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Oxidative potential of ambient water-soluble $PM_{2.5}$ in the southeastern United States: contrasts in sources and health associations between ascorbic acid (AA) and dithiothreitol (DTT) assays

Ting Fang et al.

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Semi-automated system for measuring water-soluble DTT activity

Filter extraction: Three punches of the collected Hi-Vol filter (5.07 cm^2 each) were extracted in 15 mL of deionized (DI) water (> 18 MΩ cm^{-1}) in a sterile polypropylene centrifuge tube (VWR International LLC, Suwanee, GA, USA) by sonication using an Ultrasonic Cleanser (VWR International LLC, West Chester, PA, USA) for half an hour. Extracts were then filtered using PTFE 0.45 µm syringe filters (Fisherbrand™) to remove insoluble materials.

DTT determination: The DTT assay was based on the protocol developed by Cho et al.[1] and the semi-automated DTT system has been described in detail in Fang et al.[2]. In brief, 3.5 mL of the aerosol extract, 1 mL potassium phosphate buffer (Kbuffer, 0.5 mM), and 0.5 mL of DTT solution (1mM) were incubated at 37 °C in a continuously mixed vial (400 rpm in a ThermoMixer (Eppendorf North America, Inc., Hauppauge, NY, USA)). At five time intervals (4, 13, 23, 30, and 41 min), a small aliquot (100 µL) of the incubated mixture was drawn to another vial and the DTT oxidation was quenched by adding 1 mL 1% w/v Trichloroacetic acid (TCA). 0.5 mL of a color developing agent DTNB [5,5'-dithiobis-(2-nitrobenzoic acid), 0.2 mM], with 2 mL of Tris buffer (0.08 M with 4 mM EDTA), was added to form a light absorbing product, which has a high extinction coefficient at 412 nm wavelength. Light absorbance at 412 nm and 700 nm (chosen as a baseline) for each time interval was recorded and used to calculate the consumption rate of DTT over time (nmol min^{-1}). Final DTT activity was reported as DTT consumption rate per unit of air volume (nmol min^{-1} m^{-3}), or per unit of PM mass (nmol min^{-1} μg^{-1}). The automated system was cleaned periodically (typically every 15 days) by flushing at least 3 times with methanol and then 6 times with DI water. Sample selection, various chemical reagent addition and withdrawal, and system self-cleaning were all achieved automatically by programmable syringe pumps (see details in section 2.2 AA determination).

Final DTT activity is calculated as follows:

$$\sigma DTT = -\sigma Abs \times \frac{N_0}{Abs_0} \text{ (Eq. 1)},$$

$$DTT = \frac{\sigma DTT_s - \sigma DTT_b}{\frac{V_a}{V_e} \times V_p} \text{ (Eq. 2)},$$

where σAbs is the slope of absorbance (412nm – 700nm) versus time; Abs_0 is the initial absorbance calculated from the intercept of linear regression of absorbance versus time; N_0 is the initial moles of DTT added in the reaction (500 nmol); σDTT_s (σDTT_b) is the rate of DTT consumption for sample (blank); V_e and V_a are the extraction volume (15 mL) and actual sample volume added to the reaction vial (3.5 mL, i.e., what was actually analyzed), respectively. V_p is the ambient air volume (m^3) represented by the sample in the extraction volume (V_e, i.e., considering the filter integration time and fraction of filter analyzed). DTT represents volume normalized DTT activity, in units of nmol min^{-1} m^{-3}.

Water-soluble elements

Filter preparation protocol is the same as described above in section 2.2 in the main text, except that four punches were extracted in 15 mL of DI water, and after filtering, 120 µL of high purity HNO_3 (OmniTrace® Ultra Nitric Acid, 67 - 70%, EMD Millipore Corporation, Billerica, MA, USA) was then added to 6 mL of the extract (resulting pH ≈ 0.7) to ensure the suspension of all dissolved metals. Details of the method are described in Fang et al.[3]. In brief, 5 mL of acidified sample was aerosolized using a continuous flow ultrasonic nebulizer (CETAC U5000 AT+, CETAC Technologies, Omaha, NE, USA) and directed through an evaporator at 136 °C followed by a condenser at 3 °C. The dry aerosolized sample was then neutralized by a Kr-85 ion source (Model 3077A, TSI), mixed with filtered make-up air (final flow rate = 16.7 L min^{-1}, Pall HEPA Capsule), and directed to an online aerosol element analyzer (Xact, Cooper Environmental) for X-ray fluorescence (XRF) analysis.

$PM_{2.5}$ mass

$PM_{2.5}$ mass concentration was 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[4]; water-soluble metals, and ammonium sulfate (assuming sulfate and ammonium are all $(NH_4)_2SO_4$[5], where sulfate was calculated from sulfur from XRF analysis (section 2.3.2).

Codes for health outcomes used in the epidemiological models

The health outcomes in the epidemiological models are asthma or wheeze with a primary International Classification of Disease, 9th Revision, (ICD-9) code of 493 and 786.07, congestive heart failure (428), chronic obstructive pulmonary disease (491, 492, 496), cardiovascular disease (410-414, 427, 428, 433-437, 440, 443-445, 451-453), ischemic heart disease (410-414), and pneumonia (480-486) for a patient with a home ZIP code within the Atlanta 5-county metro area (Fulton, DeKalb, Gwinnett, Cobb, Clayton) recorded in an Atlanta hospital from 8/1/1998 through 12/31/2009.

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

Month Year	Season	Anchor 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.

Table S2. Water-soluble AA and DTT activity correlations (Pearson's r) with water-soluble species in $PM_{2.5}$

