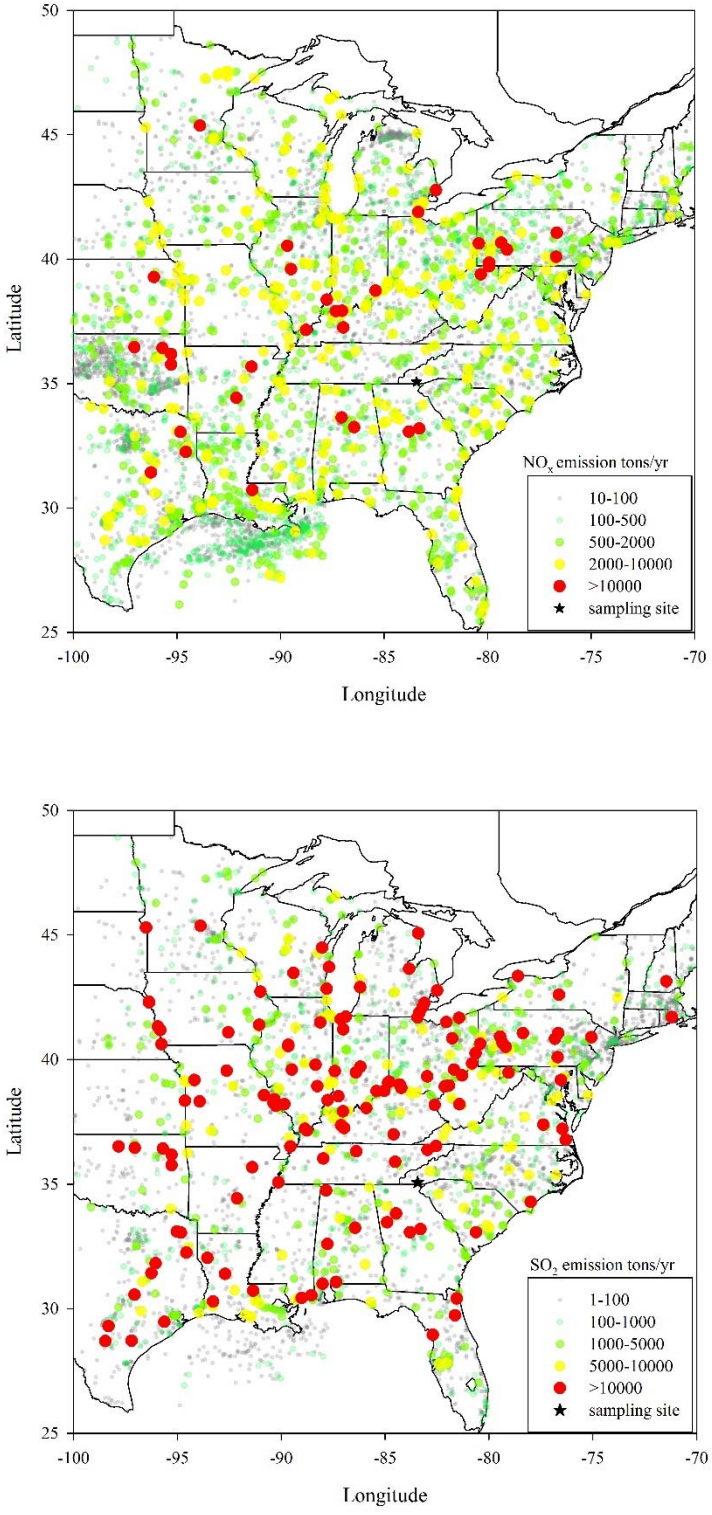

Figure S2. Emission inventories of NOx and SO_2 point sources in the eastern U.S. (2011 EPA National Emissions Inventory).

