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# Oxidative potential of PM<sub>2.5</sub> during Atlanta rush hour: Measurements of in-vehicle dithiothreitol (DTT) activity



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# HIGHLIGHTS

- In-vehicle PM<sub>2.5</sub> samples were collected during rush hour traffic in Atlanta, GA.
- Semivolatiles make important contributions to DTT activity in on-road environments.
- Compared to roadside monitors, PM collected in-vehicle may be more DTT-active.

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# G R A P H I C A L A B S T R A C T



# ABSTRACT

Although exposure to traffic emissions is frequently associated with negative health impacts, few studies have measured air pollution directly in-vehicle, and limited measurements of daily commuter exposure exist. This research, part of the Atlanta Commuter Exposures (ACE) Study, assesses on-roadway in-cabin particulate pollution (PM<sub>2.5</sub>) collected from scripted rush hour commutes on highways and on non-highway side streets. Water-soluble extracts from PM<sub>2.5</sub> filters were analyzed for oxidative potential of water-soluble species using the dithiothreitol (DTT) assay, and results suggest that there may be substantial gas-phase DTT activity in fresh emissions. We measured DTTv activities (i.e., DTT activity normalized to the sampled air volume) that were on average two times higher than comparable measurements collected by stationary roadside monitoring sites. Although some of this difference may be attributable to positive artifacts due to relatively brief (2-h) quartz filter sampling durations, the current findings provide some indication that commuters encounter notably higher exposure to redox-active PM<sub>2.5</sub> in the on-road environment. Strong correlations are observed between water-soluble DTT activity and water-soluble organic carbon (WSOC), specifically for the 'semivolatile' WSOC component (measured as the difference between denuded and non-denuded filters). Although potential for artifacts when measuring DTT activity of fresh emissions using filter-based methods is considerable, these results

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Abbreviations: ACE, Atlanta Commuter Exposures study; PM, particulate matter; DTT, dithiothreitol; DTTv, volume-normalized DTT activity; DTTm, mass-normalized DTT activity; ROS, reactive oxygen species; p-PAHs, particle-bound polyaromatic hydrocarbons; PNC, particle number concentration; EC, elemental carbon; OC, organic carbon; WSOC, water-soluble organic carbon; DEPs, diesel exhaust particles; HDDV, heavy-duty diesel vehicles; UFPs, ultrafine particles; SVOCs, semivolatile organic compounds.

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suggest that semivolatile organic species are important contributors to DTT activity, at least in environments where ambient  $PM_{2.5}$  is dominated by vehicular sources.

# 1. Introduction

Traffic-related particulate matter (PM) exposure has been widely associated with adverse impacts on health, and acute responses linked to roadway sources have been demonstrated even in healthy subjects (Larsson et al., 2007; Riediker et al., 2004; Zuurbier et al., 2011). For example, a study that monitored health responses in healthy young adults during and after the Beijing Olympics, when stringent air pollution mitigation efforts led to roughly 50% reduction in traffic volumes, observed significant negative impacts on cardiovascular and pulmonary biomarkers when traffic conditions were reverted to normal (pre-Olympic) levels (Zhang et al., 2013). In the U.S., daily vehicle commuters represent a sizable exposure cohort that likely receives a significant portion of daily PM exposure from the in-vehicle environment (Sioutas et al., 2005). The U.S. Census Bureau reports that the average commute time in the U.S. is 26 min one way, and that 86% of working Americans use personal vehicles to get to work, with 90% driving alone (Bureau, 2009-2013). A 2015 report on commuter travel distance (produced by Metropolitan Policy Program at the Brookings Institute) identified Atlanta commuters as having the longest typical travel distance of 12.8 miles (Kneebone and Holmes, 2015). Although populated roadways and long commute times are expected to result in elevated in-cabin pollutant levels, there are few realistic assessments of commuter exposure and only a small number of studies have measured in-cabin air pollution directly (Adar et al., 2007; Laumbach et al., 2010; Riediker et al., 2004; Zuurbier et al., 2011).

