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Reactive oxygen species associated with water-soluble $PM_{2.5}$ in the southeastern United States: spatiotemporal trends and source apportionment

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Abstract

We assess the potential of the water-soluble fraction of atmospheric fine aerosols in the southeastern US 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 h 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 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 %). Mineral 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. Our results indicate that the ability to generate ROS is a generic property of fine PM to which almost all major emission sources contribute to variable extents. The ubiquitous nature of the ROS generation

property of ambient particulate matter suggests widespread population exposures to aerosol components that have the ability to catalyze the production of oxidants in vivo.

1 Introduction

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

Based on this possible mechanistic route linking aerosol chemistry to health, numerous studies have been initiated in the past several years focused on measuring the oxidative properties of ambient particles. A variety of probes have been developed to quantify different aspects of PM induced oxidative stress. These include chemical systems that mimic the loss of antioxidants, such as oxidation of dithiothreitol (DTT assay, Cho et al., 2005), glutathione (GSH, Godri et al., 2011), and ascorbic acid (AA, DiStefano et al., 2009; Mudway et al., 2004), covalent bonding with glyceraldehyde-3-phosphate dehydrogenase (GAPDH, Rodrigueza et al., 2005), and hydroxyl radical generation in the presence of H_2O_2 (Shi et al., 2003). Other probes measure cellular responses when exposed to aerosols; such as macrophage ROS generation (Landreman et al., 2008), the induction of hemeoxygenase-1 (HO-1) and other stress protein expression (Li et al., 2003), and cytokine activation (Wilson et al., 2010). Each of these assays represents a plausible mode of PM toxicity and collectively they should be considered as the toolkit for deconstructing the complex mechanisms of PM ROS generation. One advantage of these assays, is that they are integrative of various aerosol chemical properties, and as pointed out by several researchers (Ayres et al., 2008; Venkatachari and Hopke, 2008; Kuenzli et al., 2004), many of them can serve as a screening step for assessing the PM samples/emission scenarios for more detailed chemical analysis and downstream health studies.

The DTT assay was devised to simulate the in-vivo generation of superoxide radicals, wherein DTT was used as a surrogate of the biological reducing agents (NADH and NADPH) (Kumagai et al., 1997, 2002). When incubated at 37 °C with a test PM sample, a decreasing DTT concentration over time is inferred as a measure of the ROS generating capability of the particles. A number of pure chemicals have been found to be associated with the response of this assay, e.g. quinones have been known to catalyze the transfer of electrons from DTT to oxygen (Kumagai et al., 2002). In a recent study, certain transition metals (e.g. Fe, Cu and Mn) have also been shown to be active in this assay (Charrier and Anastasio, 2012). However, evidences showing that any of these chemicals play a significant role in the DTT activity of ambient PM are sparse and limited in terms of their analytical efficacy. The major components of the ambient PM identified so far to be associated with the DTT activity are often bulk groups of species such as organic carbon (OC, both water-soluble (WSOC) and insoluble, WIOC) and water-soluble HULIS (Humic-like-substances) compounds (a class of WSOC characterized by strong hydrophobicity). However, most of these associations have been inferred based on statistical correlations (Ntziachristos et al., 2007; Verma et al., 2009a, b; Hu et al., 2008; Biswas et al., 2009b), which do not necessarily establish causation, while very few have used semi-mechanistic approaches such as physical separation of the organic compounds and metals (Verma et al., 2011; Lin and Yu, 2011; Charrier and Anastasio, 2012).

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

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

2 Experimental methods

2.1 Sampling plan

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

2.2 Sampling sites

A map showing the locations of all sites is shown in Fig. 1. Jefferson Street is located roughly 4 km northwest of downtown Atlanta and is representative of urban-Atlanta. The site is surrounded by commercial and residential buildings, with nearby street traffic patterns consistent with a mixed-use urban environment. The site has extensively been used in past studies characterizing urban Atlanta air quality (Hansen et al., 2006; Marmur et al., 2005) and the data used in epidemiological studies (Sarnat et al., 2008;

Strickland et al., 2010). In this study, Jefferson Street is again used as representative of urban Atlanta, to which the other three satellite measurements (discussed next) are compared.

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

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

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

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

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

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

2.3 Filter collection and extraction protocol

A high-volume sampler (HiVol, Thermo Anderson, non-denuded, nominal flow rate 1.13 $m^3 min^{-1}$, $PM_{2.5}$ impactor) was setup at each site and fine particles were collected onto pre-baked 8 × 10″ quartz filters (Pallflex® Tissuquartz™, Pall Life Sciences). 23 h integrated samples (12:00 noon–11:00 a.m. next day) were collected daily during the sampling periods (Table 1) at each site, along with periodic field blanks (at least 3 per site per month). The number of samples collected from each site, approximately 30 per site per season (total = 483) is given in Table 1. After collection, the filters were wrapped in pre-baked aluminum foil and immediately stored in a freezer (−18 °C). Prior to the chemical and oxidative potential analysis, the filters were cut using a 1″ diameter metallic punch. For the DTT activity, WSOC and BrnC analysis, three filter sections (1″ diameter each) were extracted in 15 mL of deionized water (DI, Milli-Q; >18 MΩ) via sonication in a water bath for 30 min, while additional punches were extracted separately in the same manner (15 mL of DI for 30 min of sonication time) for the metals (4 punches) and inorganic ions (1 punch) analysis. These extracts were then filtered using PTFE 0.45 µm pore syringe filters (Fisher brand). The filtered extracts for metals were acidified by adding nitric acid (high purity trace metal grade; 2 % w/v final solution), consistent with current protocols (Henshaw et al., 1989; Talbot et al., 1994).

2.4 Online instruments

$PM_{2.5}$ mass concentrations were monitored by a tapered element oscillating microbalance (Thermo Scientific TEOM 1400a), operating continuously at JST, BHM, YRK and CTR throughout the sampling period (Atmospheric Research Analysis Inc. data). At other sites (RS and GT), summed concentrations from measured chemical components (EC + 1.6 OC ions + water-soluble metals), were used as a proxy for the PM mass

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concentrations. This method has been found to agree well with the TEOM concentrations at JST and YRK sites, where co-located measurements were available (Fang et al., 2014).

2.5 Chemical analysis on PM filters

Water soluble organic carbon (WSOC) and the WSOC light absorption properties (Brown Carbon, BrnC, used as a source tracer) were measured on HiVol extracts via an automated system using an autosampler (Dionex 40AS), spectrophotometer and total organic carbon (TOC) analyzer. BrnC was measured on an aliquot (300 µL) of the extracts via a liquid waveguide capillary cell (LWCC-2100, World Precision Instruments, Sarasota, FL), which was coupled to a UV/VIS spectrophotometer (USB4000 spectrometer, Ocean Optics, Dunedin, FL) (Hecobian et al., 2010). Following the waveguide, the aliquot was conducted to a Sievers TOC analyzer (Model 900, GE Analytical Instruments; Boulder, CO) for determination of WSOC concentration.