	Site-Month. Year	BrC	WSOC	PM	S	K	Ca	Ti	Mn	Fe	Cu	Zn	As	Se	Br	Sr	Ba	Pb	DTT
	JST-June 2012	0.58	0.59	0.59	0.47	0.23	0.35	0.58	0.41	0.64	**0.91**	0.52	**0.74**	0.49	0.36	0.37	0.52	0.42	0.57
	JST-Aug. 2012	0.43	0.36	0.08	0.32	0.32	0.04	0.59	**0.65**	0.60	**0.74**	0.23	0.37	0.30	0.56	0.30	0.61	0.43	0.52
	JST-Sept. 2012	**0.69**	0.60	0.34	0.19	0.26	-0.20	0.48	0.26	0.58	**0.82**	0.54	**0.71**	0.23	0.21	0.16	0.34	0.47	0.45
	JST- Dec. 2012	0.42	**0.65**	0.56	-0.12	**0.70**	0.24	0.36	0.28	**0.66**	**0.81**	0.66	0.64	0.27	0.28	0.35	0.60	0.49	**0.70**
	JST-Feb. 2013	0.38	0.30	0.36	0.16	0.18	-0.21	-0.15	-0.06	0.14	0.29	-0.09	0.02	0.25	0.34	-0.15	-0.18	0.32	0.49
	JST-March 2013	-0.03	-0.03	-0.17	0.01	0.19	-0.08	-0.15	0.02	0.30	**0.78**	0.23	0.24	0.14	-0.30	-0.13	0.08	0.26	0.10
	GT-Aug. 2012	0.57	0.10	0.58	0.55	0.41	0.12	0.44	0.10	**0.77**	**0.75**	0.13	0.61	0.51	0.49	0.03	0.38	0.16	0.62
	GT-March 2013	0.43	0.47	0.40	0.05	0.37	0.06	0.05	0.37	0.36	0.63	0.36	0.03	0.40	0.31	-0.01	0.38	0.16	0.54
AA	GT-Sept 2013	0.18	0.08	0.27	0.10	0.32	0.27	0.38	0.37	0.35	0.52	0.18	0.17	0.07	0.33	0.10	0.45	0.07	0.39
	RS-Sept.2012	0.42	0.25	0.52	0.10	**0.72**	0.55	0.27	**0.82**	0.28	0.15	0.25	-0.29	0.17	0.28	**0.71**	0.49	-0.16	0.51
	RS-Feb.2013	0.22	0.13	-0.15	0.01	0.15	-0.07	0.17	-0.08	-0.05	**0.94**	0.14	-0.03	0.01	-0.04	0.12	0.14	-0.14	0.25
	RS-Sept 2013	0.26	0.18	0.08	0.37	0.58	0.43	0.52	0.54	0.56	**0.74**	0.50	0.33	0.21	0.67	0.06	0.62	0.40	0.13
	YRK-June.2012	0.18	0.06	0.05	-0.02	0.24	-0.22	-0.23	-0.31	0.00	**0.70**	0.11	0.02	0.06	0.27	-0.25	-0.24	0.17	0.14
	YRK-Dec.2012	0.38	0.12	0.58	0.60	0.07	-0.35	0.04	-0.10	0.29	**0.84**	0.09	0.27	0.39	0.10	-0.28	-0.04	0.54	0.49
	BHM-June 2013	0.32	0.47	0.32	0.11	0.46	0.42	0.15	0.43	0.16	**0.80**	0.24	-0.01	-0.04	0.09	0.19	0.08	-0.04	0.52
	CTR-June 2013	0.18	0.22	-0.12	0.09	0.12	-0.07	0.03	-0.29	0.14	**0.75**	0.47	0.27	0.15	0.19	-0.41	-0.24	0.38	0.10
	ESL-Aug 2013	0.32	0.27	0.15	0.08	0.17	-0.16	0.09	0.32	0.23	0.32	0.44	0.18	0.31	0.17	-0.14	0.00	0.20	0.43
	JST-June 2012	**0.77**	**0.91**	**0.85**	**0.74**	**0.71**	0.59	**0.66**	0.63	0.62	0.53	0.58	0.36	**0.69**	**0.72**	0.50	0.49	0.61	1
	JST-Aug. 2012	**0.66**	0.62	**0.80**	**0.77**	0.48	0.06	**0.68**	**0.77**	**0.90**	**0.79**	0.59	0.42	**0.74**	**0.79**	0.36	**0.65**	**0.71**	1
	JST-Sept. 2012	**0.73**	**0.65**	**0.80**	0.14	0.30	-0.23	0.53	0.52	**0.74**	0.13	**0.82**	0.13	0.20	0.28	0.10	0.55	0.27	1
	JST- Dec. 2012	**0.81**	**0.78**	**0.75**	0.07	**0.73**	0.51	0.55	0.54	**0.79**	0.63	**0.82**	**0.67**	0.43	0.38	0.39	**0.73**	0.59	1
	JST-Feb. 2013	**0.70**	**0.65**	**0.84**	**0.70**	**0.71**	0.25	-0.02	0.33	**0.70**	0.37	0.30	0.19	**0.66**	**0.77**	0.16	0.13	**0.75**	1
	JST-March 2013	**0.88**	0.63	**0.77**	0.05	**0.67**	0.26	0.63	0.51	0.57	0.36	0.58	**0.78**	**0.69**	0.44	0.44	0.58	0.52	1
	GT-Aug. 2012	0.37	0.38	0.63	0.59	0.53	0.00	0.26	0.60	**0.77**	**0.67**	0.62	0.54	0.52	0.45	0.35	0.53	0.09	1
	GT-March 2013	**0.83**	0.49	**0.88**	0.34	**0.78**	0.11	0.23	**0.71**	**0.84**	**0.83**	**0.70**	0.61	**0.74**	0.61	0.33	0.63	0.36	1
DTT	GT-Sept 2013	**0.75**	0.47	0.61	0.30	**0.65**	0.29	0.34	0.58	**0.66**	0.46	0.36	0.22	0.20	0.50	0.15	0.38	0.23	1
	RS-Sept.2012	0.59	0.51	**0.86**	0.50	0.52	0.12	0.51	0.27	0.44	0.61	0.55	-0.06	0.39	0.61	0.36	0.56	0.35	1
	RS-Feb.2013	**0.86**	0.71	**0.79**	-0.03	**0.69**	0.23	0.32	0.49	0.57	-0.11	0.60	0.63	0.33	0.57	0.20	0.34	0.34	1
	RS-Sept 2013	0.48	0.20	0.49	**0.66**	0.53	**0.77**	0.09	**0.75**	0.53	0.21	0.32	-0.13	0.41	0.64	0.16	0.29	-0.51	1
	YRK-June.2012	0.53	**0.74**	0.59	**0.74**	0.60	**0.67**	0.23	0.61	0.47	0.32	0.61	0.36	**0.67**	0.59	**0.73**	0.19	0.56	1
	YRK-Dec.2012	**0.88**	**0.84**	**0.77**	0.38	**0.74**	0.36	0.31	**0.71**	**0.69**	0.50	**0.76**	0.39	**0.83**	**0.73**	0.32	0.49	**0.74**	1
	BHM-June 2013	**0.74**	0.59	**0.74**	**0.66**	0.42	0.58	0.29	**0.65**	**0.68**	0.25	0.54	0.45	0.60	**0.69**	0.27	0.21	0.49	1
	CTR-June 2013	**0.87**	**0.77**	**0.66**	0.64	**0.66**	0.41	0.36	0.34	0.43	-0.25	0.60	0.47	0.62	0.62	0.03	0.12	0.61	1
	ESL-Aug 2013	0.16	0.38	0.57	0.47	0.48	0.27	0.17	0.44	0.40	**0.68**	0.35	0.52	0.41	0.51	0.25	0.44	0.36	1

r>0.65 in red and bold; Data below LOD was replaced by half of LOD values.