Various toxicity pathways may be elicited triggering health effects attributable to traffic pollution, including several mediated via redox imbalance and the generation of oxidative stress (de Kok et al., 2006). Previous studies have analyzed PM<sub>2.5</sub> from near-road monitoring sites with the dithiothreitol (DTT) assay in order to estimate PM oxidative potential (i.e., the ability of near-road PM to catalyze the generation of reactive oxygen species, ROS) (Cho et al., 2005; Fang et al., 2015a; Hu et al., 2008; Ntziachristos et al., 2007; Saffari et al., 2014). Broadly, the body intentionally generates ROS to eliminate xenobiotic species (e.g., inhaled PM<sub>2.5</sub>). When ROS concentrations exceed the body's antioxidant capacity, other (nonforeign) cellular species become oxidized, leading to a range of adverse health responses (Delfino et al., 2005; Donaldson et al., 2001; Li et al., 2003, 2009; Peters et al., 2006). The DTT assay acts as a surrogate that chemically mimics this antioxidant depletion (Cho et al., 2005; Kumagai et al., 1997, 2002).

DTT activity varies by PM concentration and chemical composition. Transition metals have been associated with extremely high DTT activity in some studies (Charrier and Anastasio, 2012; Charrier et al., 2015; Vejerano et al., 2015). High DTT activity has also been associated with low atmospheric dilutions (e.g., the stagnant air in a roadway tunnel) (Ntziachristos et al., 2007), which most likely corresponds to increases from particle-phase semivolatiles, which are more likely to condense under those conditions (Biswas et al., 2009; Verma et al., 2011). A roadway study that used a thermodenuder to heat ambient PM (driving semivolatiles into the gas phase) indicated that semivolatiles were responsible for 42–66% of DTT activity (Verma et al., 2011). Polyaromatic hydrocarbons (PAHs) are common semivolatile species found on the roadway environment and many are carcinogenic (Ntziachristos et al., 2007). PAHs, while not DTT active (Charrier and Anastasio, 2012) are often oxidized to produce aromatic species, such as guinones, which are another known driver of ambient PM DTT activity (Verma et al., 2015b). A study that measured particle- and vapor-phase redox activities of ambient PM2.5 (extracted in both water and in dichloromethane) indicated that-while the highest overall DTT activities were generated by water-soluble particle-phase PM<sub>2.5</sub> extracts-the dichloromethane extracts (which are more representative of organic components) indicated higher vapor-phase DTT activities, suggesting that gas-phase organics are more DTT active than particle-phase organics (Eiguren-Fernandez et al., 2010). Importantly, recent epidemiologic findings suggest that DTT activity may also comprise a more statistically relevant predictor of health outcomes than PM<sub>2.5</sub> mass (Bates et al., 2015; Yang et al., 2016). Therefore, identifying sources and environments with elevated DTT levels could help mitigate health impacts from PMrelated exposures. However, as an acellular assay that only examines one aspect of toxicity (i.e., oxidative potential), it is difficult to determine the applicability of the DTT assay as any sort of metric for human cells or health endpoints.

DTT activity measured on filters at stationary monitoring sites offers insight about area-wide ambient concentrations, however, there is a need to better characterize ROS exposures in microenvironments with known elevated levels of PM<sub>2.5</sub>. To date, oxidative potential has not been measured within an in-vehicle commuter environment, which for many millions of daily commuters, represents the single-most important microenvironmental contributor to total daily pollution exposure. The current findings are part of the larger Atlanta Commuter Exposures (ACE) study, which examines in-vehicle particle pollution and associated acute cardiorespiratory response in daily car commuters. In the first phase of the ACE study (ACE-1), exposure and acute health impacts, which were measured through a range of pulmonary and cardiovascular biomarkers, were examined in subjects following a 2-h scripted highway commute during rush hour (Mirabelli et al., 2015; Sarnat et al., 2014). Here, we present results from a sister study (ACE-2), which measured in-vehicle pollutant levels as well as DTT activity in three microenvironments. In addition to a highway commute assessed in ACE-1, the current study incorporates a non-highway (side street) commute and also an indoor environment (an Emory clinic room). We present a comparison DTT activity in different microenvironments, as well as an analysis of specific pollutant drivers of activity.

# 2. Methods

# 2.1. Study overview

In-vehicle particulate matter was measured over the course of 2-h scripted car commutes in Atlanta during morning rush hour (-7a.m-9a.m). All subjects (n = 60) drove their personal vehicles and were instructed to roll their windows up and down every 15 min throughout the commute and to set their vehicle's ventilation fan to draw in fresh air on a medium setting (i.e., no recycled air). Subjects followed either a highway commute or a "side street" commute (a route made up of non-highway surface roads), with

both the highway and side street routes composed of heavilytraveled, major roadways used daily by Atlanta commuters. Invehicle commute measurements were scheduled over the course of a year (from November 2012-August 2013) over a range of seasons and in varying meteorological conditions. Each subject participated in two exposure sessions, with at least one highway commute. Maps of the highway and side street commute routes are provided in the Supplementary Index (Fig. S1), and more specified information detailing the experimental design can be found elsewhere (Greenwald et al., 2014). In addition to the highway commute, participants were also randomly chosen to conduct either a second 2-h commute, along the side street route, or a 2-h exposure session in an indoor clinic at Emory University, each within the same 7a.m-9a.m time window. A total of 30 clinic events, 30 side street commutes, and 60 highway commutes were conducted as part of this protocol.

