

Abstract

We assess the potential of the water-soluble fraction of atmospheric fine aerosols in the southeastern United States to generate reactive oxygen species (ROS) and identify major ROS-associated emission sources. ROS-generation potential of particles was quantified by the dithiothreitol (DTT) assay and involved analysis of fine particulate matter (PM) extracted from high-volume quartz filters (23-hour integrated samples) collected at various sites in different environmental settings in the southeast, including three urban Atlanta sites, in addition to a rural site. Paired sampling was conducted with one fixed site in Atlanta (Jefferson Street), representative of the urban environment, with the others rotating among different sites, for ~250 days between June 2012 and September 2013 (N = 483). A simple linear regression between the DTT activity and aerosol chemical components revealed strong associations between PM ROS generation potential and secondary organic aerosol (WSOC) in summer, and biomass burning markers in winter. Redox-active metals were also somewhat correlated with the DTT activity, but mostly at urban and roadside sites. Positive matrix factorization (PMF) was applied to apportion the relative contribution of various sources to the ROS generation potential of water-soluble PM_{2.5} in urban Atlanta. PMF showed that vehicular emissions contribute uniformly throughout the year (12 to 25 %), while secondary oxidation processes dominated the DTT activity in summer (46 %) and biomass burning in winter (47 %). Road dust was significant only during drier periods (~12 % in summer and fall). Source apportionment by chemical mass balance (CMB) was reasonably consistent with PMF, but with higher contribution from vehicular emissions (32 %). Given the spatially large data set of PM sampled over an extended period, the study reconciles the results from

previous work that showed only region- or season-specific aerosol components or sources contributing to PM ROS activity, possibly due to smaller sample sizes. The ubiquitous nature of the major sources of PM-associated ROS suggests widespread population exposures to aerosol components that have the ability to catalyze the production of oxidants in vivo.

Keywords: ROS generation, DTT activity, Secondary organic aerosol, Biomass burning, Source apportionment, Positive matrix factorization, Chemical mass balance

1 **Reactive Oxygen Species Associated with Water-Soluble PM_{2.5} in**
2 **the Southeastern United States: Spatiotemporal Trends and Source**
3 **Apportionment**

4
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1 **Abstract**

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3 southeastern United States to generate reactive oxygen species (ROS) and identify major ROS-
4 associated emission sources. ROS-generation potential of particles was quantified by the
5 dithiothreitol (DTT) assay and involved analysis of fine particulate matter (PM) extracted from
6 high-volume quartz filters (23-hour integrated samples) collected at various sites in different
7 environmental settings in the southeast, including three urban Atlanta sites, in addition to a rural
8 site. Paired sampling was conducted with one fixed site in Atlanta (Jefferson Street),
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10 days between June 2012 and September 2013 (N = 483). A simple linear regression between the
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13 markers in winter. Redox-active metals were also somewhat correlated with the DTT activity,
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15 apportion the relative contribution of various sources to the ROS generation potential of water-
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22 period, the study reconciles the results from previous work that showed only region- or season-
23 specific aerosol components or sources contributing to PM ROS activity, possibly due to smaller

1 sample sizes. The ubiquitous nature of the major sources of PM-associated ROS suggests
2 widespread population exposures to aerosol components that have the ability to catalyze the
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7
8 **1. Introduction**

9 Substantial research has been dedicated to understand the mechanisms by which ambient
10 particulate matter (PM) causes adverse health effects in humans (Hoek et al., 2002; Samet et al.,
11 2000; Gauderman et al., 2007; Stayner et al., 1998; Riediker et al., 2004; Sun et al., 1984; Sagai
12 et al., 1993; Donaldson et al., 1996; Donaldson et al., 1997; Donaldson et al., 2003; Li et al.,
13 2003; Li et al., 2009a; Delfino et al., 2013). In many of these studies, a large number of PM
14 health effects have been attributed to the oxidative or oxidant generating properties of ambient
15 particles (Donaldson et al., 2003; Donaldson et al., 1996; Li et al., 2003; Li et al., 2009a; Delfino
16 et al., 2013). It has been hypothesized that several oxidative mechanisms can arise
17 simultaneously, leading to a cascade of events that results in high concentrations of reactive
18 oxygen species (ROS) in vivo (Tao et al., 2003; Castro and Freeman, 2001; Donaldson et al.,
19 2003). ROS concentrations in excess of the anti-oxidant capacity to neutralize them leads to
20 oxidizing other cellular components, which eventually translates into numerous health outcomes
21 (Delfino et al., 2005; Li et al., 2009a; Peters et al., 2006).

22

1 Based on this possible mechanistic route linking aerosol chemistry to health, numerous studies
2 have been initiated in the past several years focused on measuring the oxidative properties of
3 ambient particles. A variety of probes have been developed to quantify different aspects of PM
4 induced oxidative stress. These include chemical systems that mimic the loss of antioxidants,
5 such as oxidation of dithiothreitol [(DTT assay) (Cho et al., 2005)], glutathione (GSH (Godri et
6 al., 2011), and ascorbic acid [(AA) (DiStefano et al., 2009; Mudway et al., 2004)], covalent
7 bonding with glyceraldehyde-3-phosphate dehydrogenase [(GAPDH) (Rodrigueza et al., 2005)],
8 and hydroxyl radical generation in the presence of H₂O₂ (Shi et al., 2003). Other probes measure
9 cellular responses when exposed to aerosols; such as macrophage ROS generation (Landreman et
10 al., 2008), the induction of hemeoxygenase-1 (HO-1) and other stress protein expression (Li et
11 al., 2003), and cytokine activation (Wilson et al., 2010). Each of these assays represents a
12 plausible mode of PM toxicity and collectively they should be considered as the toolkit for
13 deconstructing the complex mechanisms of PM ROS generation. One advantage of these assays,
14 is that they are integrative of various aerosol chemical properties, and as pointed out by several
15 researchers (Ayres et al., 2008; Venkatachari and Hopke, 2008; Kuenzli et al., 2004), many of
16 them can serve as a screening step for assessing the PM samples/emission scenarios for more
17 detailed chemical analysis and downstream health studies.

18
19 The DTT assay was devised to simulate the in-vivo generation of superoxide radicals, wherein
20 DTT was used as a surrogate of the biological reducing agents (NADH and NADPH) (Kumagai
21 et al., 1997; Kumagai et al., 2002). When incubated at 37°C with a test PM sample, a decreasing
22 DTT concentration over time is inferred as a measure of the ROS generating capability of the
23 particles. A number of pure chemicals have been found to be associated with the response of this

1 assay, e.g. quinones have been known to catalyze the transfer of electrons from DTT to oxygen
2 (Kumagai et al., 2002). In a recent study, certain transition metals (e.g. Fe, Cu and Mn) have also
3 been shown to be active in this assay (Charrier and Anastasio, 2012). However, evidences
4 showing that any of these chemicals play a substantial role in the DTT activity of ambient PM in
5 a range of environments (locations) are limited. The major components of the ambient PM
6 identified so far to be associated with the DTT activity are often bulk groups of species such as
7 organic carbon [OC, both water-soluble (WSOC) and insoluble (WIOC)] and water-soluble
8 HULIS (Humic-like-substances) compounds [a class of WSOC characterized by strong
9 hydrophobicity]. However, most of these associations have been inferred based on statistical
10 correlations (Ntziachristos et al., 2007; Verma et al., 2009a; Verma et al., 2009b; Hu et al., 2008;
11 Biswas et al., 2009b), which do not necessarily establish causation, while very few have used
12 semi-mechanistic approaches such as physical separation of the organic compounds and metals
13 (Verma et al., 2011; Lin and Yu, 2011; Charrier and Anastasio, 2012).

14
15 Both approaches have merits, however, a major concern with the studies solely based on
16 regression analysis of DTT activity vs. chemical components is related to the sample size (N);
17 most are based on $N < 30$ with very few exceeding 100 [e.g. Delfino et. al., (2013); $N = 111$],
18 which limits the statistical significance of the inferred associations. This is partly due to
19 analytical complexity of the DTT assay, which entails a laborious and time intensive protocol.
20 To address this problem, we developed a semi-automated instrument involving minimal manual
21 operation. The instrument, which has been described in detail in Fang et al., (2014), allowed us
22 to conduct the DTT assay on a large number of aqueous samples (~1200) as part of the
23 Southeastern Center for Air Pollution and Epidemiology (SCAPE) study.

1 SCAPE is a collaborative center – combining five multi-disciplinary studies from Georgia Tech
2 and Emory University, aimed at achieving a better understanding of the ambient PM health
3 effects. Along with describing the automated DTT analytical method in our previous paper from
4 the Center studies, Fang et al., (2014) showed that the DTT activity of ambient fine aerosols
5 collected from various sites and seasons in the southeast US is generally correlated with PM
6 mass, however the strength and slope of the correlation varied ($R^2 = 0.40 - 0.90$; slope = 0.01-
7 0.05 nmol/min/ μg) among different sites and seasons. Here we discuss the detailed spatial and
8 temporal profiles of the PM ROS generation potential measured by the DTT assay on these
9 samples. The bulk and specific chemical components, i.e. OC, elemental carbon (EC), WSOC,
10 inorganic ions, water-soluble brown carbon (BrnC), and various water-soluble transition metals,
11 were also measured. Both univariate linear regression and receptor modeling techniques were
12 used to identify and apportion the contribution of major emission sources to the ROS generating
13 potential of ambient particles in the southeastern US. This analysis focuses only on the water-
14 soluble extracts from filter samples, while other reports will present results involving water-
15 insoluble components and isolated chemical fractions of both water-soluble and insoluble
16 species. The paper presents a unique and possibly the largest dataset on PM ROS generation
17 potential (N, the number of filter samples = 483), linked to a range of aerosol sources that varies
18 over seasons of the year, and thus provides a broader regional view of fine particle ROS
19 characteristics.

20

21 **2. Experimental Methods**

22 **2.1 Sampling plan**

1 The sampling plan for SCAPE involved paired simultaneous measurements using two
2 instrumented sites, one of which was fixed at the Jefferson Street SEARCH (Southeastern
3 Aerosol Research and Characterization) site (Edgerton et al., 2005, 2006; Hansen et al., 2003),
4 the other was rotated among three different satellite sites, i.e. Yorkville, Roadside Atlanta, and
5 Georgia Tech, all in Georgia. The sampling covered the period from June, 2012 to September,
6 2013; details of the sampling dates at each site are provided in Table 1. Each paired deployment
7 lasted roughly one month, and was repeated in different seasons. Based on the temperature
8 profile in Atlanta during the sampling period, shown in Figure S1, data are classified into three
9 seasons – summer (June-August, 2012), fall (September, 2012 and 2013), and winter
10 (November, 2012-March, 2013). To provide a broader perspective, additional measurements
11 (summer, June-July 2013) were made in Alabama, at the SEARCH rural-urban pair; Centreville
12 (rural) and Birmingham (urban).