Table S3. Water-soluble AA and DTT regressions with all CMB-E sources, with only signicicant (positive) sources, and with only signicicant (positive) sources without AMSULF

	Regressions		Intercept	LDGV	HDDV	SDUST	BURN	AMSULF	AMBSLF	AMNITR	OTHER_OC	*r
AA	All sources	Coefficient	0.19 ± 0.059	0.31 ± 0.046	0.28 ± 0.062	-0.020 ± 0.029	-0.098 ± 0.029	0.078 ± 0.020	0.018 ± 0.032	-0.088 ± 0.039	0.060 ± 0.020	0.71
		p-value	<0.01	<0.01	<0.01	0.50	<0.01	<0.01	0.59	0.03	<0.01	
	Significant sources	Coefficient	0.17 ± 0.055	0.32 ± 0.044	0.32 ± 0.060		-0.14 ± 0.023	0.076 ± 0.019		-0.077 ± 0.035	0.072 ± 0.019	0.69
		p-value	<0.01	<0.01	<0.01		<0.01	<0.01		0.03	<0.01	
	Significant positive sources	Coefficient	0.079 ± 0.058	0.19 ± 0.043	0.23 ± 0.064			0.063 ± 0.021			0.075 ± 0.075	0.60
		p-value	0.18	<0.01	<0.01			<0.01			<0.01	
	Significant positive sources without AMSULF	Coefficient	0.18 ± 0.047	0.19 ± 0.044	0.24 ± 0.066						0.083 ± 0.022	0.57
		p-value	<0.01	<0.01	<0.01						<0.01	
DTT	All sources	Coefficient	0.050 ± 0.025	0.11 ± 0.021	0.038 ± 0.028	0.012 ± 0.012	0.065 ± 0.012	0.023 ± 0.009	0.015 ± 0.016	-0.001 ± 0.017	0.004 ± 0.010	0.69
		p-value	0.048	<0.01	0.17	0.32	<0.01	0.011	0.35	0.94	0.68	
	Significant sources	Coefficient	0.067 ± 0.02	0.11 ± 0.02	0.045 ± 0.024		0.063 ± 0.01	0.022 ± 0.01				0.68
		p-value	<0.01	<0.01	0.07		<0.01	0.01				
	Significant sources without AMSULF	Coefficient	0.095 ± 0.018	0.11 ± 0.020	0.052 ± 0.024		0.069 ± 0.010					0.67
		p-value	<0.01	<0.01	0.04		<0.01					

*- r value represents the correlations between measured and predicted data.

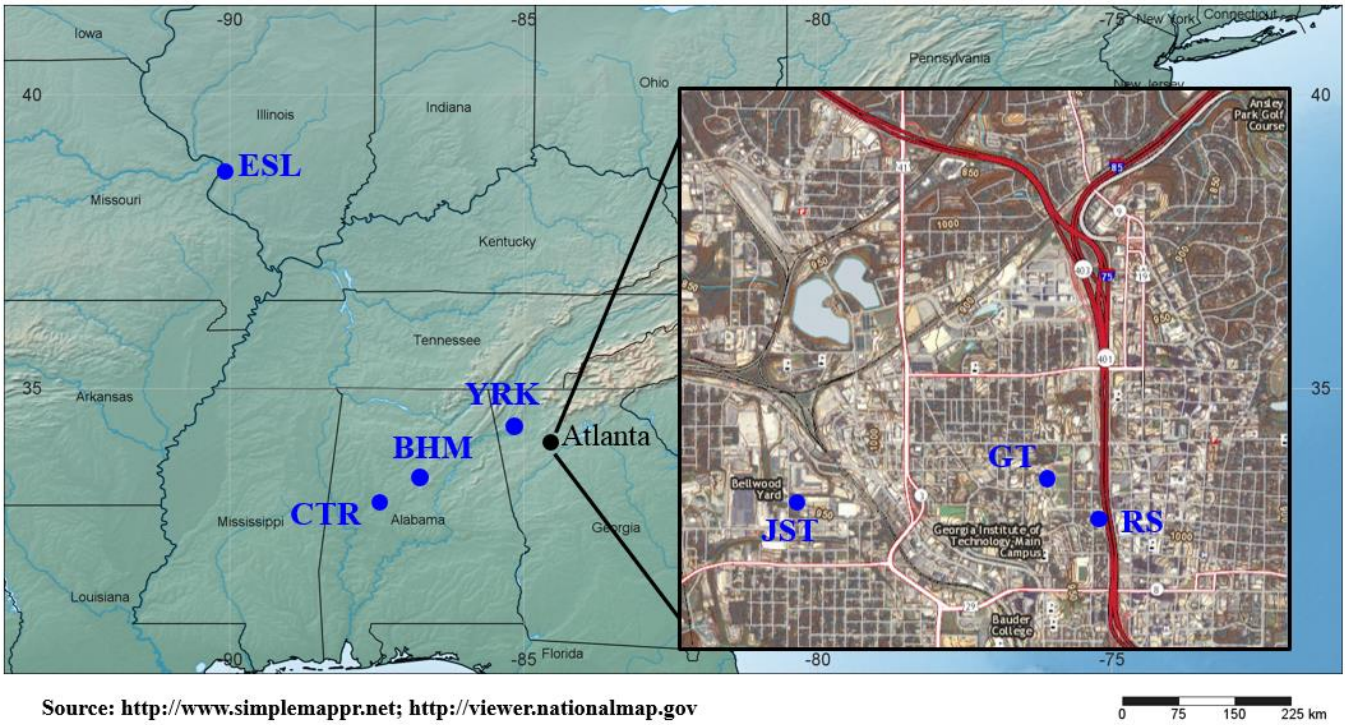
The sources are light-duty gasoline vehicles (LDGV), heavy-duty diesel vehicles (HDDV), soil dust (SDUST), biomass burning (BURN), ammonium sulfate (AMSULF), ammonium bisulfate (AMBSLF), ammonium nitrate (AMNITR), and other organic carbon (OTHER_OC) which mostly contains biogenic carbon.

Table S4. Risk ratios (95% confidence interval for interquartile range) and p-values for backcast-estimated AA and DTT activities (1998-2009) from the epidemiological analyses on asthma/wheeze, congestive heart failure (CHF), Chronic obstructive pulmunary disease (COPD), Ischemic heart disease (IHD), and Pneumonia

	Regressions	Asthma/wheeze (AS_WHZ)		Congestive heart failure (CHF)	
		Lag 0-2		Lag 0-2	
AA	**All sources**	0.999 (0.997-1.002)	p=0.64	0.998 (0.994-1.002)	p=0.29
	Significant positive sources	1.005 (0.994-1.015)	p=0.38	1.003 (0.986-1.020)	p=0.74
	Significant positive sources without AMSULF	1.008 (0.999-1.017)	p=0.07	1.005 (0.990-1.020)	p=0.50
DTT	**All sources**	1.009 (1.000-1.018)	p=0.04	1.014 (1.000-1.028)	p=0.05
	Significant positive sources	1.009 (1.001-1.018)	p=0.04	1.015 (1.000-1.029)	p=0.04
	Significant positive sources without AMSULF	1.014 (1.004-1.023)	p=0.01	1.019 (1.004-1.035)	p=0.01

	Regressions	Chronic obstructive pulmonary disease (COPD)		Ischemic heart disease (IHD)		Pneumonia	
		Lag 0-2		Lag 0-2		Lag 0-2	
AA	**All sources**	0.997 (0.992-1.002)	p=0.25	0.996 (0.993-1.000)	p=0.05	0.998 (0.995-1.001)	p=0.18
	Significant positive sources	1.010 (0.992-1.028)	p=0.29	0.991 (0.976-1.006)	p=0.25	0.996 (0.985-1.006)	p=0.38
	Significant positive sources without AMSULF	0.996 (0.979-1.013)	p=0.63	0.989 (0.975-1.003)	p=0.11	0.992 (0.982-1.002)	p=0.13
DTT	**All sources**	1.008 (0.991-1.025)	p=0.35	0.989 (0.975-1.002)	p=0.10	0.997 (0.987-1.006)	p=0.50
	Significant positive sources	0.996 (0.976-1.016)	p=0.67	0.983 (0.967-0.998)	p=0.03	0.994 (0.982-1.006)	p=0.29
	Significant positive sources without AMSULF	1.007 (0.990-1.024)	p=0.40	0.989 (0.976-1.002)	p=0.11	0.997 (0.988-1.007)	p=0.57

The AA and DTT activities were estimated from three different linear regressions including all sources from CMB-E, statistically significant (p of F-statistic of coefficient<0.05) sources with positive coefficients, and significant positive sources without AMSULF (ammonium sulfate).