Along with the inclusion of the clinic and side street microenvironments, the ACE-2 study most notably differed from the ACE-1 predecessor study (Mirabelli et al., 2015; Sarnat et al., 2014) by utilizing the DTT assay for measurements of in-vehicle oxidative potential. Another noteworthy modification in this ACE-2 study-—based on results from ACE-1 that indicated high contribution from semivolatile organic artifacts—is the incorporation of a denuded filter stream, which was placed in parallel with other filter-based measurements. Results from filter-based analyses (which include DTT activity and carbonaceous PM composition) are the primary focus of the current analysis.

#### 2.2. Experimental setup & methods

Particulate matter concentrations and composition were characterized using continuous sampling instrumentation and also via filter-based analyses (Greenwald et al., 2014). Briefly, portable sampling devices were used to conduct continuous measurements of particle number concentration (PNC) and particle-bound polycyclic aromatic hydrocarbons (i.e., PAHs on the surface of particles; referred to here as "p-PAHs") over time resolutions of 10-sec and 1sec, respectively. PNC was assessed by two TSI Inc. instruments, P-Trak Ultrafine Particle Counter 8525 and Condensation Particle Counter 3007, which both operate on principles of light scattering; and p-PAHs were measured by PAS 2000 CE (EcoChem Analytics). In the filter-based setup,  $PM_{2.5}$  was collected onto four filters (one Teflon and three quartz filters, powered by a vacuum pump) over the 2-h exposure session. Filters were then stored at -80 °C until undergoing chemical speciation.

An in-vehicle sampling manifold was designed to be placed in the front passenger's seat, with inlets located within 1 m of the participant's breathing zone. All sampling instruments (filter holders and continuous devices) fit within a  $15'' \times 21'' \times 8''$  tray, facilitating portability between sampling environments. A vacuum pump (which pulled in-cabin air through the filter-based setup) was stored in the trunk. The filter-based experimental setup is outlined in more detail below. The experimental design has been discussed, in detail, in previous manuscripts (Greenwald et al., 2014; Sarnat et al., 2014).

One 47-mm Teflon filter and three 25-mm quartz filters (one of which was preceded by a carbon monolith denuder) were aligned in parallel filter holders to collect integrated PM<sub>2.5</sub> samples using a cascade impactor (for the Teflon filter) and PM<sub>2.5</sub> impactors (for 25-mm quartz filters). The experimental flowrates for the 25-mm and 47-mm filters (15 lpm and 30 lpm, respectively) were generated by a battery-powered vacuum pump and flow was regulated by critical orifices. Flowrates were measured before and after each sampling event, and pump exhaust was filtered in order to address possible confounding impacts.

The four filters were used to measure the composition, mass. and ROS-generating potential of fine-mode particulate matter. Fig. 1 presents a schematic diagram of the filter-based setup and corresponding chemical analyses. Two of the quartz filters (one denuded and one non-denuded) were analyzed for organic and elemental carbon (OCEC) and water soluble organic carbon (WSOC) using Thermal Optical Transmittance (Sunset Labs) and Sievers 900 Portable Total Organic Carbon Analyzer (GE Analytical), respectively. A third guartz filter (non-denuded) was used solely for the DTT assay. The Teflon filter (non-denuded) was used for elemental composition analysis by ICP-MS (inductively-coupled plasma-mass spectrometry), and also for gravimetric PM2.5 mass (Mettler-Toledo), determined by the difference in mass on the filter before and after sampling. Filters were weighed 3 times before sampling and 3 times after sampling under the same controlled environment in a glovebox placed on a high-mass marble table to reduce building vibration.