The automated system was also used to measure water-soluble metals, which involved nebulizing the water extracts and directing the aerosol stream to an XRF (X-ray fluorescence) instrument (Xact™ 625 Monitoring System), capable of online measurements of a range of elements. Details of the nebulizer-XRF system would be published in a subsequent publication. Briefly, 5 mL of the acidified PM water-extracts was aerosolized using a continuous flow ultrasonic nebulizer (CETAC, U5000 AT$^+$). The resulting fine aerosol was conducted by a flow of clean filtered air through a drying system (a 136 °C heated section followed by a cooled section at −5 °C). The dried aerosol stream was neutralized by a Kr-85 source and mixed with clean filtered (Pall HEPA Capsule, Part No. 12144) air to obtain the instrument sample flow rate of 16.7 L min^{-1}. A wide range of elements were measured by the instrument, however we present only the relevant species which are either used as specific emission markers (Ca, dust; Coz et al., 2010), (K, biomass burning; Artaxo et al., 1994), or possibly play a role in ROS generation (Fe, Cu, Mn, Zn; Schoonen et al., 2006).

Elemental and organic carbon content of the PM was measured on a small section ($1.45\,\mathrm{cm}^2$) of the HiVol filters using a thermal/optical transmittance (TOT) analyzer (Sunset Laboratory) by NIOSH (The National Institute for Occupational Safety and Health) method (Birch and Cary, 1996). For the measurement of inorganic ions (SO_4^{-2}, NH_4^+, etc.) at JST and GT, ion-chromatography (IC) (LC30 chromatography oven, and Dionex CD20 conductivity detector, with IonPac® CS12A carboxylate-functionalized cation-exchange and IonPac® AS12A carbonate eluent anion-exchange columns) was performed on the aerosol extracts of HiVol filters collected from those sites.

2.6 ROS generation potential measurement

ROS generation potential of the ambient aerosols was measured by a semi-automated instrument (Fang et al., 2014) for measuring DTT activity of the PM extracts obtained from HiVol filters. The method is conceptually identical to the manual procedure described by Cho et al. (2005). The initial DTT concentration was 100 µM and loss of DTT in the reaction vial at several time steps (0, 4, 13, 23, 32 and 41 min) was monitored and used to calculate the DTT consumption rate based on the linear regression slope. The automated method provided a measurement of the DTT activity at a rate of 1 sample per hour. For each batch (consisting of either 7 or 14 samples), at least one field blank and one standard (9,10-Phenanthraquinone used as a positive control) were analyzed. Both blanks and standards were fairly consistent, with an average slope ± standard deviation of 0.38 ± 0.10 ($N = 45$) and 1.27 ± 0.19 ($N = 55$) $\mathrm{nmol\,DTT\,min^{-1}}$, respectively. The automated system was cleaned periodically (generally after every 15 days, or unless the slope of DTT reaction rate started to become non-linear) by rinsing thoroughly with methanol (at least 3 times) followed by DI (at least 6 times).

2.7 Source apportionment analysis

The emission sources contributing to ROS generation potential of the particles were investigated using regression and receptor modeling techniques. As typically done in these studies, a simple linear regression was conducted between the measured concentrations of various chemical components and DTT activity for each individual site and season. A rough indication of ROS sources was obtained based on the correlations between DTT activity and various species, and associating those species with sources. The large dataset from the combined JST and GT sites, which are representative of urban Atlanta air quality, allows a more quantitative source apportionment. Two receptor models were used - positive matrix factorization (EPA-PMF, version 3.0) and chemical mass balance (EPA-CMB, version 8.2).

Detailed description and procedural details of PMF are described elsewhere (Paatero, 1997; Norris and Vedantham, 2008). In the present PMF analysis, WSOC, BrnC, NH_4^+, SO_4^{-2}, and EC were classified as strong (high signal-to-noise ratio; S / N) species, while metals K, Ca, Mn, Fe, Cu and Zn were categorized as weak (low S / N). DTT activity was chosen as the "total variable" and thus by default assigned as weak species. Missing values in the data were replaced by the species median. For the base runs ($N = 20$), a seed of 25 was chosen and the model was executed for 4, 5 and 6 number of factors. The converged run with the highest goodness-of-fit parameter (lowest object function) was selected for five factors, which are identified as secondary WSOC, secondary SO_4^{-2}, vehicular emissions, mineral dust and biomass burning.

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

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

3 Results and discussion

3.1 PM emission characteristics

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

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

The monthly average concentrations of EC (Fig. 2a) are consistent with primary vehicular emissions being the dominant EC source; the concentrations are highly heterogeneous. Large concentration differences were observed for each pair, with highest EC at the RS, followed by urban background sites (JST, GT, and BHM), and lowest concentrations at the rural sites (YRK and CTR). The JST-GT EC concentrations were similar, suggesting that GT is not highly influenced by the roadway emissions, and so more representative of EC levels in the metro area, similar to JST. The largest contrast in EC among paired measurements is between urban and rural sites. For both summer and winter seasons, EC is more than double at the urban sites (JST and BHM) compared to their respective paired rural components (YRK and CTR) (mean ± standard deviation (1σ) of ratio = 2.9 ± 1.6 in summer, and 2.7 ± 0.9 in winter for JST/YRK, and 2.92 ± 1.42 for BHM/CTR). The RS site has the highest concentration of EC in both fall and 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).

There is little seasonal variation in the EC levels across most sites. For example, the average EC concentrations at JST in summer ($0.75 \pm 0.25\,\mu\mathrm{g\,m^{-3}}$), fall ($0.82 \pm 0.30\,\mu\mathrm{g\,m^{-3}}$), and winter ($0.67 \pm 0.33\,\mu\mathrm{g\,m^{-3}}$) were similar. The mean EC concentration at RS was slightly lower in winter ($1.18 \pm 0.43\,\mu\mathrm{g\,m^{-3}}$) than fall ($1.37 \pm 0.30\,\mu\mathrm{g\,m^{-3}}$ in September 2012 and $1.45 \pm 0.34\,\mu\mathrm{g\,m^{-3}}$ in September 2013). The marginally lower levels of EC in winter seasons in Atlanta (JST, GT and RS sites) might be attributed to higher rainfall during these periods (December–March; Supplement Fig. S1). Precipitation scavenging could have superseded the effect of generally reduced mixing height in winter on primary aerosol concentrations.