13 **2.2 Sampling sites**

14 A map showing the locations of all sites is shown in Figure 1. Jefferson Street is located roughly
15 4 km northwest of downtown Atlanta and is representative of urban-Atlanta. The site is
16 surrounded by commercial and residential buildings, with nearby street traffic patterns consistent
17 with a mixed-use urban environment. The site has extensively been used in past studies
18 characterizing urban Atlanta air quality (Hansen et al., 2006; Marmur et al., 2005) and the data
19 used in epidemiological studies (Sarnat et al., 2008; Strickland et al., 2010). In this study,
20 Jefferson Street is again used as representative of urban Atlanta, to which the other three satellite
21 measurements (discussed next) are compared.

22

1 The Roadside site is located on the Georgia Tech campus adjacent (i.e., within a few meters) to
2 the interstate highway I-75/85. The degree to which the site is under direct influence of
3 emissions from approximately 280,000 vehicles per day on a 14-lane freeway depends on wind
4 direction and wind speed. The traffic fleet is mostly (97 %) light-duty gasoline vehicles. Slow-
5 moving traffic is typical during the morning and evening rush-hour periods. Jefferson Street is
6 located roughly 2 km from this highway.

7

8 Georgia Tech site is situated between the Roadside and Jefferson Street sites on the Ford
9 Environment Sciences and Technology building top floor, ~600 m from the interstate. This site is
10 an intermediate location between the Roadside (direct freeway emissions) and urban background
11 (Jefferson Street) that could moderately be impacted by the roadway emissions.

12

13 Yorkville, also a SEARCH site, is located in a rural environment approximately 70 km west of
14 Atlanta, which is generally up-wind. The site is surrounded by agricultural land (e.g., pastures)
15 and forests, with the nearest residences at least 1 km away. There are no major roadways in the
16 vicinity of the site and nearby traffic emissions are negligible.

17

18 As a contrast to Atlanta, measurements were also made in an additional southeastern US city.
19 The urban Birmingham Alabama SEARCH site has several coking ovens within 10 km and a
20 cast iron pipe foundry located approximately 400m east. The site also receives emissions from
21 nearby (<4km) freeways (I-65, US-31 and I-20).

22

1 Centreville is the SEARCH rural pair to Birmingham, located approximately 85 km south-
2 southwest of Birmingham. The site is heavily wooded and is surrounded by the Talladega
3 National Forest with a high density of oak and pine trees. Measurements were conducted
4 simultaneously at Birmingham and Centreville and overlapped with the Southern Oxidant and
5 Aerosol Study (SOAS).

6
7 Detailed descriptions of all of the SEARCH sites used in this study can be found elsewhere
8 (Hansen et al., 2003). The Jefferson Street, Roadside, Georgia Tech, Yorkville, Birmingham and
9 Centreville sites are referred to as JST, RS, GT, YRK, BHM and CTR respectively.

10

11 **2.3 Filter collection and extraction protocol**

12 A high-volume sampler (HiVol, Thermo Anderson, non-denuded, nominal flow rate 1.13
13 m³/min, PM_{2.5} impactor) was setup at each site and fine particles were collected onto pre-baked
14 8x10” quartz filters (Pallflex® Tissuquartz™, Pall Life Sciences). 23-hour integrated samples
15 (12:00 noon-11:00 am next day) were collected daily during the sampling periods (Table 1) at
16 each site, along with periodic field blanks (at least 3 per site per month). The number of samples
17 collected from each site, approximately 30 per site per season (total = 483) is given in Table 1.
18 After collection, the filters were wrapped in pre-baked aluminum foil and immediately stored in
19 a freezer (-18 °C). The chemical and ROS-generation analysis of the filters was started in March
20 2013. Prior to the analysis, the filters were cut using a 1” diameter metallic punch. For the DTT
21 activity, WSOC and BrnC analysis, three filter sections (1” diameter each) were extracted in 15
22 mL of deionized water (DI, Milli-Q; >18 MΩ) via sonication in a water bath for 30 minutes,
23 while additional punches were extracted separately in the same manner (15 mL of DI for 30

1 minutes of sonication time) for the metals (4 punches) and inorganic ions (1 punch) analysis.
2 These extracts were then filtered using PTFE 0.45- μm pore syringe filters (Fisher brand). The
3 filtered extracts for metals were acidified by adding nitric acid (high purity trace metal grade; 2
4 % w/v final solution), consistent with current protocols (Henshaw et al., 1989; Talbot and Weiss,
5 1994).

6

7 **2.4 Online instruments**

8 $\text{PM}_{2.5}$ mass concentrations were monitored by a tapered element oscillating microbalance
9 (Thermo Scientific TEOM 1400a), operating continuously at JST, BHM, YRK and CTR
10 throughout the sampling period (Atmospheric Research Analysis Inc. data). At other sites (RS
11 and GT), summed concentrations from measured chemical components [EC + 1.6 OC + ions
12 ($\text{SO}_4^{-2} + \text{NH}_4^+ + \text{NO}_3^-$) + water-soluble metals], were used as a proxy for the PM mass
13 concentrations. This method has been found to agree well with the TEOM concentrations at JST
14 and YRK sites, where co-located measurements were available (Fang et al., 2014).

15 **2.5 Chemical analysis on PM filters**

16 Water soluble organic carbon (WSOC) and the WSOC light absorption properties (Brown
17 Carbon, BrnC, used as a source tracer) were measured on HiVol extracts via an automated
18 system using an autosampler (Dionex 40AS), spectrophotometer and total organic carbon (TOC)
19 analyzer. BrnC was measured on an aliquot (300 μL) of the extracts via a liquid waveguide
20 capillary cell (LWCC-2100, World Precision Instruments, Sarasota, FL), which was coupled to a
21 UV/VIS spectrophotometer (USB4000 spectrometer, Ocean Optics, Dunedin, FL) (Hecobian et
22 al., 2010). Following the waveguide, the aliquot was conducted to a Sievers TOC analyzer

1 (Model 900, GE Analytical Instruments; Boulder, CO) for determination of WSOC
2 concentration.

3

4 The automated system was also used to measure water-soluble metals, which involved
5 nebulizing the water extracts and directing the aerosol stream to an XRF (X-ray fluorescence)
6 instrument (Xact™ 625 Monitoring System), capable of online measurements of a range of
7 elements. Details of the nebulizer-XRF system would be published in a subsequent publication.

8 Briefly, 5 mL of the acidified PM water-extracts was aerosolized using a continuous flow
9 ultrasonic nebulizer (CETAC, U5000 AT⁺). The resulting fine aerosol was conducted by a flow
10 of clean filtered air through a drying system (a 136°C heated section followed by a cooled
11 section at -5°C). The dried aerosol stream was neutralized by a Kr-85 source and mixed with
12 clean filtered (Pall HEPA Capsule, Part No. 12144) air to obtain the instrument sample flow rate
13 of 16.7 lpm. A wide range of elements were measured by the instrument, however we present
14 only the relevant species which are either used as specific emission markers [Ca (dust; (Coz et
15 al., 2010), K (biomass burning; (Artaxo et al., 1994),] or possibly play a role in ROS generation
16 | [Fe, Cu, Mn, Zn; (Schoonen et al., 2006)].

17

18 Elemental and organic carbon content of the PM was measured on a small section (1.45 cm²) of
19 the HiVol filters using a thermal/optical transmittance (TOT) analyzer (Sunset Laboratory) by
20 NIOSH (The National Institute for Occupational Safety and Health) method (Birch and Cary,
21 1996). For the measurement of inorganic ions (SO₄⁻², NH₄⁺, NO₃⁻, etc.) at JST and GT, ion-
22 chromatography (IC) (LC30 chromatography oven, and Dionex CD20 conductivity detector,
23 with IonPac® CS12A carboxylate-functionalized cation-exchange and IonPac® AS12A carbonate

1 eluent anion-exchange columns) was performed on the aerosol extracts of HiVol filters collected
2 from those sites.

3

4 **2.6 ROS generation potential measurement**

5 ROS generation potential of the ambient aerosols was measured by a semi-automated instrument
6 (Fang et al., 2014) for measuring DTT activity of the PM extracts obtained from HiVol filters.
7 The filters (about 18) for DTT assay were extracted everyday and the extracts immediately
8 returned to the freezer (-18 °C). Approximately two-thirds (~12) of these extracts were kept for
9 the DTT activity measurement overnight and the remaining one-third (~6) were analyzed the
10 next day morning. Typical range of PM mass concentrations in the extracts used in the DTT
11 assay were 10-25 µg/mL.

12 The semi-automated instrument is based on the protocol adopted from Cho et al. (2005) and uses
13 two programmable syringe pumps (Kloehn, Inc., Las Vegas, NV, USA) for the mixing and
14 transfer of reaction mixtures and reagents. The DTT oxidation in a mixture of DTT (1 mM; 0.5
15 mL), potassium phosphate buffer (0.5 M, pH =7.4, Chelex treated; 1 mL) and PM extract (3.5
16 mL) is carried out in a single vial (conical centrifuge polypropylene tube), continuously shaken
17 and maintained at 37°C using a ThermoMixer (incubating accuracy: ±0.5 °C, Eppendorf North
18 America, Inc., Hauppauge, NY, USA). A small aliquot (100 µL) of this reaction mixture is
19 transferred to another vial at various time intervals (0, 4, 13, 23, 32 and 41 minutes) and mixed
20 with trichloroacetic acid (TCA, 1 % w/v; 1 mL), Tris buffer (0.08 M with 4 mM EDTA; 2 mL)
21 and 5,5'-dithiobis-(2- nitrobenzoic acid) (DTNB (0.2 mM; 0.5 mL). The final reaction mixture is
22 pushed through a liquid waveguide capillary cell (LWCC-M-100; World Precision Instruments,
23 Inc., FL, USA), coupled to an online spectrophotometer (Ocean Optics, Inc., Dunedin, FL,

1 USA), to measure the absorption intensity at 412 nm. The rate of DTT consumption was
2 calculated based on the linear regression slope of remaining DTT concentrations measured at
3 various time intervals. The automated method provided a measurement of the DTT activity at a
4 rate of 1 sample per hour. For each batch (consisting of either 7 or 14 samples), at least one field
5 blank and one standard [(9,10-Phenanthraquinone; 0.095 μM) used as a positive control] were
6 analyzed. Both blanks and standards were fairly consistent, with an average slope \pm standard
7 deviation of 0.38 ± 0.10 (N=45) and 1.27 ± 0.19 (N=55) $\mu\text{M}/\text{min}$, respectively. The automated
8 system was cleaned periodically (generally after every 15 days, or unless the slope of DTT
9 reaction rate started to become non-linear) by rinsing thoroughly with methanol (at least 3 times)
10 followed by DI (at least 6 times). The whole DTT analysis was completed by January 2014.
11 Given the long storage period of the filters in freezer (varying from 6 -12 months), the DTT
12 activities measured on these samples represent the ROS generation potential associated with only
13 stable PM compounds.