To analyze water-soluble parameters (i.e., DTT and WSOC), the quartz filters were extracted into deionized water (>18.2 MQ-cm) by 30-min sonication. The extracts were then filtered through PTFE 0.45-µm pore syringes. The subset of filters that were allocated for DTT analysis used 2 ml of deionized water for extraction. Following the DTT assay standard protocols, which are explained in detail elsewhere (Cho et al., 2005; Fang et al., 2015a), DTT was injected into vials containing filter extracts and buffer solutions, and subsequent reactions were quenched over 5 different time steps; the amount of DTT consumed over time was evaluated according to absorbance measurements (assessed at 412 nm) taken by a UV-VIS spectrometer (Ocean Optics) paired with a 2.5-m long Liquid Waveguide Capillary Cell (World Precision Instruments). The linearly decreasing absorbance observed from the regression of combined time steps is used to calculate the rate of DTT consumed in the experiment. This DTT loss rate (measured in nmol of DTT consumed per minute) represents the ROS-generating potential of particulate matter in a given sample. Water-soluble organic species in the extracts (such as brown carbon) do not have a significant influence on interfering with absorbance at 412 nm.

Normalizing DTT consumption rates by the total volume of air that passes through the filter (i.e., volume-normalized DTT activity, or "DTTv") represents an exposure-relevant measure of oxidative potential. In this case, DTTv indicates the average oxidative potential expected per unit-volume of air that participants were exposed to while inside a car during Atlanta rush hour. In addition to characterizing DTTv, we normalized DTT consumption rates by PM<sub>2.5</sub> mass (i.e., mass-normalized DTT activity, or "DTTm"), which represents the intrinsic DTT activity of PM<sub>2.5</sub> mass. In this study, all DTT results report the water-soluble portion of DTT activity. Data were characterized using descriptive statistics, graphical displays, t-tests, ANOVA, and Pearson's correlation coefficients (r). Statistical analyses were computed using R 3.3.2. (R Core Team, 2016) Statistical significance is reported at the 0.05 level.

# 2.3. Limits of detection (LOD)

Data quality and method detection limits are described here for filter-based parameters (i.e., OCEC, WSOC, PM<sub>2.5</sub> mass, and DTT). As previously mentioned, to conduct realistic in-cabin measurements of multiple PM components, filters were sampled in the same microenvironment (within 1 m of the subject) and over the same duration of time that the subject spent in-commute or in-clinic (~2 h). Due to the relatively short sampling duration and small filter size, total mass loadings were typically low for all parameters (with the exception of non-denuded OC), with fractions of samples below the blank-determined limits of detection (Table 1). This was especially true for sampling conducted within the indoor clinic



Fig. 1. The ACE-2 experimental setup for filter-based PM<sub>2.5</sub> collection is portrayed. Four parallel sampling lines and the corresponding analyses are shown along with respective flowrates and filter characteristics.

environment, designed as a clean "control" microenvironment, which had multiple pollutant parameters with >50% of samples below detection.

On average, the PM<sub>2.5</sub> mass measured on the side street and highway filters (~50  $\pm$  16  $\mu$ g and ~61  $\pm$  22  $\mu$ g, respectively) more than doubled the mass measured in the clinic (~20  $\pm$  11  $\mu$ g). Due to lower relative mass loadings, a higher proportion of clinic samples fell below method LOD. For the carbonaceous measurements, OCEC blanks (n = 70) and WSOC blanks (n = 51) were used to determine the limit of detection (i.e., blank mean + 2 $\sigma$ ). All data above the LOD has been blank-corrected. For all descriptive analyses, data below LOD has been replaced with ½ LOD values (rather than removing the values) to avoid biasing mean concentrations towards higher values. All ½ LOD values were excluded from correlation analyses, however, to avoid introducing distributional biases resulting from the use of arbitrarily assigned concentrations.

The DTT measurements shown in the results include all analyzed samples corrected by blank-subtraction only—even for samples that fell below LOD—in order to permit more comparisons between measured parameters. The proportions of DTT samples above the blank mean  $+ 2\sigma$  (n = 10 blanks; in units of nmol min<sup>-1</sup>) are included in Table 1 to demonstrate that many DTT results were in close range of the field blanks (even though DTT activity was notably high when normalized by mass and volume). For the highway and side street, PM mass concentrations in the watersoluble filter extracts were ~12 µg ml<sup>-1</sup> on average. Massnormalized DTT activity has previously shown non-linear correlations to PM mass for samples dominated by Mn and Cu (Charrier

#### Table 1

Percent of analyzed samples above detection limit are shown for indoor (clinic) and commute (side street, highway) microenvironments; all parameters measured on 25-mm quartz filters are listed (PM<sub>2.5</sub>, OC, EC, WSOC, DTT). The total number of analyzed samples are shown in parentheses. The limit of detection was set according to the blank mean +  $2\sigma$ . The percent of DTT samples above detection (in nmol min<sup>-1</sup>) are included to demonstrate that many DTT results were close to the blanks. However, DTT data used in the results have only been corrected by blank-subtraction in order to permit more comparisons between parameters.