Source: http://www.simplemappr.net; http://viewer.nationalmap.gov

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.

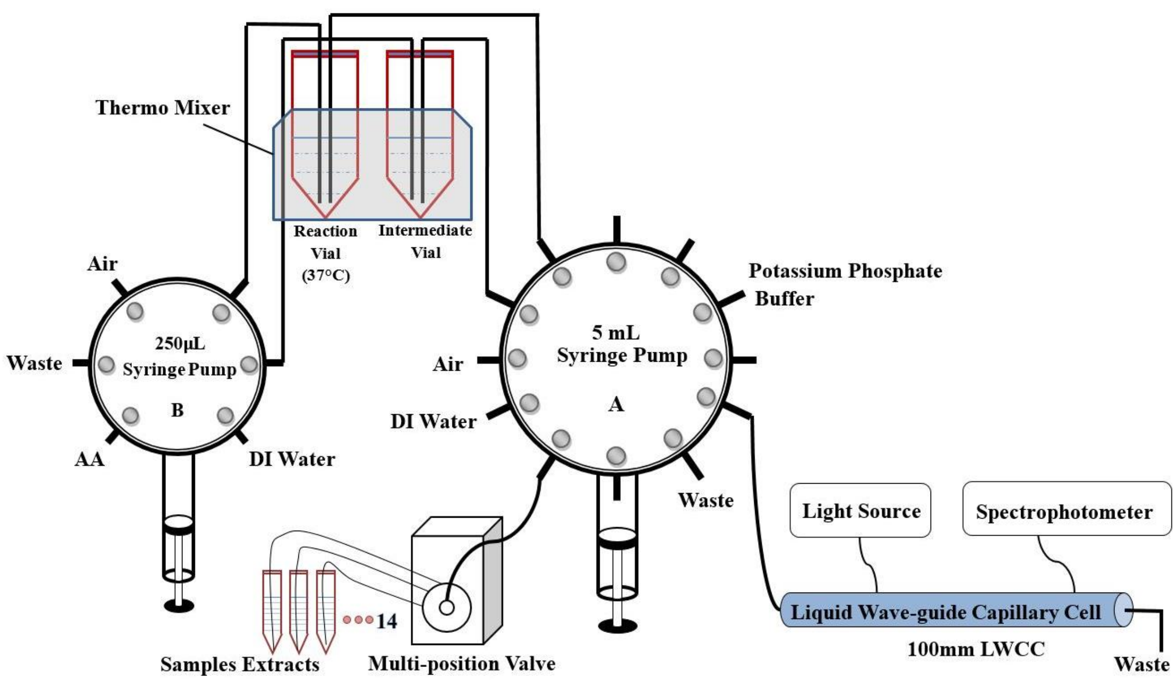


Figure S2. Semi-automated system setup for Ascorbic Acid activities determination

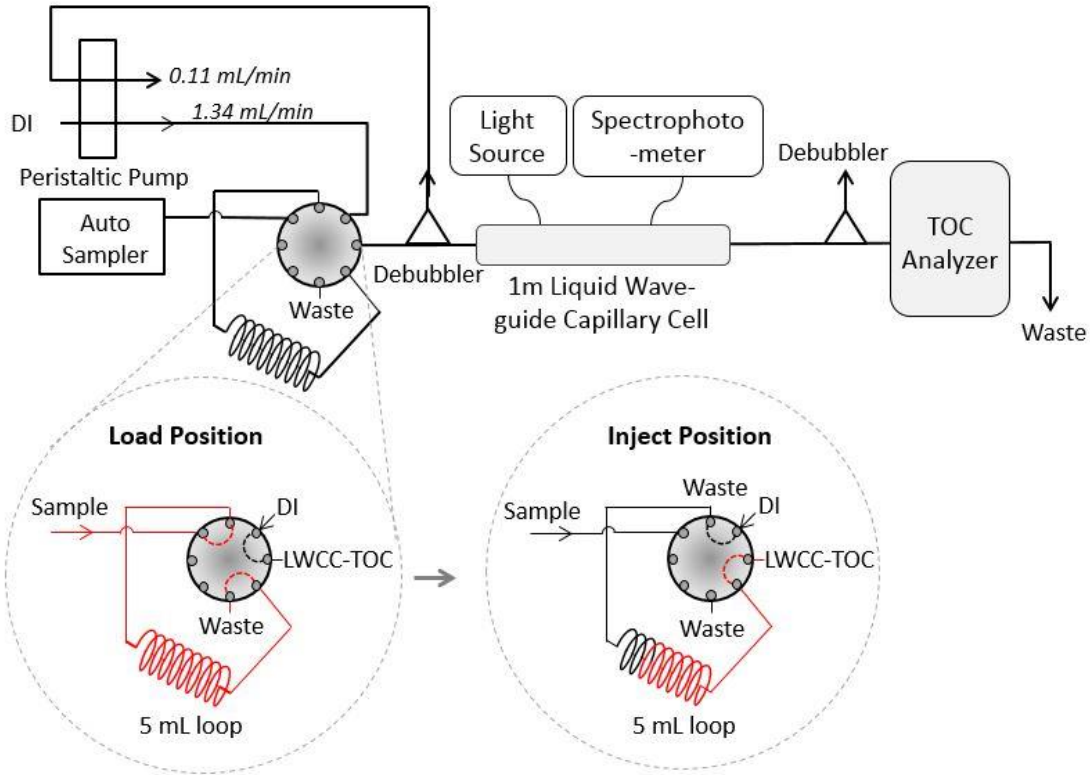


Figure S3. Automated system that utilized an auto-sampler (AS40, DIONEX Corporation, Sunnyvale, CA, USA), a SelectPro two-position fluid processor valve (Alltech, Deerfield, IL, USA), and a peristaltic pump (Ismatec, Cole-Parmer Instrument Company, Vernon Hills, IL, USA) for measuring water-soluble organic carbon (WSOC) and brown carbon (BrC) from aqueous extracts.

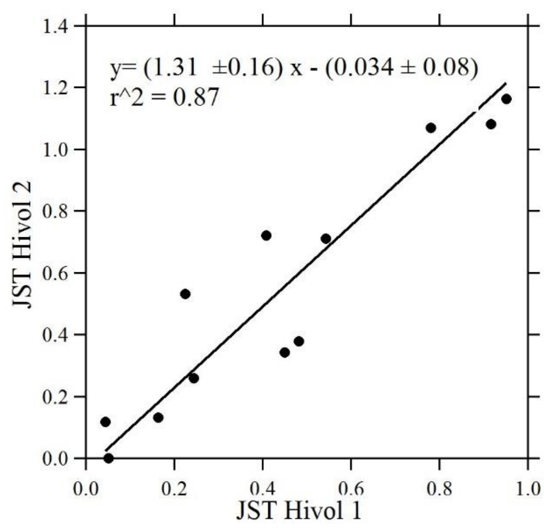


Figure S4. Collocated measurements using two Hi-Vol samplers deployed at JST during November 2012 (Analysis was done by orthogonal regression.)