Unlike EC, WSOC was more spatially uniform, but varied substantially between different seasons. WSOC concentrations at the paired sites were very similar indicating that major WSOC sources extend to regional scales. These sources are mainly secondary organic aerosol (SOA) formation and biomass burning, (Zhang et al., 2010, 2012), with possibly minor influence from primary WSOC associated with vehicular emissions at the urban sites (Yan et al., 2009). An overall stronger influence of summertime SOA than wintertime biomass burning on WSOC in the region is apparent from a gradually decreasing averaged concentration profile at JST from summer to winter ($3.8 \pm 2.2\,\mu g\,m^{-3}$, $3.2 \pm 1.7\,\mu g\,m^{-3}$ and $2.0 \pm 1.1\,\mu g\,m^{-3}$ in summer, fall and winter). Similar decreases are also noted at other sites ($3.7 \pm 1.9\,\mu g\,m^{-3}$ in summer to $1.8 \pm 0.8\,\mu g\,m^{-3}$ in winter at YRK, and $3.3 \pm 1.1\,\mu g\,m^{-3}$ and $3.9 \pm 2.3\,\mu g\,m^{-3}$ in fall, 2012 and 2013, respectively to $1.6 \pm 1.3\,\mu g\,m^{-3}$ in winter, 2013 at RS). These results are consistent with a more detailed analysis of the WSOC spatial and seasonal distribution conducted two years before in the southeast US (Zhang et al., 2010).

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

3.1.2 Water-soluble metals

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

Rural sites, YRK and CTR, have generally lower metals concentrations, while GT and JST levels are moderate.

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

3.2 PM ROS generation potential

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

Time series of daily average DTT activity from the sites in different months is shown in Fig. 4a and b. The rate of consumption of DTT is normalized by both the volume of sampled air (DTTv; expressed in units of nmol min^{-1} m^{-3}, Fig. 4a) and the particulate mass (DTTm; expressed in units of nmol min^{-1} μg^{-1}, Fig. 4b). While volume normalized activity is a function of strength of the emission source, and thus an extrinsic property, mass normalized levels represent an intrinsic property of PM, independent of its mass concentration and a characteristic of the specific source.

Our measurements of both volume and mass normalized DTT activity are generally in the typical range (0.1–1.5 nmol min^{-1} m^{-3} for DTTv and 0.005–0.1 nmol min^{-1} μg^{-1} for DTTm, as summarized in Fang et al., 2014) observed for ambient particles at other locations. Figure 4 shows that in general, both the extrinsic (DTTv) and intrinsic (DTTm) activity of ambient PM is spatially uniform. There is no consistent and substantial difference in DTT activity of ambient PM at the two sites for any paired measurement, except the JST-YRK pair in winter [DTTv(YRK) < DTTv(JST)] and GT-RS pair in fall [DTTm(RS) > DTTm(GT)]. Intrinsic DTT activity is fairly uniform even on day-to-day scales for most sites, suggesting that the sources of ROS-associated aerosol components don't change rapidly. There is, however, a substantial daily variability in the extrinsic activity, which reflects variations in emissions, dispersion and sinks, factors that also control overall PM mass concentrations.

A summary of the spatial and seasonal trends in mean DTT activity (both DTTv and DTTm) for the individual sampling periods and at various sites is shown in Fig. 5. A significant seasonal variability in both the volume and mass normalized DTT activity is evident; the levels are generally higher in the colder months than summer. A one-sample t-test showed that the DTTv at JST in December was significantly ($p \leq 0.05$) higher from that in June–July (51 ± 34 %), August (48 ± 22 %), and September (27 ± 14 %). These results are in agreement with a recent study conducted in the Los Angeles Basin, which showed a generally higher DTT activity (both mass and volume normalized) of quasi-ultrafine particles in cooler months compared to warmer periods (Saffari et al., 2014). The authors in that study attributed the higher DTT activity to an elevated concentration of redox-active semi-volatile organic compounds (SVOC) caused by their enhanced partitioning to the particulate phase and the lowered atmospheric mixing height in winter. Although, SVOC have been suggested to make a substantial contribution to the DTT activity of ultrafine particles (Verma et al., 2011), the $PM_{2.5}$ samples collected via HiVol filters in our study are not expected to contain a significant fraction of these species due to losses associated with large flow-rate and long sampling duration (Ashbaugh and Eldred, 2004).

The seasonal variability is even more pronounced in the intrinsic DTT activity. For example, differences in DTTm levels in December vs. June–July (119 ± 48 %), August (86 ± 31 %) and September (44 ± 14 %) are higher compared to the respective differences in DTTv levels. Similar increases in the intrinsic DTT activity in winter were observed at other sites too (38 ± 13 % at GT from average of August 2012 and September 2013, and 53 ± 24 % at YRK), but not at RS, where average fall level ($0.032 \pm 0.009\,\text{nmol}\,\text{min}^{-1}\,\mu\text{g}^{-1}$) was nearly the same as in winter ($0.036 \pm 0.008\,\text{nmol}\,\text{min}^{-1}\,\mu\text{g}^{-1}$).

To further assess the spatiotemporal variability in DTTv activity in the region, correlation coefficients (R^2) were calculated for all of the site pairs and are shown in Fig. 6. To put the DTT activity comparison in a larger context, we have also included the corresponding coefficients for EC and WSOC. A high spatial correlation for a species indicates it has more spatially uniform emission sources in the region, on the scale of distances between the paired sites.

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

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

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

3.3 Sources of PM ROS generation potential

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

3.3.1 Linear regression of DTT activity with PM chemical composition

Pearson's correlation coefficients for the linear regression between DTT activity and the measured chemical components were calculated for each site and season and are shown in Table 2. Considering the limited daily variability in mass normalized DTT activity at most sites in a given season, the regression was conducted on the volume normalized levels of DTT activity (nmol min^{-1} m^{-3}) and chemical components (µg m^{-3}). To consolidate the data for convenience, individual time-series at JST and GT sites from June-to-August were merged (named "JST-GT Summer"), given their similar concentration profiles. Similarly, JST and GT time series from December to March were merged as "JST-GT winter". The complete regression matrix showing the correlation between all pairs of selected species, for each site and season, is provided in the Supplement (Table S1).

DTT activity is almost always correlated with OC in the present study. OC results from all major sources in the region (e.g. vehicular emissions, SOA, and biomass burning) and comprises the greatest fraction of PM mass (OM/PM$_{2.5}$ > 60 %, not shown).

Thus, the strong correlation of OC underlines the general contribution of PM organic compounds in the ROS generation potential, and also likely accounts for the DTT correlation with PM mass, as reported in Fang et al. (2014). However, it does not yield any novel information on the specific PM species or the emission sources associated with the DTT activity. Associations between water-soluble DTT activity and organic compounds are consistent with a number of previous studies (Biswas et al., 2009a; Verma et al., 2012; Cho et al., 2005; Yang et al., 2014), but in contrast to other reports showing metals as the major drivers in this reaction (Charrier and Anastasio, 2012).