14

15 **2.7 Source apportionment analysis**

16 The emission sources contributing to ROS generation potential of the particles were investigated
17 using regression and receptor modeling techniques. As typically done in these studies, a simple
18 linear regression was conducted between the measured concentrations of various chemical
19 components and DTT activity for each individual site and season. A rough indication of ROS
20 sources was obtained based on the correlations between DTT activity and various species, and
21 associating those species with sources. The large dataset from the combined JST and GT sites,
22 which are representative of urban Atlanta air quality, allows a more quantitative source

1 apportionment. Two receptor models were used - positive matrix factorization (EPA-PMF,
2 version 3.0) and chemical mass balance (EPA-CMB, version 8.2).
3
4 Detailed description and procedural details of PMF are described elsewhere (Paatero, 1997;
5 Norris and Vedantham, 2008). The uncertainties for each chemical species used in PMF and
6 CMB were the overall uncertainties obtained by propagating the uncertainties at each step
7 starting from filter collection to analysis. The analytical uncertainties were obtained by analyzing
8 the standards (e.g. 9, 10-Phenanthrenequinone for DTT, sucrose solution for OC and WSOC,
9 copper sulfate for Cu, and ammonium iron (II) sulfate hexahydrate for Fe, etc.) or the same
10 ambient sample (e.g. for BrnC) multiple times ($N > 6$) and calculating the standard deviation from
11 the measurement. WSOC, BrnC, NH_4^+ , SO_4^{2-} , and EC were classified as strong [high signal-to-
12 noise ratio) (S/N)] species, while metals K, Ca, Mn, Fe, Cu and Zn were categorized as weak
13 (low S/N). DTT activity was chosen as the “total variable” and thus by default assigned as weak
14 species. Missing values in the data were replaced by the species median. For the base runs ($N =$
15 20), a seed of 25 was chosen and the model was executed for 4, 5 and 6 number of factors. The
16 converged run with the highest goodness-of-fit parameter (lowest object function) was selected
17 for five factors, which are identified as secondary WSOC, secondary SO_4^{2-} , vehicular emissions,
18 road dust and biomass burning. With fewer factors, the individual tracer species started merging
19 (e.g. dust and WSOC came in the same factor in four factor solution). For more than five factors,
20 a converged solution was not obtained. The correlation among individual factors was tested by
21 G-space plots. The solution space of these plots was filled by the contribution values indicating
22 the independence of different factors.
23

1 In the CMB approach (Coulter, 2004), source contributions to $PM_{2.5}$ at JST were first determined
2 and then the sources most associated with DTT activity were identified through correlations. The
3 model was run using eight yearly average source profiles, which were derived from JST in a
4 previous study (Marmur et al., 2005). Profiles included primary sources from gasoline vehicles
5 (LDGV), diesel vehicles (HDDV), soil dust (SDUST), biomass burning (BURN), and coal fired
6 power plants (CFPP). Secondary source profiles included ammonium sulfate (AMSULF),
7 ammonium bisulfate (AMBSULF) and other OC (OTHROC), which is taken to be secondary OC
8 (SOC). Using the JST-GT-combined HiVol concentration data, which includes inorganic ions,
9 water-soluble metals, OC and EC, contributions of each source to the measured concentration of
10 various species were predicted at JST on a daily basis. DTT activity was then related to these
11 CMB-identified $PM_{2.5}$ source contributions through a stepwise regression analysis using Akaike
12 Information Criterion (AIC) approach (Akaike, 1974), with DTT activity as the dependent
13 variable and sources contributions as the independent variables. Note, the source profiles used
14 total metals, whereas the fitting data were water-soluble metals; however, using total metals data
15 from the SEARCH data archive for the sampling period showed little effect on the final DTT
16 source apportionment. More detailed analysis based on the improved source profiles recently
17 developed by an ensemble approach (Balachandran et al., 2014) is underway and here we only
18 present the study average results from CMB to compare and validate the PMF analysis.

19 Data from YRK, RS and Alabama sites (CTR and BHM), were not included in PMF and CMB
20 as they represent more extreme and generally different conditions than JST and GT, the sites
21 representative of urban Atlanta. These other sites also had insufficient data for their own source
22 apportionment analyses.

23

1 **3. Results and Discussion**

2 **3.1 PM emission characteristics**

3 **3.1.1 Elemental, water-soluble organic and brown carbon (EC, WSOC, BrnC)**

4 Figure 2 (a, b and c) shows the ambient concentrations of EC, WSOC and BrnC at all sites for
5 different months of sampling. EC and WSOC are discussed first since they represent the diverse
6 PM emissions characteristics at these sites, followed by BrnC. EC is a marker for incomplete
7 combustion, such as vehicular emissions (Schauer, 2003), while secondary oxidation processes
8 (Weber et al., 2007) and biomass burning (Zhang et al., 2010) are the major sources of WSOC in
9 the southeast. From these figures, contrasts can be made between paired sites, and seasonal
10 trends can be discerned. Measurements in the Atlanta region can also be contrasted to the
11 Alabama sites.

12
13 The monthly average concentrations of EC (Figure 2a) are consistent with primary vehicular
14 emissions being the dominant EC source; the concentrations are highly heterogeneous. Large
15 concentration differences were observed for each pair, with highest EC at the RS, followed by
16 urban background sites (JST, GT, and BHM), and lowest concentrations at the rural sites (YRK
17 and CTR). The JST-GT EC concentrations were similar, suggesting that GT is not highly
18 influenced by the roadway emissions, and so more representative of EC levels in the metro area,
19 similar to JST. The largest contrast in EC among paired measurements is between urban and
20 rural sites. For both summer and winter seasons, EC is more than double at the urban sites (JST
21 and BHM) compared to their respective paired rural components (YRK and CTR) [mean ±
22 standard deviation (1σ) of ratio = 2.9 ± 1.6 in summer, and 2.7 ± 0.9 in winter for JST/YRK, and

1 2.92 ± 1.42 for BHM/CTR]. The RS site has the highest concentration of EC in both fall and
2 winter seasons (RS/JST = 1.81±0.67 in fall, and 1.9±0.8 in winter, and RS/GT = 1.95±0.5 in fall).
3 There is little seasonal variation in the EC levels across most sites. For example, the average EC
4 concentrations at JST in summer (0.75±0.25 µg/m³), fall (0.82±0.30 µg/m³), and winter
5 (0.67±0.33 µg/m³) were similar. The mean EC concentration at RS was slightly lower in winter
6 (1.18±0.43 µg/m³) than fall (1.37±0.30 µg/m³ in September, 2012 and 1.45±0.34 µg/m³ in
7 September, 2013). The marginally lower levels of EC in winter seasons in Atlanta (JST, GT and
8 RS sites) might be attributed to higher rainfall during these periods (December-March; Figure
9 S1). Precipitation scavenging could have superseded the effect of generally reduced mixing
10 height in winter on primary aerosol concentrations.

11 Unlike EC, WSOC was more spatially uniform, but varied substantially between different
12 seasons (Figure 2b). WSOC concentrations at the paired sites were very similar indicating that
13 major WSOC sources extend to regional scales. These sources are mainly secondary organic
14 aerosol (SOA) formation and biomass burning, (Zhang et al., 2010; Zhang et al., 2012), with
15 possibly minor influence from primary WSOC associated with vehicular emissions at the urban
16 sites (Yan et al., 2009). An overall stronger influence of summertime SOA than wintertime
17 biomass burning on WSOC in the region is apparent from a gradually decreasing averaged
18 concentration profile at JST from summer to winter (3.8±2.2 µg/m³, 3.2±1.7 µg/m³ and 2.0 ±1.1
19 µg/m³ in summer, fall and winter). Similar decreases are also noted at other sites (3.7±1.9 µg/m³
20 in summer to 1.8±0.8 µg/m³ in winter at YRK, and 3.3±1.1 µg/m³ and 3.9±2.3 µg/m³ in fall, 2012
21 and 2013, respectively to 1.6±1.3 µg/m³ in winter, 2013 at RS). These results are consistent with
22 a more detailed analysis of the WSOC spatial and seasonal distribution conducted two years
23 before in the southeast US (Zhang et al., 2010).

1 BrnC denotes the water-soluble organic compounds that absorb light in the UV-region of the
2 UV-Vis spectrum (Hecobian et al., 2010). Biomass burning is by far the largest source of these
3 compounds with additional contributions from vehicular sources and possibly aged SOA
4 (Hecobian et al., 2010; Zhang et al., 2011). The spatial profile of BrnC (Figure 2c) is
5 intermediate between EC (heterogeneous) and WSOC (homogeneous), indicating the diversity of
6 its sources. The moderate impact of vehicular emissions on BrnC is probably reflected in
7 generally higher concentrations of BrnC at RS and other urban sites (JST, GT, BHM) than rural
8 (CTR, YRK). However, the strong seasonality is evident from its extreme values in winter
9 periods resulting from biomass burning [average levels at JST in winter = $0.97 \pm 0.78 \text{ Mm}^{-1}$,
10 compared to $0.42 \pm 0.25 \text{ Mm}^{-1}$ in summer and $0.53 \pm 0.33 \text{ Mm}^{-1}$ in fall).

11

12 **3.1.2 Water-soluble metals**

13 The selected elements (Figure 3), have a wide range of concentrations at various sites and
14 differing seasonal trends, pointing to heterogeneous sources. A more in-depth discussion on the
15 distribution of the measured water-soluble elements will follow in a subsequent publication, here
16 we only briefly discuss the major trends in selected metals. BHM, a site heavily impacted by
17 industrial emissions, has very high concentrations of all metals, with Ca, Mn, and Zn the highest
18 among all sites. After BHM, RS has the highest levels of most metals among all sites in the
19 Atlanta region (i.e. JST, GT, YRK, RS), indicating either road dust and/or direct vehicular
20 emissions as their major source. Rural sites, YRK and CTR, have generally lower metals
21 concentrations, while GT and JST levels are moderate.