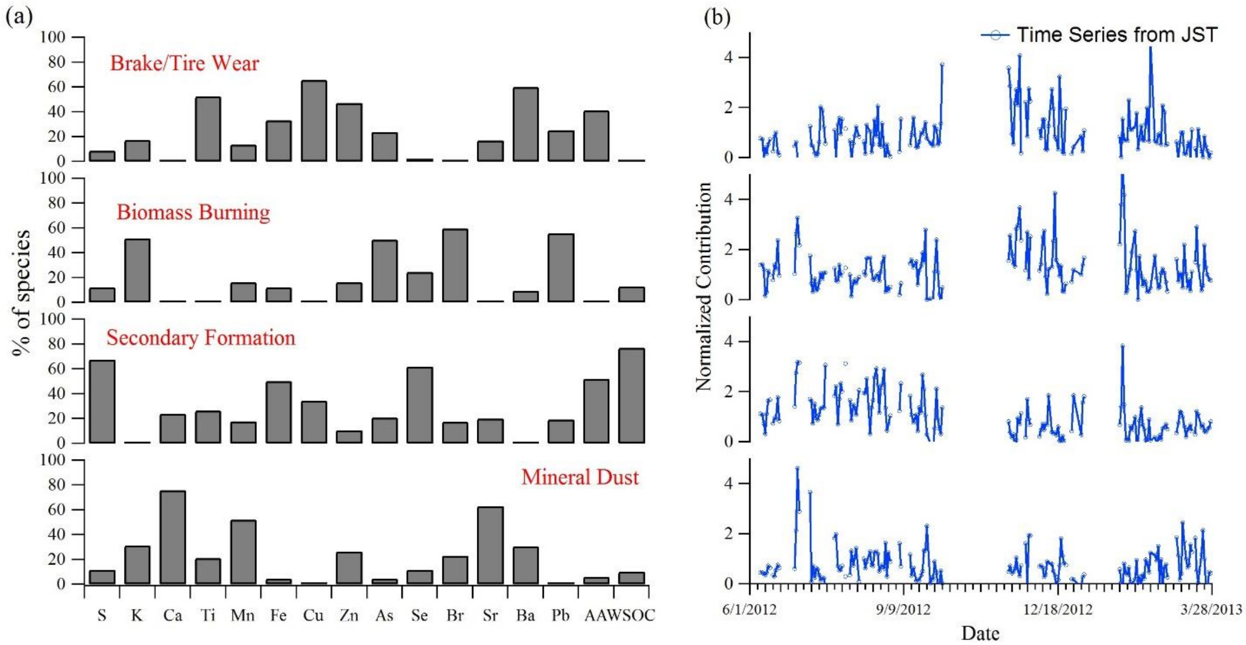


Figure S5. Loading of various water-soluble species and AA activity into various factors resolved by PMF analyses for all Atlanta urban sites (JST, GT, and RS) (a) and factors' time series (b) from the JST site.

Hardware and software details of the Kloehn Control syringe pumps (Kloehn, Inc., Las Vegas, Nevada, USA):

Pump A:

VersaPump 6, 48k resolution drive pump (P/N 55022);

12-way distribution rotary valve (P/N 24105);

5 mL syringe (P/N 17599);

Pump B:

VersaPump 3, 12k resolution drive pump (P/N 23254);

6-way distribution valve (P/N 23327);

250 µL syringe (P/N 23166);

Software: Kloehn Control version 1.04.

Kloehn Control program code for conducting the AA method (Address 2 - pump A**;** Address 1 - pump B)**:**

Line	Line Label	Address	Command	Command Data
1		2	CONSTANT <varName> = <float>	dILarge,12
2		2	CONSTANT <varName> = <float>	AirLarge,5
3		2	CONSTANT <varName> = <float>	WasteLarge,6
4		2	CONSTANT <varName> = <float>	Kbuffer,2
5		2	CONSTANT <varName> = <float>	LWCC,9
6		2	CONSTANT <varName> = <float>	Sample,7
7		2	CONSTANT <varName> = <float>	IVLarge,4
8		2	CONSTANT <varName> = <float>	RVLarge,3
9		2	CONSTANT <varName> = <float>	BVLarge, 1
10		1	CONSTANT <varName> = <float>	dISmall,6
11		1	CONSTANT <varName> = <float>	AirSmall,4
12		1	CONSTANT <varName> = <float>	WasteSmall,5
13		1	CONSTANT <varName> = <float>	AA,3
14		1	CONSTANT <varName> = <float>	IVSmall,2
15		1	CONSTANT <varName> = <float>	RVSmall,1
16				
17				
18	HomePosition	2	SET out2 = <bit>	1
19		2	SET out2 = <bit>	0
20		2	SET out2 = <bit>	1
21		2	SET out1 = <bit>	1

22				
23	PreloadKbuffer	2	VALVE_PORT = <int> [CCW]	Kbuffer
24		2	SET speed = <float>	400
25		2	POSITION <float> [IMM or SYNC]	1000
26		2	VALVE_PORT = <int> [CCW]	WasteLarge
27		2	POSITION <float> [IMM or SYNC]	0
28				
29	PreloadAA	1	VALVE_PORT = <int> [CCW]	AA
30		1	SET speed = <float>	30
31		1	POSITION <float> [IMM or SYNC]	250
32		1	VALVE_PORT = <int> [CCW]	WasteSmall
33		1	POSITION <float> [IMM or SYNC]	0
34				
35				
36	CleanLarge+Small		DO	
37		2	VALVE_PORT = <int> [CCW]	dILarge
38		2	SET speed = <float>	400
39		2	POSITION <float> [IMM or SYNC]	5000
40		2	VALVE_PORT = <int> [CCW]	WasteLarge
41		2	POSITION <float> [IMM or SYNC]	0
42		1	VALVE_PORT = <int> [CCW]	dISmall
43		1	POSITION <float> [IMM or SYNC]	250
44		1	VALVE_PORT = <int> [CCW]	WasteSmall
45		1	POSITION <float> [IMM or SYNC]	0
46			LOOP <int>	2
47				
48			DO	
49	ChangeSample	2	SET out1 = <bit>	0
50		2	SET out1 = <bit>	1
51				
52	MixSample	2	VALVE_PORT = <int> [CCW]	Sample
53		2	SET speed = <float>	300
54		2	POSITION <float> [IMM or SYNC]	5000
55		2	DELAY <float>	1
56		2	VALVE_PORT = <int> [CCW]	Sample
57		2	POSITION <float> [IMM or SYNC]	0
58			DO	
59		2	VALVE_PORT = <int> [CCW]	AirLarge
60		2	SET speed = <float>	400
61		2	POSITION <float> [IMM or SYNC]	5000
62		2	VALVE_PORT = <int> [CCW]	Sample
63		2	SET speed = <float>	800
64		2	POSITION <float> [IMM or SYNC]	0
65			LOOP <int>	3