In summer, DTT activity is well correlated with WSOC at all sites; JST-GT ($R = 0.81$), YRK ($R = 0.79$), CTR ($R = 0.78$) and BHM ($R = 0.67$). Inorganic ions such as SO_4^{-2} and NH_4^+ are also correlated with WSOC and DTT activity ($R > 0.60$ at most sites) indicating secondary photochemical formation as their common source in summer. This is consistent with the results of ambient (Verma et al., 2009a) and chamber studies (McWhinney et al., 2013; Li et al., 2009b) suggesting higher DTT activity of secondary organic compounds than their parent gases and primary particles.

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

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

In fall, DTT activity appears to be derived from a mixed contribution from primary vehicular emissions and secondary formation, as supported by its correlation with WSOC

($R = 0.72$), and EC ($R = 0.90$) at JST. Metals such as Fe and Zn are also correlated with DTT activity ($R = 0.70$ and 0.82) and EC ($R = 0.90$ and 0.75) at JST. The stronger correlation of primary emissions (EC) than secondary species (WSOC, SO_4^{-2}, NH_4^+) indicates a diminishing effect of photochemistry on the DTT activity. This is even more apparent in fall 2013, when the highest correlation of DTT at GT is with EC ($R = 0.78$), while the correlation with WSOC is low ($R = 0.47$).

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

In winter months, DTT activity is again correlated with WSOC at all sites; JST-GT ($R = 0.69$), YRK ($R = 0.84$), and RS ($R = 0.78$), however, this correlation is not accompanied by a similar correlation with inorganic ions ($R < 0.55$ for SO_4^{-2} and NH_4^+) as in summer months. It implies that another emission source of WSOC – biomass burning, starts contributing more to the DTT activity in winter. This is further reflected in the strong correlation of BrnC and K with DTT activity and WSOC ($R > 0.65$; Table 2 and Supplement Table S1) at all sites. In a study conducted in Los Angeles, the ambient concentrations of K and WSOC were elevated (~ 2 ×) during the 2007 Southern California wildfires compared to the post-fire period (Verma et al., 2009b). More importantly, these wood-smoke particles were found to be at least two times more oxidative than the post-fire ambient $PM_{2.5}$ typically dominated by vehicular emissions. The redox-active WSOC emitted in the biomass burning particles probably explain the higher intrinsic DTT activity of ambient PM in winter compared to other seasons in the present study (Figs. 4 and 5).

Interestingly, EC is also highly correlated with DTT activity ($R \geq 0.75$) in winter at all sites. However, the concurrent correlation of EC with BrnC and K ($R > 0.60$ at all sites;

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

3.3.2 Source contributions to DTT activity

To provide a more quantitative assessment of the contribution of various sources to the fine particle oxidative properties in urban Atlanta, a PMF analysis was conducted using the DTT activity and measured chemical composition data. The five factors resolved by PMF are shown in Fig. 7. Factors 1 and 2 are characterized with high WSOC and high inorganic ions (NH_4^+ and SO_4^{-2}) loadings, respectively. Both of these factors have higher relative contributions in summer and therefore are thought to be mostly associated with secondary oxidation processes, however a significant EC fraction in factor 1 suggests some contribution of vehicular emissions to SOA. The lack of WSOC loading in secondary factor 2 is curious. Previous $PM_{2.5}$ source apportionment studies conducted in Southeast US (Zhang et al., 2012; Zhang et al., 2010) also showed a very low but non-zero WSOC fraction in this PMF factor. The results suggest that multiple mechanisms are involved in the formation of secondary WSOC and SO_4^{-2}. More detailed analysis of the specific components of SOA to DTT activity will be reported in the future. Here we assume that factor 2 is more representative of regional secondary aerosols, including some redox-active SOA, as there are no studies showing the DTT activity associated with inorganic ions NH_4^+ and SO_4^{-2}.

Factor 3 has a very high loading of all metals and is attributed to mineral dust, however a slight EC fraction in this factor might also imply some association with vehicular emissions. This factor is also most significant in summer and fall, which is consistent with Fig. 3 showing a generally lowered concentration of metals in winter. Factor 4 has a clear signature of biomass burning with very high concentrations of BrnC and K, and is prominent in winter. Lastly, the EC peak in factor 5 is a distinct feature suggesting it is linked to primary vehicular emissions. Also consistent with the vehicular sources, this factor does not have an obvious seasonal pattern.

The time-series of reconstituted DTT activity resolved by the five PMF factors, along with the residuals (not predicted), and a distribution of these factors in each season, is shown in Fig. 8. In summer, secondary oxidation processes (WSOC (29 %) + SO_4^{-2} (17 %), factors 1 and 2) are the dominant contributors (46 %) to DTT activity, with additional contributions from biomass burning (24 %, factor 4) and vehicle emissions (19 %, factor 5). In fall, the contribution from secondary formation drops to 32 % (22 % associated with WSOC and only 10 % with SO_4^{-2} factors) with an increase in the contribution from vehicle emissions (25 %). Biomass burning dominates the ROS generation potential in winter, contributing 47 % to the DTT activity, while relatively low contribution from secondary formation (20 %) and vehicle emissions (12 %) is observed. Mineral dust (factor 3), possibly including road-dust resuspension also makes a non-zero contribution to DTT activity, but is significant only in summer (13 %) and fall (11 %).

Relative loadings of individual species in various PMF factors, and the contributions of each of these factors to the DTT activity, could provide some insights on the specific chemical components in an emission source driving the aerosol oxidative potential. For example, WSOC has been associated with the DTT activity in previous studies (Verma et al., 2012; Biswas et al., 2009a) and our results showing the substantial DTT activity associated with factor 1 (Figs. 7 and 8) support these findings. A few laboratory studies have also noted the capability of transition metals, particularly Fe, Cu and Mn to transfer the electrons from DTT, (Charrier and Anastasio, 2012). In this study, metals were mostly concentrated in factor 3, i.e. mineral dust, which has the smallest contribution suggesting a lesser role for metals. However, the substantial contribution of biomass burning aerosols (factor 4) to DTT activity could be attributed in part to metals, along with WSOC components. The occurrence of trace amount of redox-active metals (Fe, Cu, Mn and Zn) in other factors (1, 2 and 5) might also be contributing to the DTT activity associated with those factors. It is noteworthy that at BHM and RS sites, where metals concentrations tend to be higher (Fig. 3), DTT activity is not significantly different from that of the corresponding paired site (CTR, JST and GT). Overall, these data do not suggest that metals are the only dominant players in driving the DTT activity of water-soluble $PM_{2.5}$ in the southeast, but they likely play an important role. This is addressed in a subsequent paper where multiple linear regression is used to asses the contributions of specific organic components and metals to the observed DTT activity.