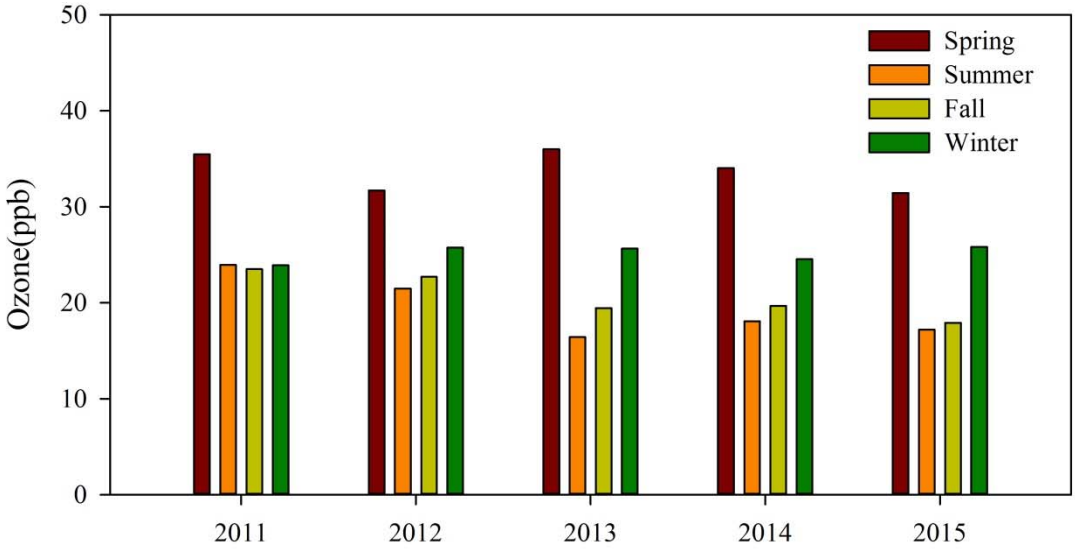

Figure S3. Seasonal ozone average concentrations from 2011 to 2015 at Coweeta sampling site (Spring: March, April and May; Summer: June, July and August; Fall: September, October and November; Winter: December, January and February).

Back trajectory cluster analysis

Backward air mass trajectories were calculated for select periods using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003) with NOAA ARL EDAS 40 km meteorological data. Hourly trajectories for each sampling days were run for 72hr (120hr for regional biomass burning event towards end of October 2015) periods at an arriving height of 1000 m above the ground level. In order to better understand different synoptic circulation patterns, clusters of back trajectories were analyzed (Dorling et al., 1992; Dorling and Davies, 1995). The assignment of individual trajectories to a given cluster was carried out by minimizing the internal variability within the group of trajectories and maximizing the external variability between different groups based on the trajectory co-ordinates. Back trajectories and cluster analysis were computed by HYSPLIT 4. The number of clusters was determined by identifying a sudden change (criterion set at 30%) in the total spatial variance, which is the sum of all the cluster spatial variances.

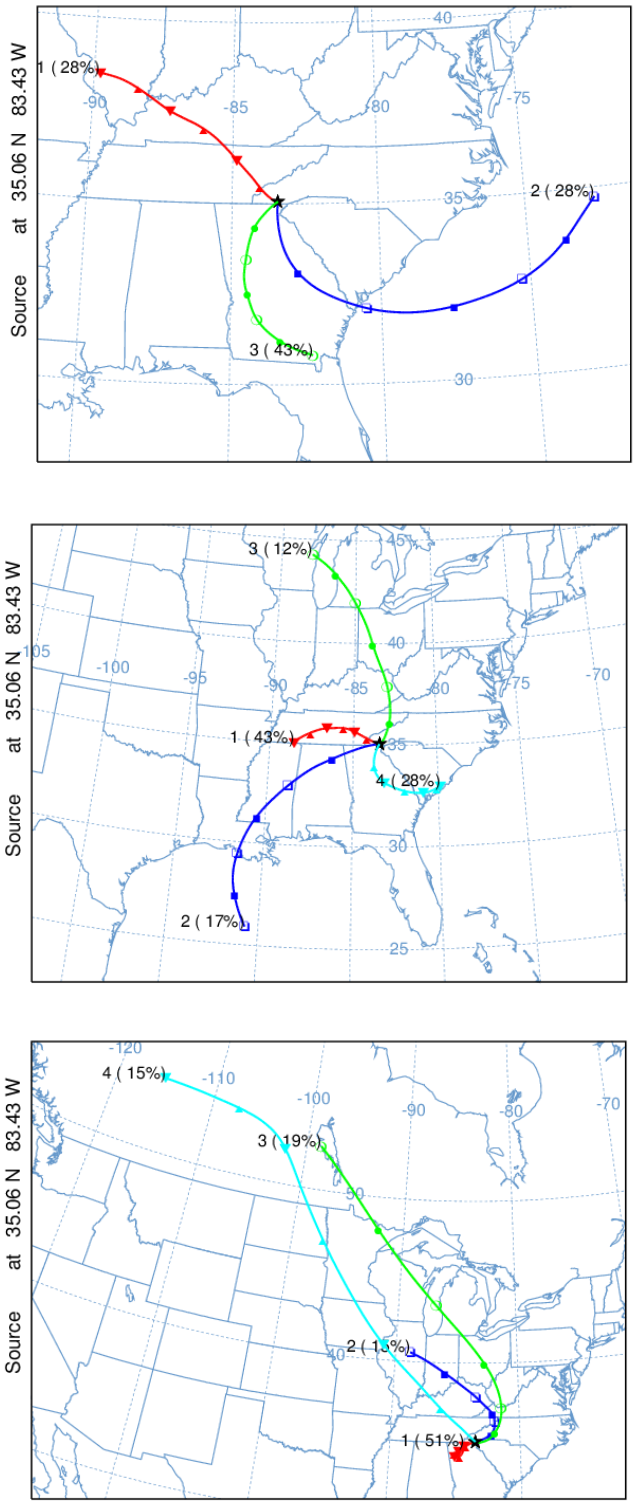

Figure S4. Back trajectory clusters for spring, summer and fall 2015(from top to bottom) at Coweeta for intensive sampling periods.