22

1 Higher rainfall in winter compared to summer months could also affect the metals concentrations
2 since the re-entrainment of road dust, which is a major source of metals, is most effective in dry
3 periods. The metals of predominantly crustal and vehicular origin (e.g. Ca, Fe, Mn and Cu) are
4 generally higher in summer and fall compared to the winter (Figure 3). For example, the average
5 Ca concentration at JST was 155 ± 116 , 160 ± 87 , and 67 ± 37 ng/m^3 in summer, fall, and winter,
6 respectively. Exceptions are K and Zn, which despite being associated with crustal dust [K; (Coz
7 et al., 2010)] or vehicular sources [Zn; (Liu et al., 2008)] are also emitted in biomass burning
8 (Echalar et al., 1995), which could account for a weaker seasonal variability due to multiple
9 sources; average K concentration is 62 ± 25 , 59 ± 22 and 65 ± 32 ng/m^3 in summer, fall and winter,
10 while the respective Zn concentration is 9.6 ± 4.7 , 9.3 ± 4.8 and 9.9 ± 5.8 ng/m^3 at JST.

11

12 **3.2 PM ROS generation potential**

13 Temporal and spatial differences in the water-soluble DTT activity are discussed to provide an
14 overview of the PM ROS generation potential in Southeastern US.

15

16 Time series of daily average DTT activity from the sites in different months is shown in our
17 previous publication (Fang et al., 2014) and also reproduced in the supplemental information
18 (Figure S2). The rate of DTT consumption is normalized by both the volume of sampled air
19 (DTTv; expressed in units of $\text{nmol}/\text{min}/\text{m}^3$, Figure S2a) and the particulate mass (DTTm;
20 expressed in units of $\text{nmol}/\text{min}/\mu\text{g}$, Figure S2b). A summary of the spatial and seasonal trends in
21 mean DTT activity (both DTTv and DTTm) for the individual sampling periods and at various
22 sites is shown in Figure 4. Our measurements of both volume and mass normalized DTT activity
23 are generally in the typical range [0.1 - 1.5 $\text{nmol}/\text{min}/\text{m}^3$ for DTTv and 0.005 - 0.1 $\text{nmol}/\text{min}/\mu\text{g}$

1 for DTTm, as summarized in Fang et al., (2014)] observed for ambient particles at other
2 locations. Figure 4 shows that in general, both the extrinsic (DTTv) and intrinsic (DTTm)
3 activity of ambient PM is spatially uniform. There is no substantial difference in DTT activity of
4 ambient PM at the two sites for any paired measurement, except the JST-YRK pair in winter
5 [DTTv(YRK) < DTTv(JST)] and GT-RS pair in fall [DTTm(RS) > DTTm(GT)].

6
7 A significant seasonal variability in both the volume and mass normalized DTT activity is
8 evident; the levels are generally higher in the colder months than summer (Figure 4). A one-
9 sample t-test showed that the DTTv at JST in December was significantly ($p \leq 0.05$) higher from
10 that in June-July (51 ± 34 %), August (48 ± 22 %), and September (27 ± 14 %). These results are in
11 agreement with a recent study conducted in the Los Angeles Basin, which showed a generally
12 higher DTT activity (both mass and volume normalized) of quasi-ultrafine particles in cooler
13 months compared to warmer periods (Saffari et al., 2014). The authors in that study attributed the
14 higher DTT activity to an elevated concentration of redox-active semi-volatile organic
15 compounds (SVOC) caused by their enhanced partitioning to the particulate phase and the
16 lowered atmospheric mixing height in winter. Although, SVOC have been suggested to make a
17 substantial contribution to the DTT activity of ultrafine particles (Verma et al., 2011), the $PM_{2.5}$
18 samples collected via HiVol filters in our study are not expected to contain a significant fraction
19 of these species due to losses associated with large flow-rate and long sampling duration
20 (Ashbaugh and Eldred, 2004; Warner et al., 2001).

21
22 The seasonal variability is even more pronounced in the intrinsic DTT activity (Figure 4). For
23 example, differences in DTTm levels in December vs. June-July (119 ± 48 %), August (86 ± 31 %)

1 and September (44 ± 14 %) are higher compared to the respective differences in DTTv levels.
2 Similar increases in the intrinsic DTT activity in winter were observed at other sites too (38 ± 13
3 % at GT from average of August, 2012 and September, 2013, and 53 ± 24 % at YRK), but not at
4 RS, where average fall level (0.032 ± 0.009 nmol/min/ μ g) was nearly the same as in winter
5 (0.036 ± 0.008 nmol/min/ μ g).

6

7 To further assess the spatiotemporal variability in DTTv activity in the region, correlation
8 coefficients (R^2) were calculated for all of the site pairs and are shown in Figure 5. To put the
9 DTT activity comparison in a larger context, we have also included the corresponding
10 coefficients for EC and WSOC. A high spatial correlation for a species indicates it has more
11 spatially uniform emission sources in the region, on the scale of distances between the paired
12 sites.

13

14 The site pair JST-GT shows high correlation coefficients ($R^2 > 0.5$) for many PM species (DTT,
15 EC and WSOC), which was expected given their spatial proximity and absence of nearby strong
16 sources, e.g., roadways. The other site pairs show disparate patterns for the different PM species
17 depending upon their sources. For example, EC has relatively low correlation coefficients for the
18 urban-rural site pairs, i.e. JST-YRK in both summer ($R^2 = 0.42$) and winter (0.45), and BHM-
19 CTR ($R^2 = 0.39$), as expected. Despite relatively close proximity, the low correlation in fall for
20 JST-RS pair ($R^2 = 0.10$) and GT-RS pair ($R^2 = 0.48$) for EC is due to the strong influence of
21 freeway emissions (I-85) at the RS site. However, the JST-RS correlation is high in February
22 ($R^2 = 0.74$), possibly suggesting some contributions from a common source of EC, such as
23 biomass burning.

1 WSOC on the other hand exhibits high correlations for most site pairs (JST-YRK, JST-GT,
2 CTR-BHM; $R^2 > 0.5$) in all seasons (Figure 5). The correlations are generally higher in summer
3 ($R^2 > 0.70$), indicating a more regional influence of SOA formation as a source of WSOC in
4 summertime, compared to biomass burning in winter ($R^2 < 0.65$). The correlations are generally
5 weaker for the pairs involving RS ($R^2 = 0.08-0.46$), probably due to the added contribution of
6 freeway emissions to WSOC.

7
8 Compared to WSOC and EC, the spatial correlations for DTT activity are moderate in all
9 seasons. For example, R^2 for DTT are not as high as for EC for the sites in closer proximity ($R^2 =$
10 0.68 and 0.67 for JST-GT in fall and winter, respectively). Similarly, in summer when the
11 correlations for WSOC are very high even for the far-apart sites (JST-YRK and CTR-BHM),
12 correlations for DTT are only moderate ($R^2 = 0.47$ and 0.59). It appears that DTT activity is
13 impacted by both regional sources and local emissions associated with individual site
14 characteristics. The role of various emission sources in the DTT activity of ambient PM in
15 different seasons and sites is the major point of discussion in the next section and also the
16 subsequent papers from this study.

17 18 **3.3. Sources of PM ROS generation potential**

19 Sources of ROS generation potential were identified and apportioned using combination of linear
20 regression, factor analysis and chemical mass balance techniques as described below.

21 **3.3.1 Linear regression of DTT activity with PM chemical composition**

22 Pearson's correlation coefficients for the linear regression between DTT activity and the
23 measured chemical components were calculated for each site and season and are shown in Table

1 2. Considering the limited daily variability in mass normalized DTT activity at most sites in a
2 given season (Figure S2b), the regression was conducted on the volume normalized levels of
3 DTT activity ($\text{nmol}/\text{min}/\text{m}^3$) and chemical components ($\mu\text{g}/\text{m}^3$). To consolidate the data for
4 convenience, individual time-series at JST and GT sites from June-to-August were merged
5 (named “JST-GT Summer”), given their similar concentration profiles. Similarly, JST and GT
6 time series from December to March were merged as “JST-GT winter”. The complete regression
7 matrix showing the correlation between all pairs of selected species, for each site and season, is
8 provided in the supplemental information (Table S1).

9
10 DTT activity is almost always correlated with OC in the present study. OC results from all major
11 sources in the region (e.g. vehicular emissions, SOA, and biomass burning) and comprises the
12 greatest fraction of PM mass [$\text{OM}/\text{PM}_{2.5} > 60\%$, not shown]. Thus, the strong correlation of OC
13 underlines the general contribution of PM organic compounds in the ROS generation potential,
14 and also likely accounts for the DTT correlation with PM mass, as reported in Fang et al.,
15 (2014). However, it doesn’t yield any novel information on the specific PM species or the
16 emission sources associated with the DTT activity. Associations between water-soluble DTT
17 activity and organic compounds are consistent with a number of previous studies (Biswas et al.,
18 2009a; Verma et al., 2012; Cho et al., 2005; Yang et al., 2014), but in contrast to other reports
19 showing metals as the major drivers in this reaction (Charrier and Anastasio, 2012).

20
21 In summer, DTT activity is well correlated with WSOC at all sites; JST-GT ($R=0.81$), YRK
22 ($R=0.79$), CTR ($R=0.78$) and BHM ($R=0.67$). Inorganic ions such as SO_4^{-2} and NH_4^+ are also
23 correlated with WSOC and DTT activity ($R > 0.60$ at most sites) indicating secondary

1 photochemical formation as their common source in summer. This is consistent with the results
2 of ambient (Verma et al., 2009a) and chamber studies (McWhinney et al., 2013; Li et al., 2009b)
3 suggesting higher DTT activity of secondary organic compounds than their parent gases and
4 primary particles.

5
6 In addition to WSOC, summertime DTT activity at urban sites, i.e. JST-GT and BHM, is also
7 correlated with certain transition metals [Mn (R=0.72), Fe (0.78), and Cu (0.71) at JST-GT, and
8 Mn (0.75), Fe (0.66) and Zn (0.66) at BHM]. At BHM, the iron foundry and coke oven plants are
9 the likely sources of these DTT-correlated metals. None of these metals are strongly correlated
10 with any specific emission markers at JST-GT. However, a moderate correlation of EC with
11 DTT activity (R=0.69) and also somewhat with metals (R= 0.59, 0.75 and 0.58 for Mn, Fe, and
12 Cu; Table S1), suggests that vehicular emissions could be one of their common source.

13
14 BrnC is also correlated with DTT activity in summer at JST-GT, CTR, and BHM sites (R>0.65).
15 However, its correlation with both WSOC and EC (R>0.65 at all sites; Table S1) doesn't allow
16 isolating its predominant source. Both vehicular emissions and possibly aged SOA appear to
17 contribute to these chromophores in summer.

18 In fall, DTT activity appears to be derived from a mixed contribution from primary vehicular
19 emissions and secondary formation, as supported by its correlation with WSOC (R=0.72), and
20 EC (R=0.90) at JST. Metals such as Fe and Zn are also correlated with DTT activity (R=0.70 and
21 0.82) and EC (R=0.90 and 0.75) at JST. The stronger correlation of primary emissions (EC) than
22 secondary species (WSOC, SO_4^{-2} , NH_4^+) indicates a diminishing effect of photochemistry on the

1 DTT activity. This is even more apparent in fall 2013, when the highest correlation of DTT at
2 GT is with EC (R=0.78), while the correlation with WSOC is low (R=0.47).