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

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

$$\begin{aligned}\mathrm{DTTv} &= 0.10\ \mathrm{LDGV} + 0.072\ \mathrm{HDDV} + 0.065\ \mathrm{BURN} + 0.023\ \mathrm{AMSULF} \\ &\quad + 0.028\ \mathrm{SOC} + 0.0069\ \mathrm{PMOther}\end{aligned} \tag{1}$$

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

The aggregate contribution of each of these sources to the $PM_{2.5}$ DTT activity over the whole study period is also shown in Fig. 9b. Overall, CMB yielded a similar picture as PMF; biomass burning (BURN) and secondary oxidation processes (SOC + AMSULF) were the dominant sources of DTT activity in Atlanta with contributions of 33 and 29 %, respectively, in addition to vehicular sources (LDGV + HDDV, 32 %). CMB-identified vehicle sources also include resuspended dust, which may explain, to some extent, a higher vehicular contribution to DTT activity by CMB compared to PMF.

4 Conclusions

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

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

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

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

Season, Year	Sapling dates Start date	End date	Sampling Site Fixed site	Samples collected (*N*)	Mobile site	Samples collected (*N*)
Summer, 2012	8 Jun 2012	20 Jul 2012	JST	31	YRK	33
	24 Jul 2012	31 Aug 2012	JST	37	GT	38
Fall, 2012	6 Sep 2012	4 Oct 2012	JST	26	RS	29
Winter, 2012–2013	15 Nov 2012	30 Nov 2012	JST	13	JST	14
	6 Dec 2012	4 Jan 2013	JST	22	YRK	22
	27 Jan 2013	27 Feb 2013	JST	30	RS	31
	5 Mar 2013	27 Mar 2013	JST	23	GT	22
Summer, 2013	**16 Jun 2013**	**16 Jul 2013**	**CTR**	**31**	**BHM**	**31**
Fall, 2013	9 Sep 2013	3 Oct 2013	GT	25	RS	25
Total number of samples				238		245

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

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

Season	Site	WSOC	BrnC	Inorganic ions		OC	EC	Water-soluble metals					
				SO_4^{-2}	NH_4^+			K	Ca	Mn	Fe	Cu	Zn
Summer, 2012	*JST-GT*	**0.81**	**0.67**	**0.68**	**0.73**	**0.81**	**0.69**	0.49	0.20	**0.72**	**0.78**	**0.71**	0.62
	YRK	**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	*JST*	**0.72**	**0.81**	0.49	0.52	**0.83**	**0.90**	0.61	−0.08	0.37	**0.74**	0.20	**0.82**
	RS	**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, 2012–2013	*JST-GT*	**0.69**	**0.78**	0.15	0.13	**0.85**	**0.82**	**0.78**	−0.13	0.46	**0.65**	0.63	0.63
	YRK	**0.84**	**0.88**	0.34	0.45	**0.82**	**0.80**	**0.75**	0.31	**0.68**	0.04	0.43	**0.72**
	RS	**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	*CTR*	**0.78**	**0.88**	**0.71**	**0.78**	**0.77**	**0.72**	**0.66**	0.23	0.36	0.41	−0.12	0.62
	BHM	**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	*GT*	0.47	**0.75**	0.39	0.37	**0.79**	**0.78**	**0.65**	0.29	0.58	**0.66**	0.46	0.46
	RS	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.

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Reactive oxygen species associated with water-soluble $PM_{2.5}$

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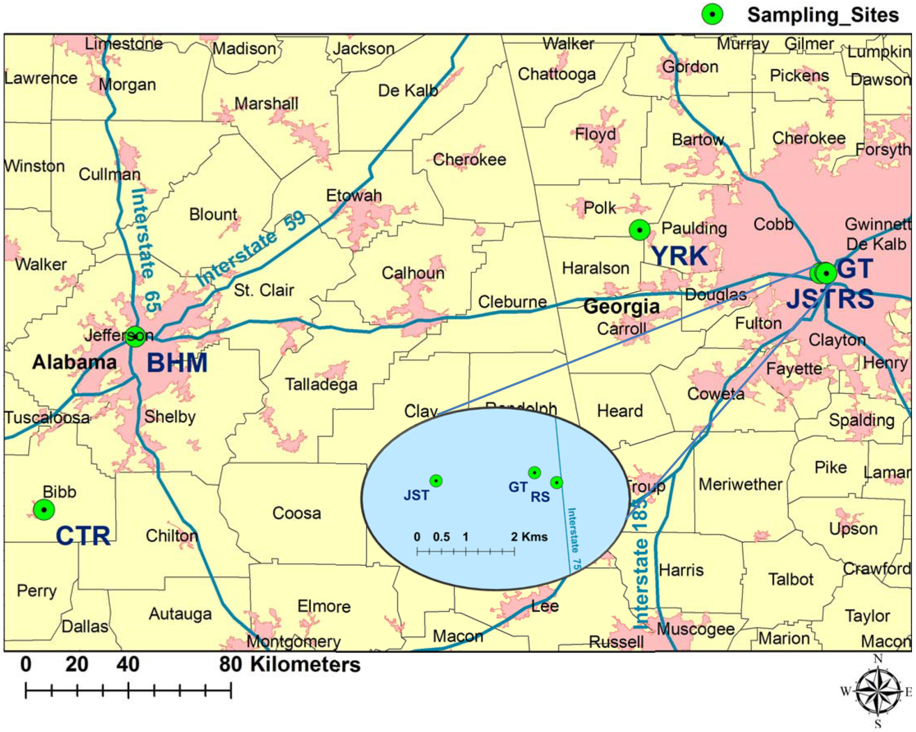
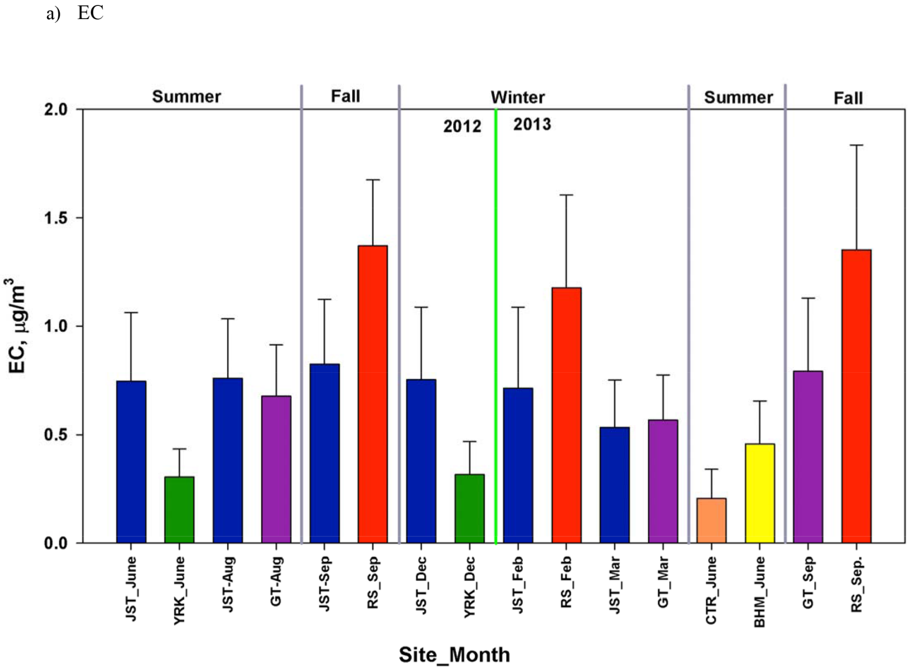