66				
67	PreLoad Sample	2	VALVE_PORT = <int> [CCW]	Sample
68		2	SET speed = <float>	200
69		2	POSITION <float> [IMM or SYNC]	1000
70		2	DELAY <float>	1
71		2	VALVE_PORT = <int> [CCW]	WasteLarge
72		2	POSITION <float> [IMM or SYNC]	0
73				
74				
75	LoadReactionVial	2	VALVE_PORT = <int> [CCW]	Kbuffer
76		2	POSITION <float> [IMM or SYNC]	300
77		2	VALVE_PORT = <int> [CCW]	RVLarge
78		2	POSITION <float> [IMM or SYNC]	0
79		2	VALVE_PORT = <int> [CCW]	Sample
80		2	SET speed = <float>	200
81		2	POSITION <float> [IMM or SYNC]	2400
82		2	DELAY <float>	1
83		2	VALVE_PORT = <int> [CCW]	RVLarge
84		2	SET speed = <float>	400
85		2	POSITION <float> [IMM or SYNC]	0
86		2	VALVE_PORT = <int> [CCW]	RVLarge
87		2	SET speed = <float>	800
88		2	POSITION <float> [IMM or SYNC]	3000
89		2	VALVE_PORT = <int> [CCW]	RVLarge
90		2	POSITION <float> [IMM or SYNC]	0
91		2	VALVE_PORT = <int> [CCW]	AirLarge
92		2	POSITION <float> [IMM or SYNC]	1000
93		2	VALVE_PORT = <int> [CCW]	RVLarge
94		2	POSITION <float> [IMM or SYNC]	0
95				
96	Draw1	1	VALVE_PORT = <int> [CCW]	RVSmall
97		1	POSITION <float> [IMM or SYNC]	250
98		1	VALVE_PORT = <int> [CCW]	WasteSmall
99		1	POSITION <float> [IMM or SYNC]	0
100		1	VALVE_PORT = <int> [CCW]	RVSmall
101		1	POSITION <float> [IMM or SYNC]	250
102		1	VALVE_PORT = <int> [CCW]	RVSmall
103		1	POSITION <float> [IMM or SYNC]	200
104		1	VALVE_PORT = <int> [CCW]	IVSmall
105		1	POSITION <float> [IMM or SYNC]	110
106		1	VALVE_PORT = <int> [CCW]	RVSmall
107		1	POSITION <float> [IMM or SYNC]	0
108		1	VALVE_PORT = <int> [CCW]	AirSmall
109		1	POSITION <float> [IMM or SYNC]	250

110		1	VALVE_PORT = <int> [CCW]	RVSmall
111		1	POSITION <float> [IMM or SYNC]	0
112		1	VALVE_PORT = <int> [CCW]	dISmall
113		1	POSITION <float> [IMM or SYNC]	250
114		1	VALVE_PORT = <int> [CCW]	WasteSmall
115		1	POSITION <float> [IMM or SYNC]	0
116		1	VALVE_PORT = <int> [CCW]	dISmall
117		1	POSITION <float> [IMM or SYNC]	250
118		1	VALVE_PORT = <int> [CCW]	IVSmall
119		1	POSITION <float> [IMM or SYNC]	0
120		1	VALVE_PORT = <int> [CCW]	dISmall
121		1	POSITION <float> [IMM or SYNC]	250
122		1	VALVE_PORT = <int> [CCW]	IVSmall
123		1	POSITION <float> [IMM or SYNC]	0
124				
125	DiluteTo3mL1	2	VALVE_PORT = <int> [CCW]	dILarge
126		2	SET speed = <float>	400
127		2	POSITION <float> [IMM or SYNC]	3500
128		2	VALVE_PORT = <int> [CCW]	WasteLarge
129		2	POSITION <float> [IMM or SYNC]	0
130		2	VALVE_PORT = <int> [CCW]	dILarge
131		2	POSITION <float> [IMM or SYNC]	3500
132		2	VALVE_PORT = <int> [CCW]	WasteLarge
133		2	POSITION <float> [IMM or SYNC]	0
134		2	VALVE_PORT = <int> [CCW]	dILarge
135		2	POSITION <float> [IMM or SYNC]	2410
136		2	VALVE_PORT = <int> [CCW]	IVLarge
137		2	POSITION <float> [IMM or SYNC]	0
138		2	VALVE_PORT = <int> [CCW]	IVLarge
139		2	POSITION <float> [IMM or SYNC]	3000
140		2	VALVE_PORT = <int> [CCW]	IVLarge
141		2	POSITION <float> [IMM or SYNC]	0
142		2	VALVE_PORT = <int> [CCW]	AirLarge
143		2	SET speed = <float>	800
144		2	POSITION <float> [IMM or SYNC]	1000
145		2	VALVE_PORT = <int> [CCW]	IVLarge
146		2	POSITION <float> [IMM or SYNC]	0
147		2	VALVE_PORT = <int> [CCW]	IVLarge
148		2	POSITION <float> [IMM or SYNC]	3000
149		2	VALVE_PORT = <int> [CCW]	IVLarge
150		2	POSITION <float> [IMM or SYNC]	0
151		2	VALVE_PORT = <int> [CCW]	AirLarge
152		2	POSITION <float> [IMM or SYNC]	1000
153		2	VALVE_PORT = <int> [CCW]	IVLarge

154		2	POSITION <float> [IMM or SYNC]	0
155				
156	IVtoLWCC1	2	VALVE_PORT = <int> [CCW]	IVLarge
157		2	SET speed = <float>	400
158		2	POSITION <float> [IMM or SYNC]	3000
159		2	VALVE_PORT = <int> [CCW]	WasteLarge
160		2	POSITION <float> [IMM or SYNC]	2000
161		2	SET speed = <float>	100
162		2	VALVE_PORT = <int> [CCW]	LWCC
163		2	POSITION <float> [IMM or SYNC]	500
164		2	VALVE_PORT = <int> [CCW]	WasteLarge
165		2	SET speed = <float>	400
166		2	POSITION <float> [IMM or SYNC]	0
167				
168	RinseIV1	2	VALVE_PORT = <int> [CCW]	IVLarge
169		2	SET speed = <float>	700
170		2	POSITION <float> [IMM or SYNC]	1000
171		2	VALVE_PORT = <int> [CCW]	WasteLarge
172		2	POSITION <float> [IMM or SYNC]	0
173			DO	
174		1	VALVE_PORT = <int> [CCW]	dISmall
175		1	SET speed = <float>	50
176		1	POSITION <float> [IMM or SYNC]	250
177		1	VALVE_PORT = <int> [CCW]	IVSmall
178		1	POSITION <float> [IMM or SYNC]	0
179		1	VALVE_PORT = <int> [CCW]	AirSmall
180		1	POSITION <float> [IMM or SYNC]	250
181		1	VALVE_PORT = <int> [CCW]	IVSmall
182		1	POSITION <float> [IMM or SYNC]	0
183		2	VALVE_PORT = <int> [CCW]	dILarge
184		2	POSITION <float> [IMM or SYNC]	4000
185		2	VALVE_PORT = <int> [CCW]	IVLarge
186		2	POSITION <float> [IMM or SYNC]	0
187		2	VALVE_PORT = <int> [CCW]	IVLarge
188		2	POSITION <float> [IMM or SYNC]	4500
189		2	VALVE_PORT = <int> [CCW]	WasteLarge
190		2	POSITION <float> [IMM or SYNC]	0
191			LOOP <int>	3
192				
193	ReloadRV	2	VALVE_PORT = <int> [CCW]	RVLarge
194		2	SET speed = <float>	400
195		2	POSITION <float> [IMM or SYNC]	3000
196		2	VALVE_PORT = <int> [CCW]	WasteLarge
197		2	POSITION <float> [IMM or SYNC]	2000