3
4 However, at the RS site, road-dust also appears to be a significantly contributing factor to DTT
5 activity in fall as indicated from the moderate to strong correlation (R=0.61-0.84) of certain
6 metals including those from crustal sources (Cu and Zn in fall 2012, and K, Ca, Mn, and Zn in
7 fall 2013). The added contribution from dust probably dilutes the association of DTT activity
8 with other emission sources. For example, DTT at RS is not as strongly correlated with EC
9 (R≤0.55) or WSOC (R =0.71 and 0.21 in Fall, 2012 and 2013, respectively) as at JST and GT.

10
11 In winter months, DTT activity is again correlated with WSOC at all sites; JST-GT (R=0.69),
12 YRK (R=0.84), and RS (R=0.78), however, this correlation is not accompanied by a similar
13 correlation with inorganic ions (R <0.55 for SO_4^{2-} and NH_4^+) as in summer months. It implies
14 that another emission source of WSOC – biomass burning, starts contributing more to the DTT
15 activity in winter. This is further reflected in the strong correlation of BrnC and K with DTT
16 activity and WSOC (R>0.65; Table 2 and Table S1) at all sites. In a study conducted in Los
17 Angeles, the ambient concentrations of K and WSOC were elevated (~2x) during the 2007
18 Southern California wildfires compared to the post-fire period (Verma et al., 2009b). More
19 importantly, these wood-smoke particles were found to be at least two times more oxidative than
20 the post-fire ambient $\text{PM}_{2.5}$ typically dominated by vehicular emissions. The redox-active WSOC
21 emitted in the biomass burning particles probably explain the higher intrinsic DTT activity of
22 ambient PM in winter compared to other seasons in the present study (Figure 4).

23

1 Interestingly, EC is also highly correlated with DTT activity ($R \geq 0.75$) in winter at all sites.
2 However, the concurrent correlation of EC with BrnC and K ($R > 0.60$ at all sites; Table S1)
3 somewhat confounds the contribution of vehicular sources with biomass burning to the DTT
4 activity in winter. Although, EC/OC ratio for wood smoke can be very low [0.2-0.3 (Harrison et
5 al., 2012)], it is possible that some fraction of EC at the sampling sites is also contributed by
6 biomass burning in addition to the vehicular emissions. Transition metals are also correlated with
7 DTT activity in winter months at JST-GT [Fe ($R=0.65$), Cu ($R=0.63$) and Zn ($R=0.63$)], and
8 YRK [Mn ($R=0.68$), and Zn ($R=0.72$)]. However, the co-variability of major emission markers
9 in winter (i.e. EC, WSOC, K and BrnC) makes it difficult to identify their dominant source(s) at
10 these sites.

11

12 **3.3.2 Source contributions to DTT activity**

13 To provide a more quantitative assessment of the contribution of various sources to the fine
14 particle oxidative properties in urban Atlanta, a PMF analysis was conducted using the DTT
15 activity and measured chemical composition data. The five factors resolved by PMF are shown
16 in Figure 6. Factors 1 and 2 are characterized with high WSOC and high inorganic ions (NH_4^+
17 and SO_4^{2-}) loadings, respectively. Both of these factors have higher relative contributions in
18 summer and therefore are thought to be mostly associated with secondary oxidation processes,
19 however a significant EC fraction in factor 1 suggests some contribution of vehicular emissions
20 to SOA. The lack of WSOC loading in secondary factor 2 is curious. Previous $\text{PM}_{2.5}$ source
21 apportionment studies conducted in Southeast US (Zhang et al., 2012; Zhang et al., 2010) also
22 showed a very low but non-zero WSOC fraction in this PMF factor. The results suggest that
23 multiple mechanisms are involved in the formation of secondary WSOC and SO_4^{2-} . More

1 detailed analysis of the specific components of SOA to DTT activity will be reported in the
2 future. Here we assume that factor 2 is more representative of regional secondary aerosols,
3 including some redox-active SOA, as there are no studies showing the DTT activity associated
4 with inorganic ions NH_4^+ and SO_4^{2-} .

5
6 Factor 3 has a very high loading of all metals and is attributed to road-dust. This factor is also
7 most significant in summer and fall, which is consistent with Figure 3 showing a generally
8 lowered concentration of metals in winter. Factor 4 has a clear signature of biomass burning with
9 very high concentrations of BrnC and K, and is prominent in winter. Lastly, the EC peak in
10 factor 5 is a distinct feature suggesting it is linked to primary vehicular emissions. Also
11 consistent with the vehicular sources, this factor does not have an obvious seasonal pattern.

12
13 The time-series of reconstituted DTT activity resolved by the five PMF factors, along with the
14 residuals (not predicted), and a distribution of these factors in each season, is shown in Figure 7.
15 In summer, secondary oxidation processes [WSOC (29 %) + SO_4^{2-} (17%), factors 1 and 2] are the
16 dominant contributors (46 %) to DTT activity, with additional contributions from biomass
17 burning (24 %, factor 4) and vehicle emissions (19 %, factor 5). In fall, the contribution from
18 secondary formation drops to 32% (22 % associated with WSOC and only 10 % with SO_4^{2-}
19 factors) with an increase in the contribution from vehicle emissions (25 %). Biomass burning
20 dominates the ROS generation potential in winter, contributing 47 % to the DTT activity, while
21 relatively low contribution from secondary formation (20 %) and vehicle emissions (12%) is
22 observed. Road dust (factor 3) also makes a non-zero contribution to DTT activity, but is
23 significant only in summer (13 %) and fall (11 %).

1 The seasonal contributions of various emission sources to DTT activity were averaged over the
2 complete sampling year to estimate their aggregate contributions. Figure 8a shows that the major
3 drivers of DTT activity of fine PM in Atlanta are biomass burning and secondary aerosols, with
4 their respective annual contributions of 35 % and 31 %. This is followed by vehicle emissions
5 contributing 16 % annually, while road dust contributes minimally (9 %) to the DTT activity of
6 PM_{2.5}. Together, all of these emission sources explained 91 % of the water-soluble DTT activity
7 and 70 % of its variability (R^2 between reconstituted and measured DTT activity = 0.70; not
8 shown) in Atlanta, demonstrating the robustness of our PMF model.

9
10 For the CMB analysis, step-wise regression provided a method for selecting the source
11 contributions that significantly affect DTT activity, the others were removed from the regression
12 to avoid over-fitting. Thus, *SDUST*, *CFPP* and *AMBSULF* were removed from the regression
13 through this process. The final regression was:

$$14 \quad DTT_v = 0.10 LDGV + 0.072 HDDV + 0.065 BURN + 0.023 AMSULF + 0.028 SOC + 0.0069 PMOther \quad Eq. (1)$$

15 *PMOther*, or the residual, was calculated by difference between the measured PM_{2.5} mass and
16 sum of the significant source contributions (i.e., *LDGV*, *HDDV*, *BURN*, *AMSULF*, *SOC*), for
17 each day. All coefficients have p-values less than 0.01 except *PMOther*. The resulting Pearson's
18 correlation coefficients (R) between DTT_v and the various sources were; *LDGV* 0.60, *HDDV*
19 0.27, *SDUST* 0.15, *BURN* 0.49, *CFPP* 0.16, *AMSULF* 0.33, *AMBSLF* 0.03, and *SOC* 0.44.

20 The aggregate contribution of each of these sources to the PM_{2.5} DTT activity over the whole
21 study period is also shown in Figure 8b. Overall, CMB yielded a similar picture as PMF;
22 biomass burning (*BURN*) and secondary oxidation processes (*SOC*+ *AMSULF*) were the
23 dominant sources of DTT activity in Atlanta with contributions of 33 % and 29 %, respectively,

1 in addition to vehicular sources (*LDGV+HDDV*, 32 %). CMB-identified vehicle sources also
2 include road dust, which may explain, to some extent, a higher vehicular contribution to DTT
3 activity by CMB compared to PMF.

4 **4. Conclusion**

5 Based on a large data set (N=483), the ability of water-soluble PM_{2.5} to generate oxidants
6 determined by the DTT assay was linked with aerosol sources in the Southeastern US. Spatial
7 and temporal profiles of DTT activity in the region were produced from more than a year of
8 sampling conducted intermittently at multiple sites, ranging from urban to rural environments.
9 PM chemical components indicated diverse emission characteristics at these sites in different
10 seasons. While WSOC was spatially uniform from widespread summertime SOA formation and
11 wintertime biomass burning emissions, primary pollutants such as EC and metals were less
12 uniformly distributed and were higher at the urban sites. The results show that DTT activity per
13 volume of air sampled is also spatially uniform, but has seasonal variability, with significantly
14 higher levels in winter compared to summer and fall.

15
16 Despite the spatial uniformity, the moderate correlations of DTT activity between paired sites
17 indicate the influence of both regional and local emissions on the PM's ability to generate ROS.
18 A simple linear regression conducted between DTT activity and chemical components at each
19 site in various seasons indicated that DTT activity is associated with WSOC in summer at both
20 urban and rural sites, and probably influenced by vehicle emissions at urban sites. The DTT
21 activity associations with WSOC moderated in fall while those with vehicular emissions and
22 road dust increased. In winter, DTT activity was best correlated with biomass burning (BrnC and
23 K) at both urban and rural sites.

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PMF analysis was conducted on the representative urban Atlanta dataset to quantify the contribution from each of these sources to the ROS generating potential of PM. Biomass burning and secondary aerosol formation were quantified as the strongest sources of DTT activity, with their respective study-average (summer 2012 to spring 2013) contribution of 35 %, and 31 %, followed by vehicular emissions (16 %). There was strong seasonality in the contribution from secondary and biomass burning aerosols, i.e. secondary processes dominated in summer accounting for 46 % of the DTT activity, while biomass burning in winter (47 %). The dust contribution was minimal (9%) and was significant only in summer and fall. Source apportionment conducted using an alternative approach, CMB, also yielded similar study-average contributions from secondary sources (29 %) and biomass burning (33 %), but higher contributions from vehicular emissions (32 %), which is partly due to road dust included in the CMB-identified vehicular source.

This is perhaps the first study integrating an extensive dataset on PM ROS generating potential with chemical components using source apportionment models and was made possible by a recently developed automated DTT analytical system. Previous studies, relying on a small sample size collected from single sites and typically in a specific season have associated similar chemical species to aerosol DTT activity, but often from a limited range of sources. Further analysis is underway to resolve the specific components of SOA and biomass burning that contributed to the DTT activity. Finally, we note that the large spatial distribution of two major sources of DTT activity, secondary aerosols and biomass burning emissions, suggests a wide-

1 spread exposure of populations to aerosol species capable of generating oxidants in vivo, and
2 possibly leading to oxidative stress induced adverse health effects.