Figure 1. Map of sampling sites.



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

Figure 2. Monthly average ambient concentrations of EC **(a)** WSOC **(b)** and BrnC **(c)** at the sampling sites.

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Reactive oxygen species associated with water-soluble PM$_{2.5}$

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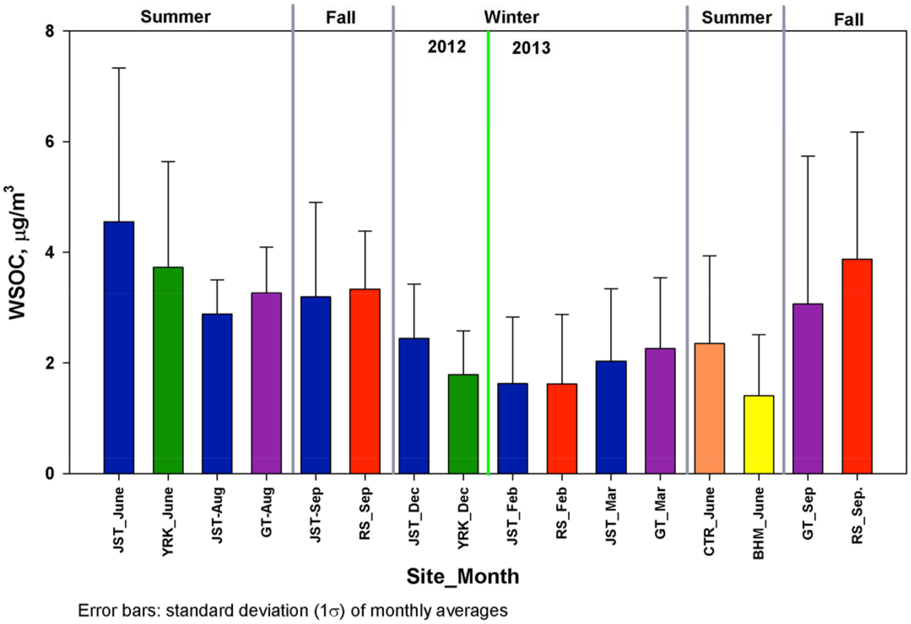
b) WSOC



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c) BrnC

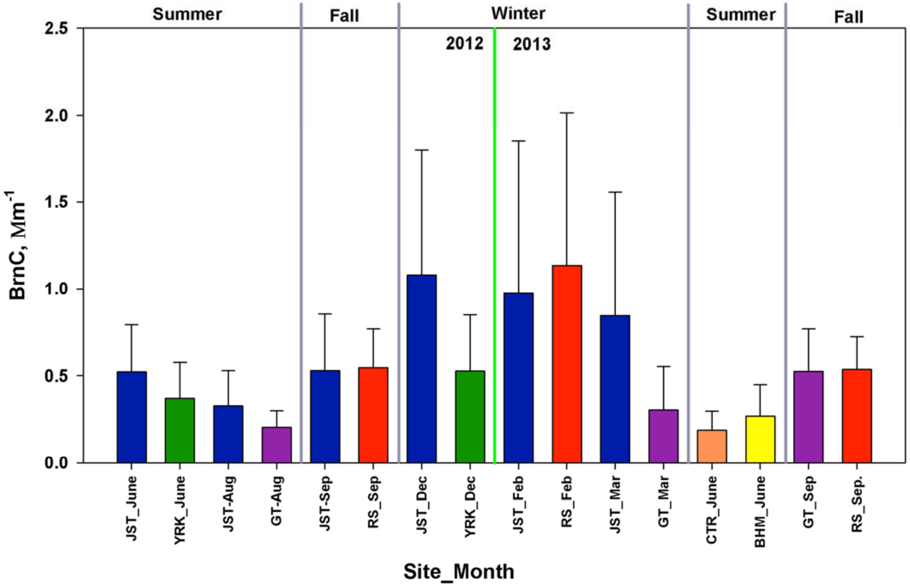

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Figure 2. Continued.

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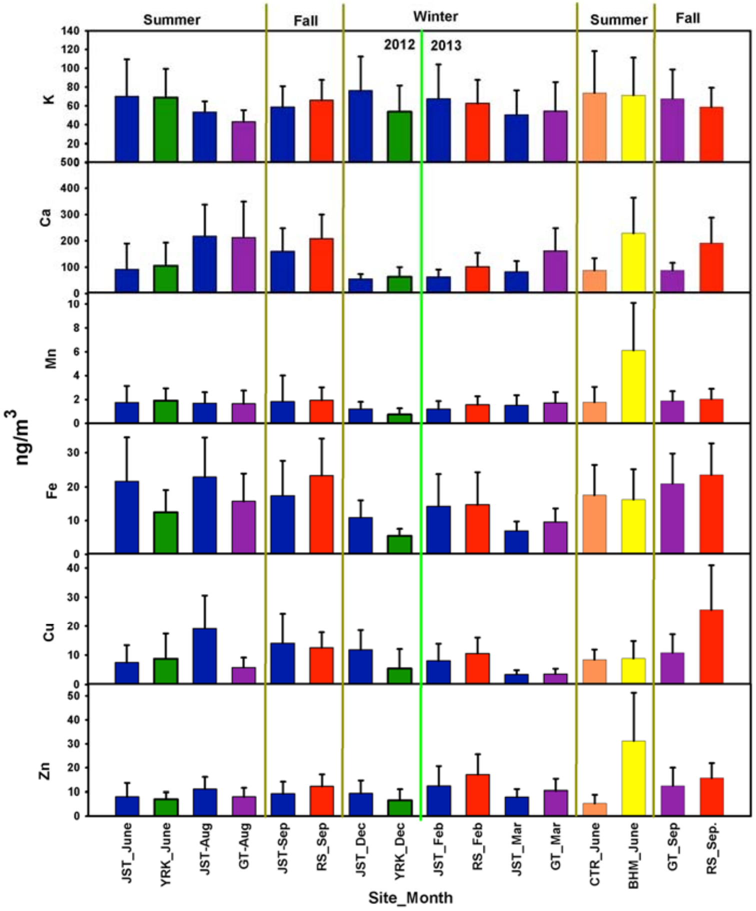

Error bars: standard deviation (1σ) of monthly averages

Figure 3. Monthly average ambient concentrations of water-soluble metals at the sampling sites.