198		2	VALVE_PORT = <int> [CCW]	RVLarge
199		2	POSITION <float> [IMM or SYNC]	200
200		2	VALVE_PORT = <int> [CCW]	WasteLarge
201		2	POSITION <float> [IMM or SYNC]	0
202		2	VALVE_PORT = <int> [CCW]	AirLarge
203		2	POSITION <float> [IMM or SYNC]	1500
204		2	VALVE_PORT = <int> [CCW]	RVLarge
205		2	POSITION <float> [IMM or SYNC]	0
206				
207	AddAA	1	VALVE_PORT = <int> [CCW]	AA
208		1	POSITION <float> [IMM or SYNC]	250
209		1	VALVE_PORT = <int> [CCW]	RVSmall
210		1	SET speed = <float>	40
211		1	POSITION <float> [IMM or SYNC]	50
212		1	VALVE_PORT = <int> [CCW]	WasteSmall
213		1	POSITION <float> [IMM or SYNC]	0
214		1	VALVE_PORT = <int> [CCW]	AirSmall
215		1	POSITION <float> [IMM or SYNC]	250
216		1	VALVE_PORT = <int> [CCW]	RVSmall
217		1	POSITION <float> [IMM or SYNC]	0
218		2	VALVE_PORT = <int> [CCW]	RVLarge
219		2	SET speed = <float>	800
220		2	POSITION <float> [IMM or SYNC]	2500
221		2	VALVE_PORT = <int> [CCW]	RVLarge
222		2	POSITION <float> [IMM or SYNC]	0
223		2	VALVE_PORT = <int> [CCW]	AirLarge
224		2	POSITION <float> [IMM or SYNC]	1000
225		2	VALVE_PORT = <int> [CCW]	RVLarge
226		2	POSITION <float> [IMM or SYNC]	0
227		2	POSITION <float> [IMM or SYNC]	2500
228		2	VALVE_PORT = <int> [CCW]	RVLarge
229		2	POSITION <float> [IMM or SYNC]	0
230		2	VALVE_PORT = <int> [CCW]	AirLarge
231		2	POSITION <float> [IMM or SYNC]	1000
232		2	VALVE_PORT = <int> [CCW]	RVLarge
233		2	POSITION <float> [IMM or SYNC]	0
234			DO	
235		1	VALVE_PORT = <int> [CCW]	dISmall
236		1	SET speed = <float>	30
237		1	POSITION <float> [IMM or SYNC]	250
238		1	VALVE_PORT = <int> [CCW]	WasteSmall
239		1	POSITION <float> [IMM or SYNC]	0
240			LOOP <int>	2
241				

242			DO	
243	Clean Lsyringe	2	VALVE_PORT = <int> [CCW]	dILarge
244		2	SET speed = <float>	400
245		2	POSITION <float> [IMM or SYNC]	4500
246		2	VALVE_PORT = <int> [CCW]	WasteLarge
247		2	POSITION <float> [IMM or SYNC]	0
248			LOOP <int>	2
249				
250			DO	
251	CleanLWCC	2	VALVE_PORT = <int> [CCW]	dILarge
252		2	POSITION <float> [IMM or SYNC]	4000
253		2	VALVE_PORT = <int> [CCW]	WasteLarge
254		2	POSITION <float> [IMM or SYNC]	3500
255		2	VALVE_PORT = <int> [CCW]	LWCC
256		2	SET speed = <float>	100
257		2	POSITION <float> [IMM or SYNC]	500
258		2	VALVE_PORT = <int> [CCW]	WasteLarge
259		2	SET speed = <float>	400
260		2	POSITION <float> [IMM or SYNC]	0
261				
262	Draw	1	VALVE_PORT = <int> [CCW]	RVSmall
263		1	SET speed = <float>	30
264		1	POSITION <float> [IMM or SYNC]	250
265		1	VALVE_PORT = <int> [CCW]	RVSmall
266		1	POSITION <float> [IMM or SYNC]	0
267		1	VALVE_PORT = <int> [CCW]	AirSmall
268		1	POSITION <float> [IMM or SYNC]	250
269		1	VALVE_PORT = <int> [CCW]	RVSmall
270		1	POSITION <float> [IMM or SYNC]	0
271		1	VALVE_PORT = <int> [CCW]	RVSmall
272		1	POSITION <float> [IMM or SYNC]	250
273		1	VALVE_PORT = <int> [CCW]	WasteSmall
274		1	POSITION <float> [IMM or SYNC]	0
275		1	VALVE_PORT = <int> [CCW]	RVSmall
276		1	POSITION <float> [IMM or SYNC]	250
277		1	VALVE_PORT = <int> [CCW]	RVSmall
278		1	POSITION <float> [IMM or SYNC]	200
279		1	VALVE_PORT = <int> [CCW]	IVSmall
280		1	POSITION <float> [IMM or SYNC]	100
281		1	VALVE_PORT = <int> [CCW]	RVSmall
282		1	POSITION <float> [IMM or SYNC]	0
283		1	VALVE_PORT = <int> [CCW]	AirSmall
284		1	POSITION <float> [IMM or SYNC]	250
285		1	VALVE_PORT = <int> [CCW]	RVSmall