3

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13

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5 Table 1: Sampling plan and details of sampling dates at each site.

Season, Year	Sapling dates		Sampling Site			
	Start Date	End Date	Fixed Site	Samples collected (N)	Mobile Site	Samples collected (N)
Summer, 2012	6/8/2012	7/20/2012	JST	31	YRK	33
	7/24/2012	8/31/2012	JST	37	GT	38
Fall, 2012	9/6/2012	10/4/2012	JST	26	RS	29
	11/15/2012	11/30/2012	JST	13	JST	14
Winter, 2012-13	12/6/2012	1/4/2013	JST	22	YRK	22
	1/27/2013	2/27/2013	JST	30	RS	31
	3/5/2013	3/27/2013	JST	23	GT	22
<i>Summer, 2013</i>	<i>6/16/2013</i>	<i>7/16/2013</i>	<i>CTR</i>	<i>31</i>	<i>BHM</i>	<i>31</i>
Fall, 2013	9/9/2013	10/3/2013	GT	25	RS	25
Total Number of Samples				238		245

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7 Note: In the summer of 2013 (shown in italics) measurements were made at sites outside of the
 8 State of Georgia as part of other studies to provide a greater context and were not part of the
 9 paired sampling approach with JST as the central site.

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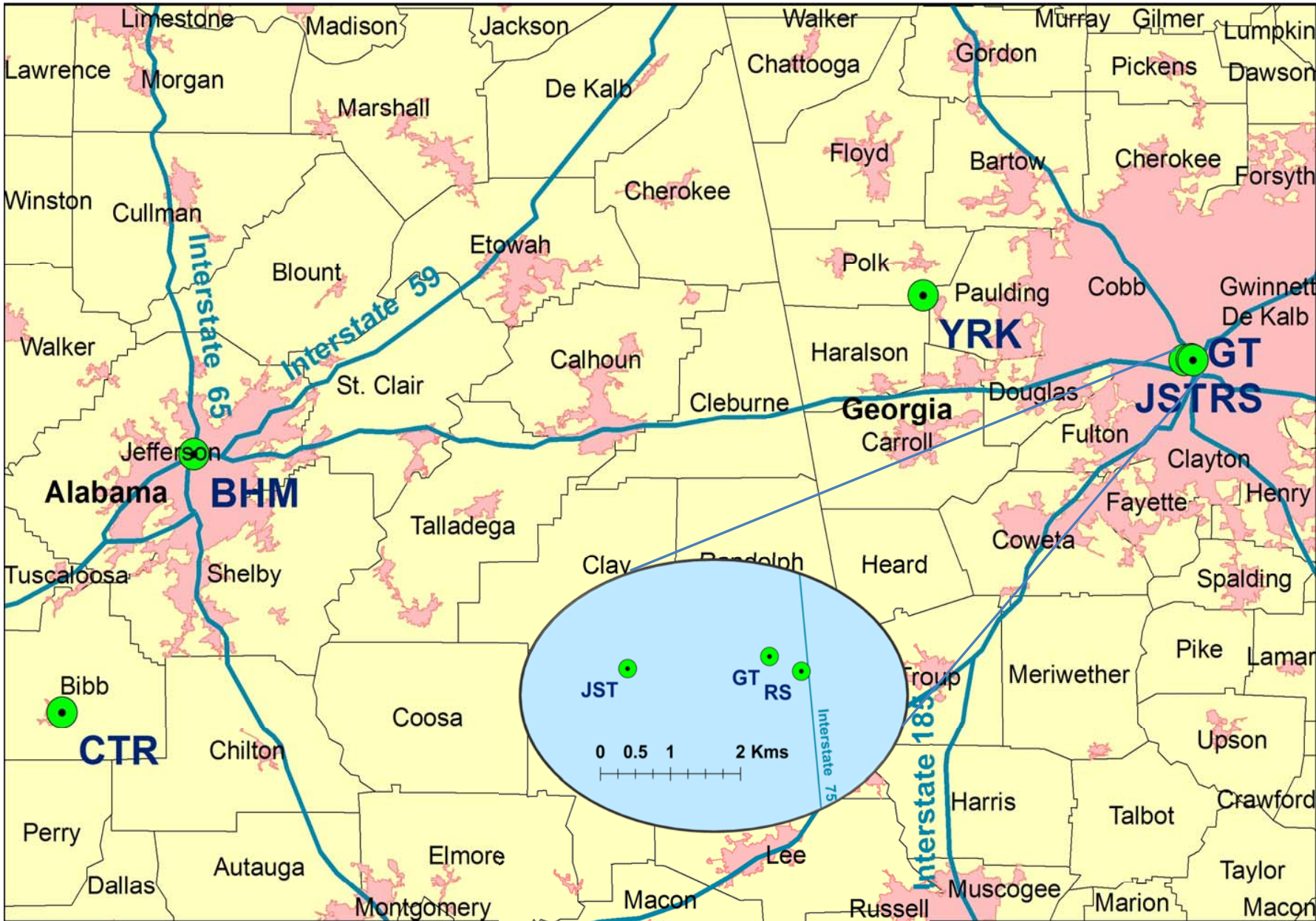
Table 2: Regression analysis (Pearson’s R) between DTT activity and selected PM components

Season	Site	Inorganic ions						Water-soluble metals					
		WSOC	BrnC	SO ₄ ⁻²	NH ₄ ⁺	OC	EC	K	Ca	Mn	Fe	Cu	Zn
Summer, 2012	<i>JST-GT</i>	0.81	0.67	0.68	0.73	0.81	0.69	0.49	0.20	0.72	0.78	0.71	0.62
	<i>YRK</i>	0.79	0.53	0.58	0.59	0.76	0.56	0.51	0.68	0.63	0.48	0.09	0.48
Fall, 2012	<i>JST</i>	0.72	0.81	0.49	0.52	0.83	0.90	0.61	-0.08	0.37	0.74	0.20	0.82
	<i>RS</i>	0.71	0.59	0.62	0.66	0.77	0.55	0.52	0.12	0.28	0.44	0.61	0.68
Winter, 2012-13	<i>JST-GT</i>	0.69	0.78	0.15	0.13	0.85	0.82	0.78	-0.13	0.46	0.65	0.63	0.63
	<i>YRK</i>	0.84	0.88	0.34	0.45	0.82	0.80	0.75	0.31	0.68	0.04	0.43	0.72
	<i>RS</i>	0.78	0.86	0.47	0.52	0.86	0.75	0.69	0.31	0.49	0.57	0.35	0.60
Summer, 2013	<i>CTR</i>	0.78	0.88	0.71	0.78	0.77	0.72	0.66	0.23	0.36	0.41	-0.12	0.62
	<i>BHM</i>	0.67	0.74	0.66	0.66	0.85	0.68	0.41	0.55	0.75	0.66	0.23	0.66
Fall, 2013	<i>GT</i>	0.47	0.75	0.39	0.37	0.79	0.78	0.65	0.29	0.58	0.66	0.46	0.46
	<i>RS</i>	0.21	0.48	0.60	0.47	0.58	0.53	0.74	0.79	0.84	0.53	-0.09	0.74

Note: R>0.65 are bolded.

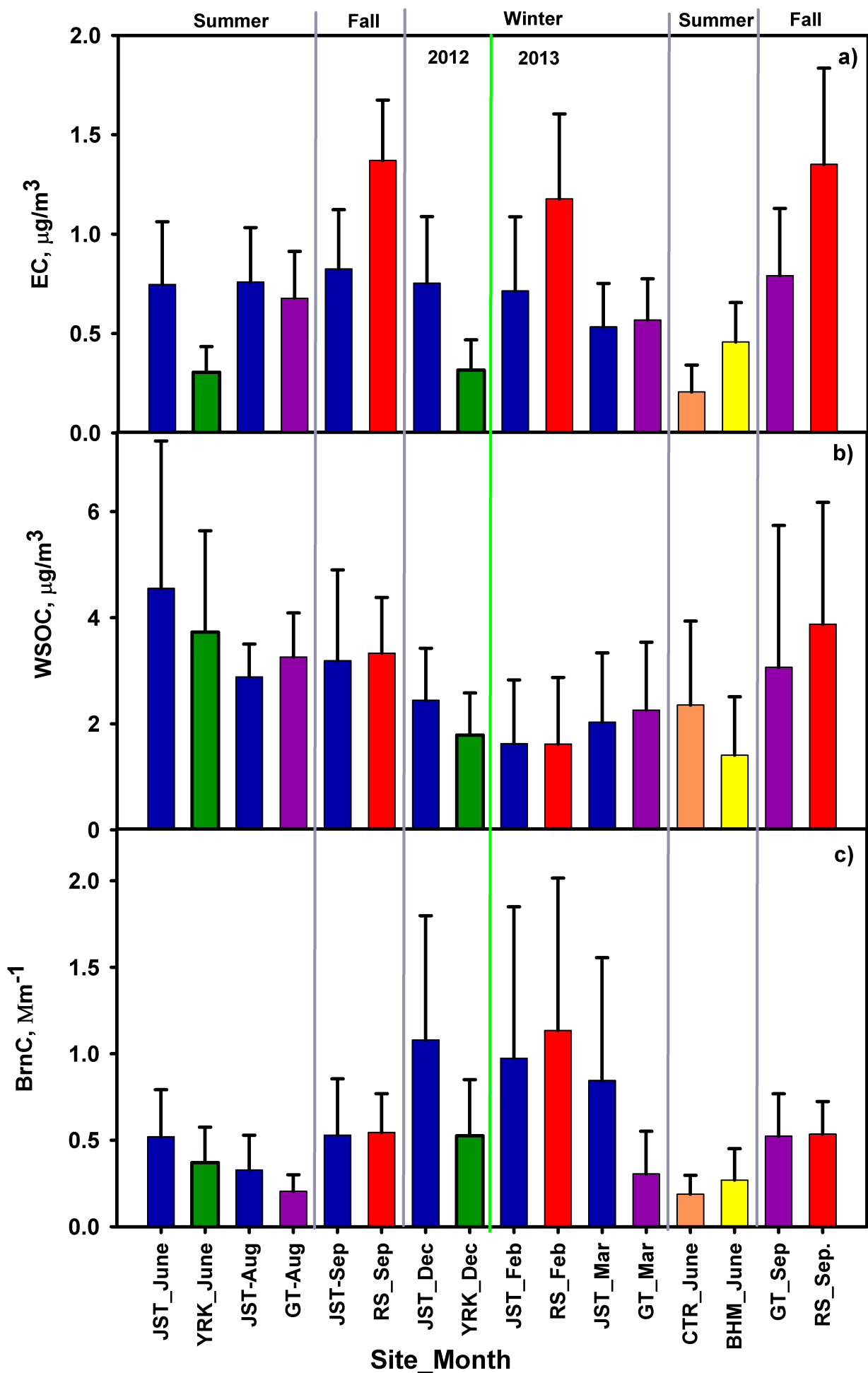
- 1 Figure 1: Map of Sampling Sites
- 2 Figure 2: Monthly average ambient concentrations of EC (a) WSOC (b) and BrnC (c) at the
3 sampling sites
- 4 Figure 3: Monthly average ambient concentrations of water-soluble metals at the sampling sites
- 5 Figure 4: Monthly averages of volume- (DTTv) and mass-normalized (DTTm) DTT activity at
6 the sampling sites
- 7 Figure 5: Site-to-site correlations (R^2) for volume normalized DTT activity (DTTv), elemental
8 carbon (EC) and water-soluble carbon (WSOC) of $PM_{2.5}$.
- 9 Figure 6: Composition profiles (% of each species) for the five factors resolved by PMF (left
10 panel), and the time series of their relative contribution (right panel).
- 11 Figure 7: Time series of $PM_{2.5}$ DTT activity segregated into different factors as predicted by
12 PMF and their season-wise contributions
- 13 Figure 8: Annual aggregate contributions of different sources identified by PMF (Figure 8a) and
14 CMB method (Figure 8b) to the water-soluble DTT activity of ambient $PM_{2.5}$ in urban Atlanta
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● Sampling_Sites