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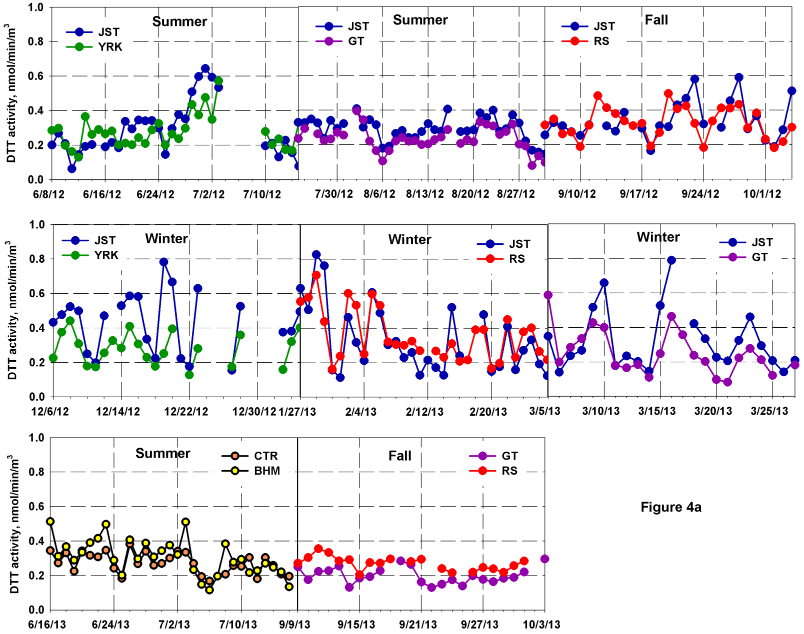


Figure 4. Time-series of the daily average DTT activity (DTTv; **a** and DTTm; **b**) of ambient $PM_{2.5}$ at the sampling site.

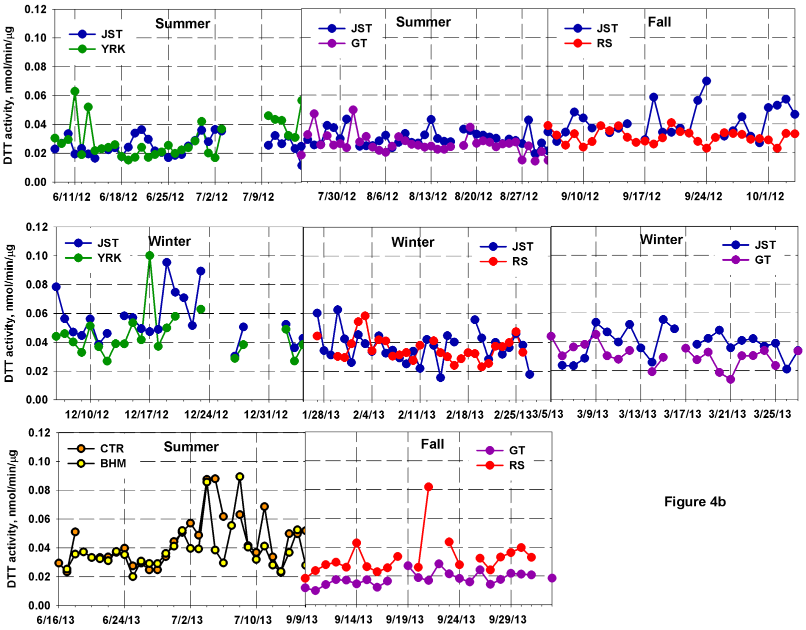


Figure 4b

Figure 4. Continued.

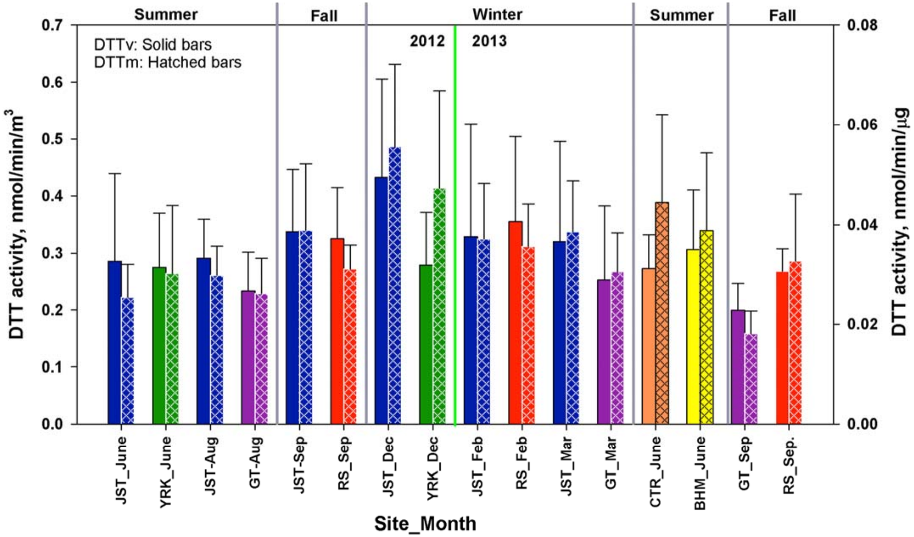


Figure 5. Monthly averages of volume- (DTTv) and mass-normalized (DTTm) DTT activity at the sampling sites.