286		1	POSITION <float> [IMM or SYNC]	0
287		1	VALVE_PORT = <int> [CCW]	dISmall
288		1	POSITION <float> [IMM or SYNC]	250
289		1	VALVE_PORT = <int> [CCW]	WasteSmall
290		1	POSITION <float> [IMM or SYNC]	0
291		1	VALVE_PORT = <int> [CCW]	dISmall
292		1	POSITION <float> [IMM or SYNC]	250
293		1	VALVE_PORT = <int> [CCW]	IVSmall
294		1	POSITION <float> [IMM or SYNC]	0
295		1	VALVE_PORT = <int> [CCW]	dISmall
296		1	POSITION <float> [IMM or SYNC]	250
297		1	VALVE_PORT = <int> [CCW]	IVSmall
298		1	POSITION <float> [IMM or SYNC]	0
299				
300	Dilute to 3ml	2	VALVE_PORT = <int> [CCW]	dILarge
301		2	SET speed = <float>	400
302		2	POSITION <float> [IMM or SYNC]	2400
303		2	VALVE_PORT = <int> [CCW]	IVLarge
304		2	POSITION <float> [IMM or SYNC]	0
305		2	VALVE_PORT = <int> [CCW]	IVLarge
306		2	POSITION <float> [IMM or SYNC]	3000
307		2	VALVE_PORT = <int> [CCW]	IVLarge
308		2	POSITION <float> [IMM or SYNC]	0
309		2	VALVE_PORT = <int> [CCW]	AirLarge
310		2	SET speed = <float>	800
311		2	POSITION <float> [IMM or SYNC]	1000
312		2	VALVE_PORT = <int> [CCW]	IVLarge
313		2	POSITION <float> [IMM or SYNC]	0
314		2	VALVE_PORT = <int> [CCW]	IVLarge
315		2	POSITION <float> [IMM or SYNC]	3000
316		2	VALVE_PORT = <int> [CCW]	IVLarge
317		2	POSITION <float> [IMM or SYNC]	0
318		2	VALVE_PORT = <int> [CCW]	AirLarge
319		2	POSITION <float> [IMM or SYNC]	1000
320		2	VALVE_PORT = <int> [CCW]	IVLarge
321		2	POSITION <float> [IMM or SYNC]	0
322				
323	IVtoLWCC	2	VALVE_PORT = <int> [CCW]	IVLarge
324		2	POSITION <float> [IMM or SYNC]	3000
325		2	VALVE_PORT = <int> [CCW]	WasteLarge
326		2	POSITION <float> [IMM or SYNC]	2000
327		2	SET speed = <float>	100
328		2	VALVE_PORT = <int> [CCW]	LWCC
329		2	POSITION <float> [IMM or SYNC]	500

330		2	VALVE_PORT = <int> [CCW]	WasteLarge
331		2	POSITION <float> [IMM or SYNC]	0
332				
333	RinseIV	2	VALVE_PORT = <int> [CCW]	IVLarge
334		2	SET speed = <float>	700
335		2	POSITION <float> [IMM or SYNC]	1000
336		2	VALVE_PORT = <int> [CCW]	WasteLarge
337		2	POSITION <float> [IMM or SYNC]	0
338			DO	
339		1	VALVE_PORT = <int> [CCW]	dISmall
340		1	SET speed = <float>	50
341		1	POSITION <float> [IMM or SYNC]	250
342		1	VALVE_PORT = <int> [CCW]	IVSmall
343		1	POSITION <float> [IMM or SYNC]	0
344		1	VALVE_PORT = <int> [CCW]	AirSmall
345		1	POSITION <float> [IMM or SYNC]	250
346		1	VALVE_PORT = <int> [CCW]	IVSmall
347		1	POSITION <float> [IMM or SYNC]	0
348		2	VALVE_PORT = <int> [CCW]	dILarge
349		2	POSITION <float> [IMM or SYNC]	4000
350		2	VALVE_PORT = <int> [CCW]	IVLarge
351		2	POSITION <float> [IMM or SYNC]	0
352		2	VALVE_PORT = <int> [CCW]	IVLarge
353		2	POSITION <float> [IMM or SYNC]	4500
354		2	VALVE_PORT = <int> [CCW]	WasteLarge
355		2	POSITION <float> [IMM or SYNC]	0
356			LOOP <int>	3
357			LOOP <int>	5
358				
359	Rinse RV	1	VALVE_PORT = <int> [CCW]	dISmall
360		1	SET speed = <float>	50
361		1	POSITION <float> [IMM or SYNC]	250
362		1	VALVE_PORT = <int> [CCW]	RVSmall
363		1	POSITION <float> [IMM or SYNC]	0
364		1	VALVE_PORT = <int> [CCW]	dISmall
365		1	POSITION <float> [IMM or SYNC]	250
366		1	VALVE_PORT = <int> [CCW]	RVSmall
367		1	POSITION <float> [IMM or SYNC]	0
368		1	VALVE_PORT = <int> [CCW]	AirSmall
369		1	POSITION <float> [IMM or SYNC]	250
370		1	VALVE_PORT = <int> [CCW]	RVSmall
371		1	POSITION <float> [IMM or SYNC]	0
372		2	VALVE_PORT = <int> [CCW]	RVLarge
373		2	SET speed = <float>	400

374		2	POSITION <float> [IMM or SYNC]	2000
375		2	VALVE_PORT = <int> [CCW]	WasteLarge
376		2	POSITION <float> [IMM or SYNC]	0
377			DO	
378		2	VALVE_PORT = <int> [CCW]	dILarge
379		2	POSITION <float> [IMM or SYNC]	3000
380		2	VALVE_PORT = <int> [CCW]	RVLarge
381		2	POSITION <float> [IMM or SYNC]	0
382		2	VALVE_PORT = <int> [CCW]	RVLarge
383		2	POSITION <float> [IMM or SYNC]	3500
384		2	VALVE_PORT = <int> [CCW]	WasteLarge
385		2	POSITION <float> [IMM or SYNC]	0
386			LOOP <int>	3
387				
388	RecleanLWCC	2	VALVE_PORT = <int> [CCW]	dILarge
389		2	SET speed = <float>	400
390		2	POSITION <float> [IMM or SYNC]	5000
391		2	VALVE_PORT = <int> [CCW]	WasteLarge
392		2	POSITION <float> [IMM or SYNC]	4000
393		2	VALVE_PORT = <int> [CCW]	LWCC
394		2	SET speed = <float>	100
395		2	POSITION <float> [IMM or SYNC]	1000
396		2	VALVE_PORT = <int> [CCW]	WasteLarge
397		2	SET speed = <float>	400
398		2	POSITION <float> [IMM or SYNC]	0
399			LOOP <int>	14

References

1. Cho, A. K.; Sioutas, C.; Miguel, A. H.; Kumagai, Y.; Schmitz, D. A.; Singh, M.; Eiguren-Fernandez, A.; Froines, J. R., Redox activity of airborne particulate matter at different sites in the Los Angeles Basin. *Environmental research* **2005,** *99*, (1), 40-47.
2. Fang, T.; Verma, V.; Guo, H.; King, L. E.; Edgerton, E. S.; Weber, R. J., A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE). *Atmos. Meas. Tech.* **2015,** *8*, (1), 471-482.
3. Fang, T.; Guo, H.; Verma, V.; Peltier, R. E.; Weber, R. J., PM2.5 water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies. *Atmos. Chem. Phys. Discuss.* **2015,** *15*, (12), 17189-17227.
4. Turpin, B. J.; Lim, H.-J., Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* **2001,** *35*, (1), 602-610.
5. Zhang, X.; Hecobian, A.; Zheng, M.; Frank, N. H.; Weber, R. J., Biomass burning impact on PM 2.5 over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis. *Atmos. Chem. Phys.* **2010,** *10*, (14), 6839-6853.
6. Hand, J. L.; Schichtel, B. A.; Malm, W. C.; Pitchford, M. L., Particulate sulfate ion concentration and SO2 emission trends in the United States from the early 1990s through 2010. *Atmos. Chem. Phys.* **2012,** *12*, (21), 10353-10365.

7. Hidy, G. M.; Blanchard, C. L.; Baumann, K.; Edgerton, E.; Tanenbaum, S.; Shaw, S.; Knipping, E.; Tombach, I.; Jansen, J.; Walters, J., Chemical climatology of the southeastern United States, 1999-2013. *Atmos. Chem. Phys.* **2014,** *14*, (21), 11893-11914.