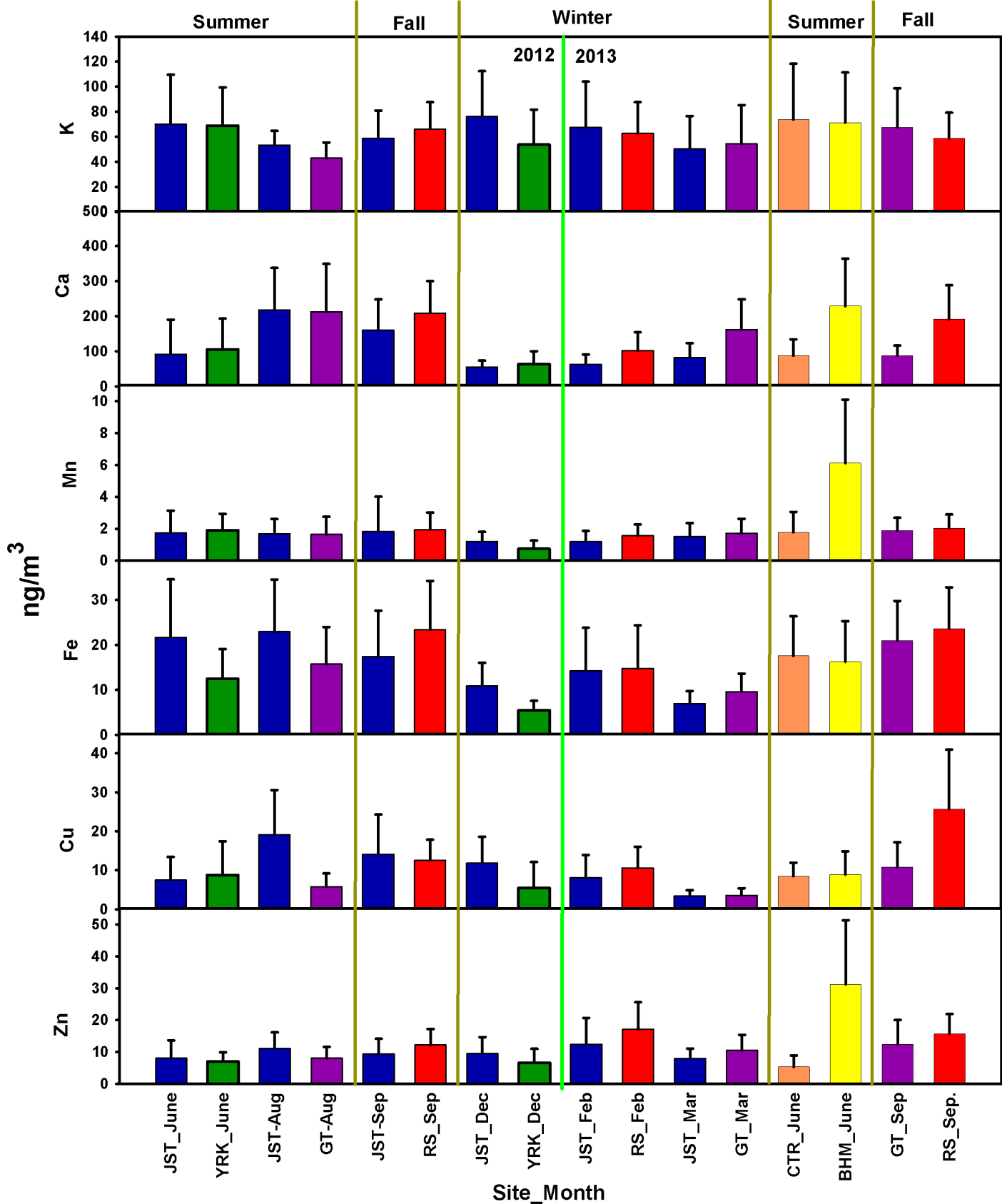


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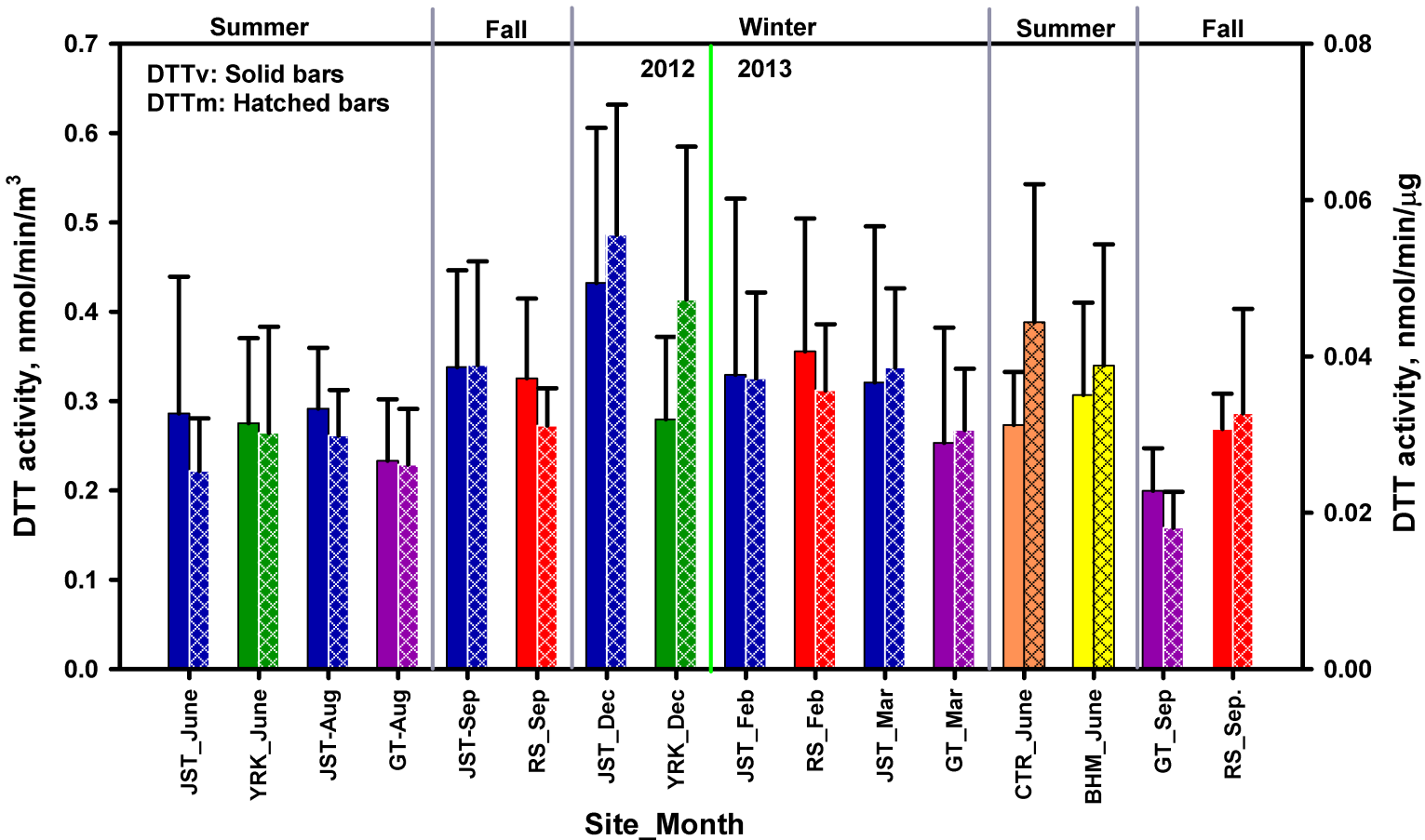