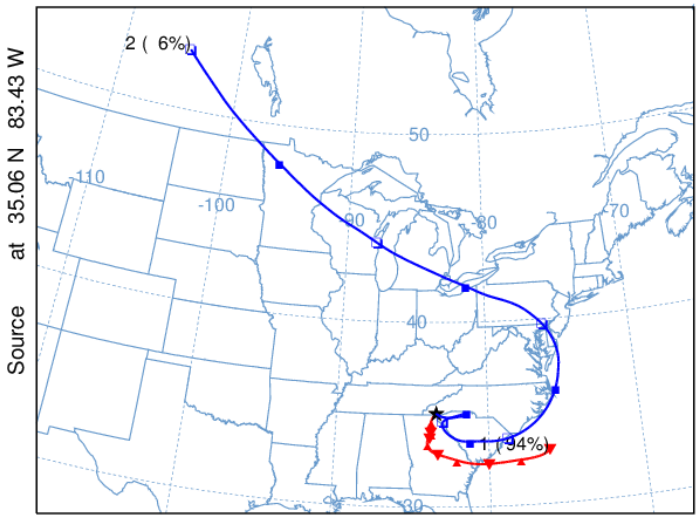

Figure S5. Back trajectory (120hr periods) clusters for regional biomass burning event on October 24th and 25th 2015 at Coweeta.

PMF analysis and results

To identify potential sources or processes related to particulate WSOC and WSON, bulk OC and EC, major inorganic ions (NH_4^+, SO_4^{2-}), organosulfates, nitro-aromatic compounds, terpenoic acids and levoglucosan were included for PMF analysis. Due to the small sample number, organosulfates, nitro-aromatic compounds and terpenoic acids were combined within each group based on the correlation of concentrations and potential sources. Among the 15 inputs species, two isoprene derived organosulfates and three monoterpene derived organosulfates are included. Iso_OS1 represents the combination of $C_5H_{10}O_6S$, $C_4H_8O_7S$ and $C_5H_{12}O_7S$; Iso_OS2 is $C_5H_{11}NO_9S$; Mono_OS1 is the sum of $C_{10}H_{18}O_5S$ and $C_{10}H_{16}O7S$; Mono_OS2 is composed of $C_{10}H_{17}NO_8S$ and $C_{10}H_{17}NO_9S$; Mono_OS3 is $C_{10}H_{17}NO_7S$; Iso_SOA includes methyltetrols, 2-methylglyceric acid and C-5 alkene triols; NitroArom and T_acids represent the sum of all nitro-aromatic compounds and terpenoic acids measured in this work, respectively. The uncertainties associated with each input species were estimated by: $unc = \sqrt{(20\% \times Conc.)^2 + (blk)^2}$

where *Conc.* is the measured concentration of each species and *blk* is the average of the field blank measurements. Due to the low filed blank contamination, each input species has a signal to noise ratio higher than 3. The missing species observation was replaced by the geometric mean of the remaining observations, and the associated uncertainty was set as four times the geometric mean.

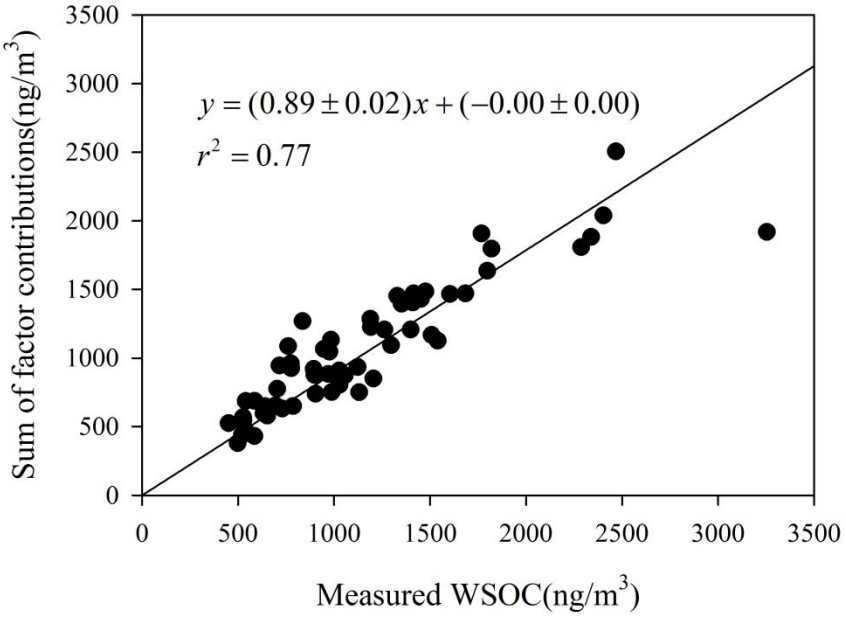

Figure S6. Linear regression between integrated PMF resolved factor contributions and measured WSOC.

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