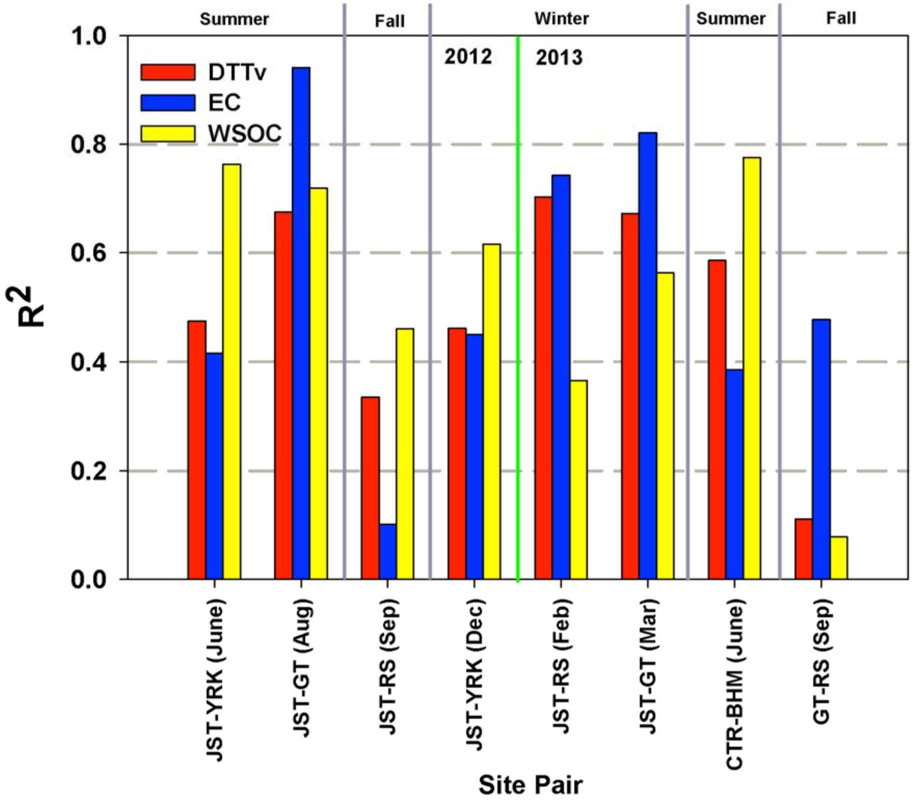
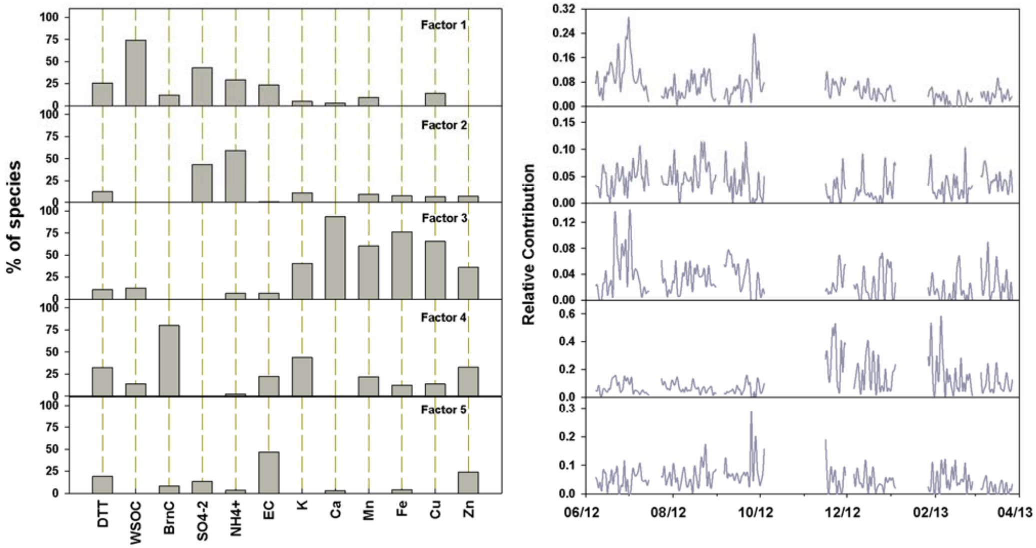


Figure 6. Site-to-site correlations (R^2) for volume normalized DTT activity (DTTv), elemental carbon (EC) and water-soluble carbon (WSOC) of $PM_{2.5}$.



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

Figure 7. Composition profiles (% of each species) for the five factors resolved by PMF (left panel), and the time series of their relative contribution (right panel).

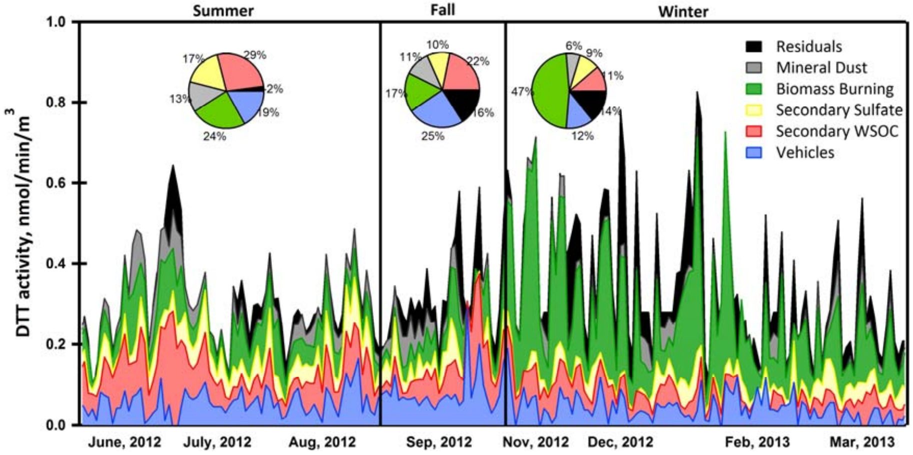


Figure 8. Time series of $PM_{2.5}$ DTT activity segregated into different factors as predicted by PMF and their season-wise contributions.

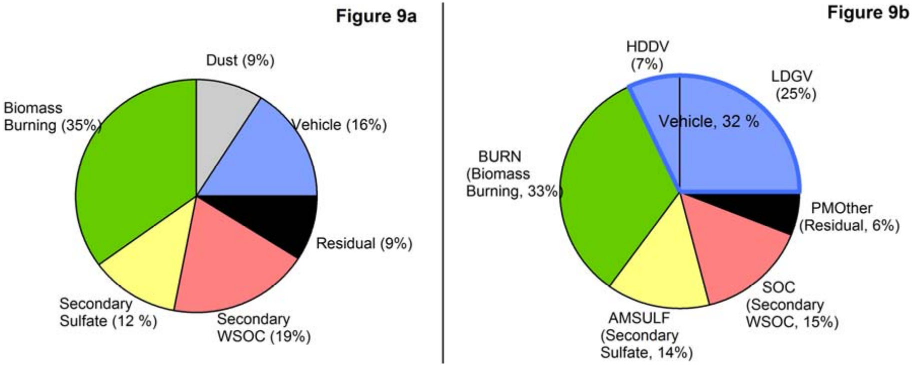


Figure 9. Annual aggregate contributions of different sources identified by PMF **(a)** and CMB method **(b)** to the water-soluble DTT activity of ambient $PM_{2.5}$ in urban Atlanta.