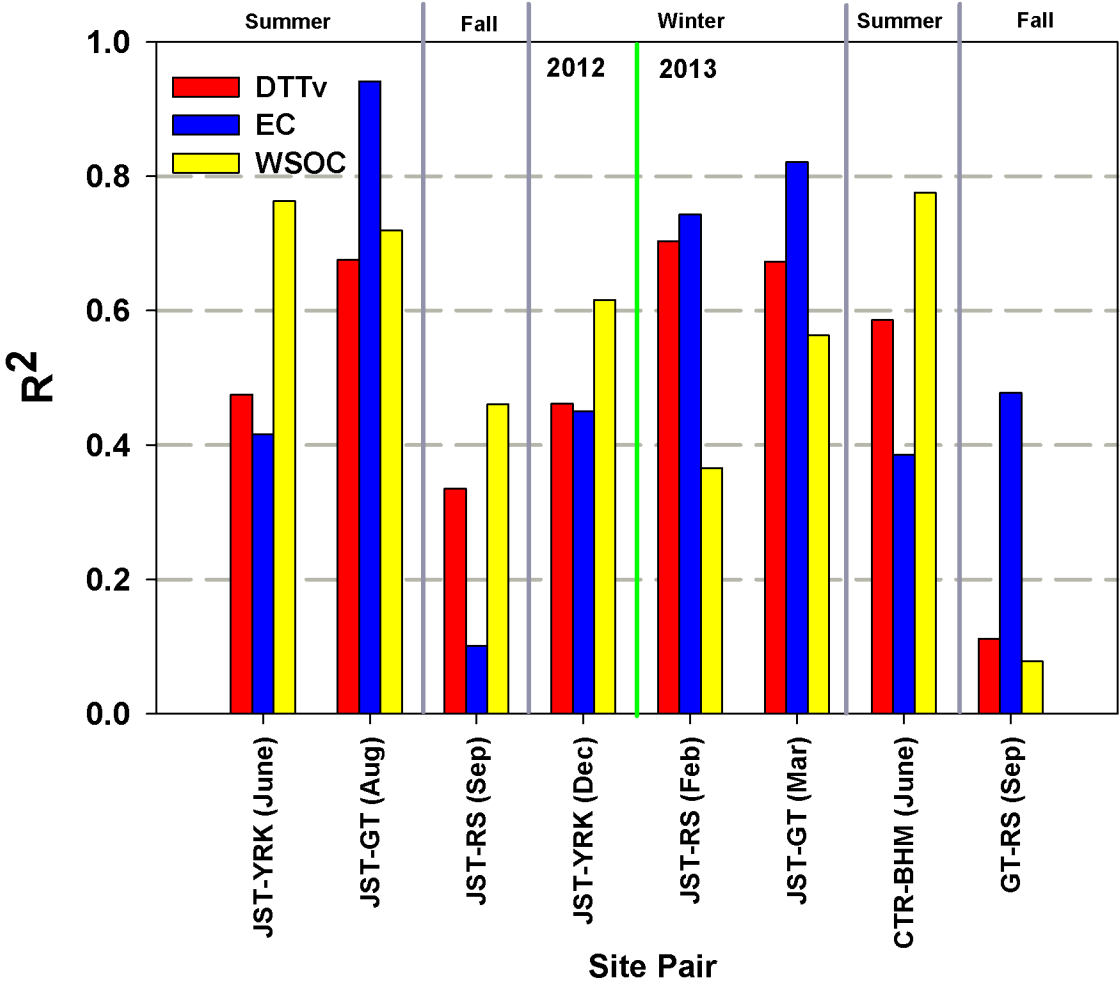
Error bars: standard deviation (1σ) of monthly averages

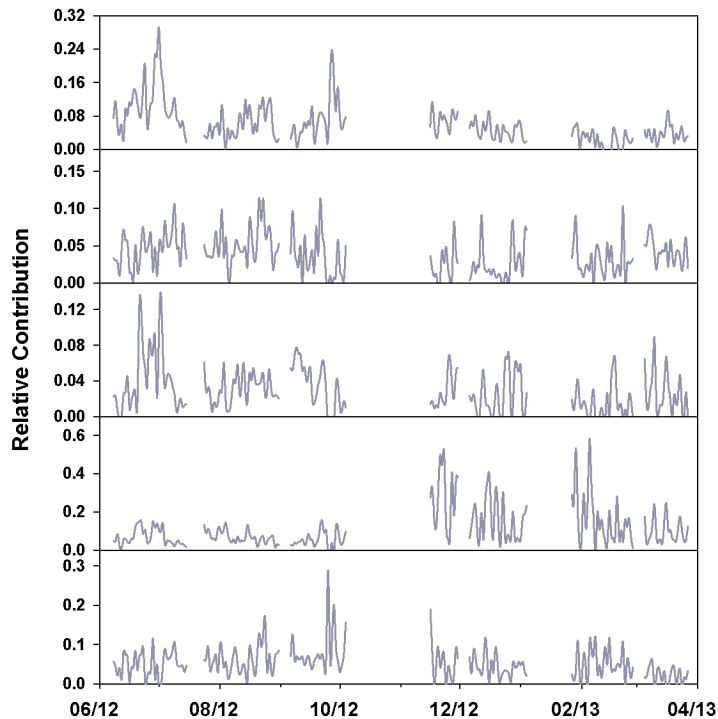
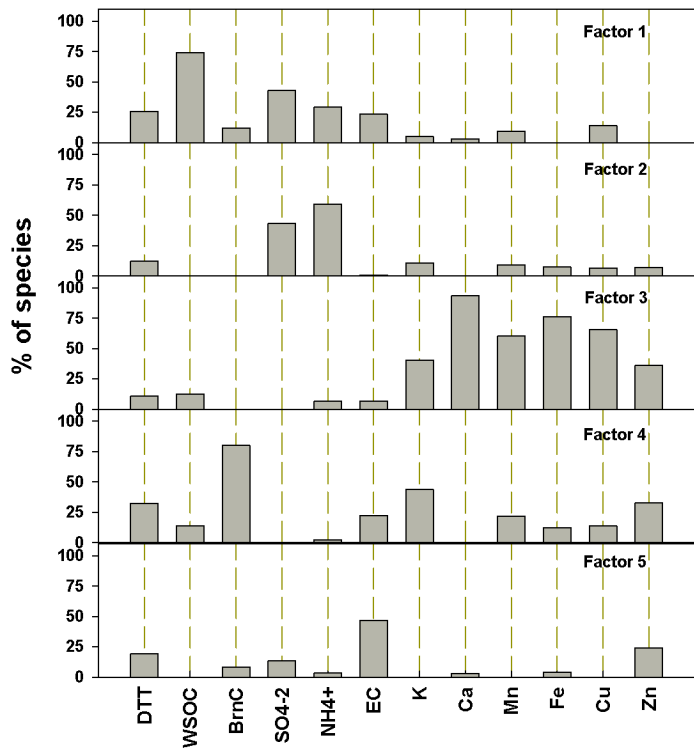


Error bars: standard deviation (1σ) of monthly averages

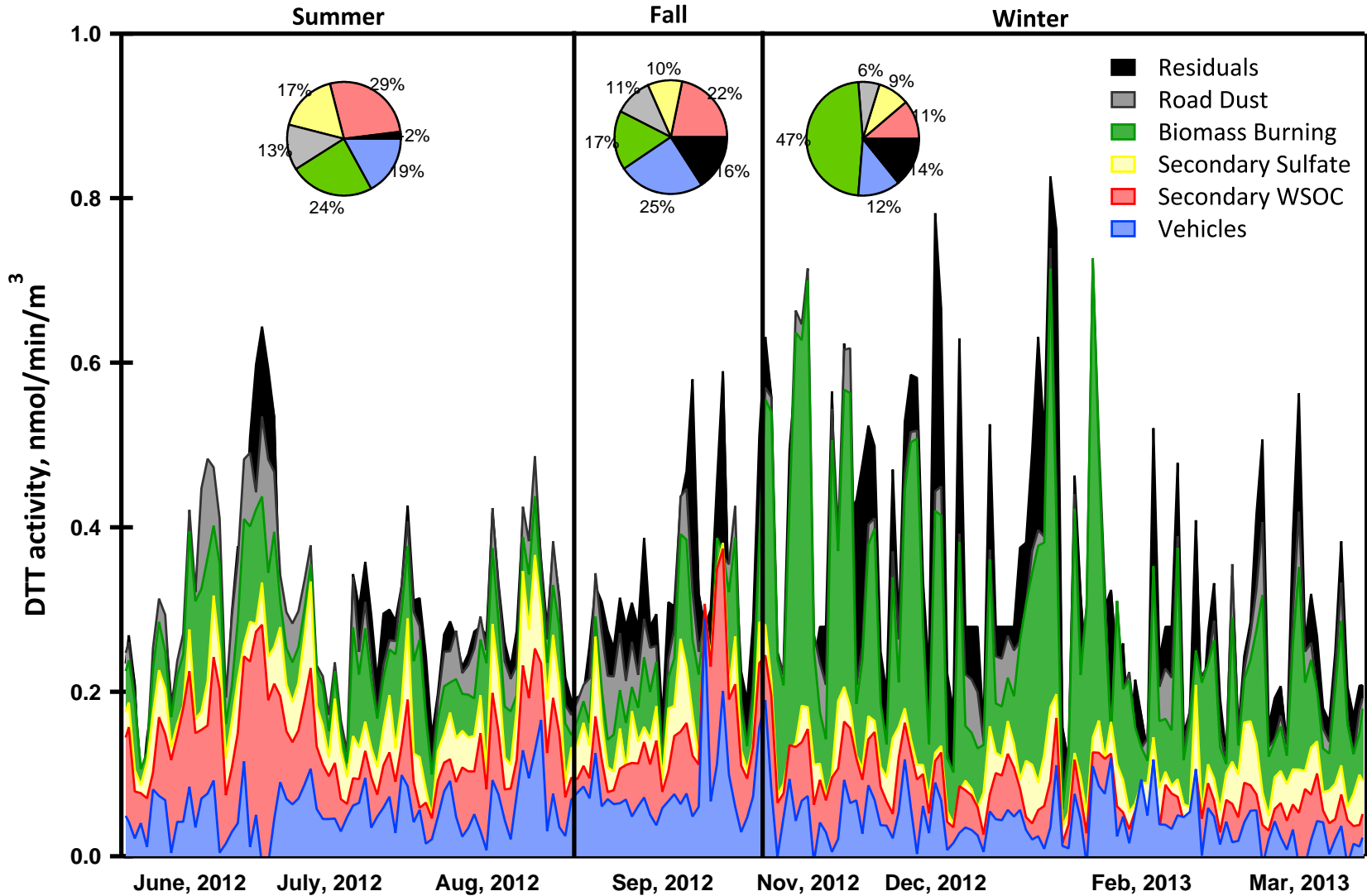


Error bars: standard deviation (1σ) of monthly averages

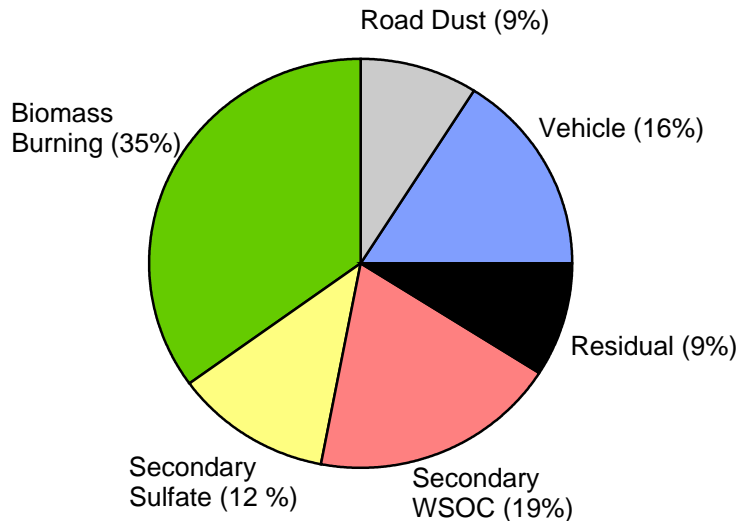




The scale for relative contribution of various factors (Y-axis of the right-side panel) has a different range for each factor.



a)



b)