Percent of samples above LOD: %(N)						
Parameter	Clinic	Side street	Highway			
PM <sub>2.5</sub> mass	89.7% (29)	100.0% (29)	100.0% (58)			
OC	100.0% (25)	100.0% (25)	100.0% (47)			
OC den.	80.0% (25)	100.0% (28)	100.0% (48)			
EC	16.7% (24)	65.4% (26)	96.0% (46)			
EC den.	26.1% (23)	63.0% (27)	93.6% (47)			
WSOC	83.3% (24)	73.9% (23)	82.6% (46)			
WSOC den.	38.5% (26)	41.7% (24)	46.8% (47)			
DTT <sup>a</sup>	31.2% (15)	50.0% (18)	62.5% (32)			

<sup>a</sup> Shown only for observational purposes—DTT measurements in resulting analysis are determined by blank-subtraction only. and Anastasio, 2012). However, mass-normalized DTT activity did not show a dependence on the mass concentration of analyzed extract ( $\mu$ g ml<sup>-1</sup>) for the highway—though some evidence for an inverse relation was observed for the side street data—suggesting that a potential nonlinear response of DTT due to metals is not a significant bias for the mass-normalized DTT data reported here. Clinic DTT levels are not reported due to sensitivity issues associated with the low PM mass concentrations in the water-soluble filter extracts (~6  $\mu$ g ml<sup>-1</sup> on average for clinic samples).

# 3. Results and discussions

#### 3.1. Overview of results

DTTv measurements for both side street and highway commutes were generally elevated and highly variable, with in-vehicle DTTv ranging from 0.04 to 3.70 nmol min<sup>-1</sup> m<sup>-3</sup> (25th and 75th percentiles of 0.47 and 1.23 nmol min<sup>-1</sup> m<sup>-3</sup>, respectively). The wide distribution in concentrations may be related to the use of different personal vehicles, driver actions/lane preferences, and to the day-to-day variability of point source emissions that would be expected from mobile sampling as compared to stationary monitoring. Considering that stationary monitors are located further away from point sources, observed PM from vehicular sources would be more diluted and well-mixed compared to direct on-road sampling.

The rate of DTT consumption depends on PM chemical composition, and while both highway and side street commutes are clearly dominated by rush hour primary traffic emissions, the amount of emissions generated—and the vehicular fleets generating those emissions—may vary substantially. Table 3 provides medians and interquartile ranges for in-cabin carbonaceous measurements and DTTv activities, and distributions of side street and highway results are shown as side-by-side boxplots embedded along the diagonal. Specific trace metal species (Cu, Mn, Zn, and V), PNCs, and surface-bound PAHs, which were all uncorrelated with water-soluble DTT activity, are presented in the Supplementary Index. DTTm levels for the side street and highway commutes measure  $0.05 \pm 0.03$  nmol min<sup>-1</sup>  $\mu$ g<sup>-1</sup> and 0.07  $\pm$  0.07 nmol min<sup>-1</sup>  $\mu$ g<sup>-1</sup> respectively.

Both mass- and volume-normalized DTT activities were not statistically different between highway and side street commutes using ANOVA testing (see Supplementary Index). Similarly, with the exception of EC, PNC, and PAHs, the measured PM pollutants did not statistically differ by on-road commute type. Interestingly, commute distributions most noticeably differed in regards to EC, which can be DTT active but is not water-soluble (Cho et al., 2005); thus, potential redox activity associated with elemental carbon is, therefore, unlikely to be captured by our water-soluble DTT analyses. PNC measured for Dp > 20 nm were 1.9 times higher on the highway than side street commutes, and PNC for smaller particle diameters (Dp > 10 nm) were 2.3 times higher on the highway than side street, indicating a higher portion of ultrafine particles (UFPs) overall on the highway. This is expected since the elevated EC points to greater contributions from heavy-duty diesel vehicles (HDDV), a predominant source of UFPs (Matti Maricq, 2007), which are also more prevalent along the scripted highway routes in this protocol.

Most measured pollutant metrics were a factor of 5–20 times higher in the in-vehicle environments as compared to the clinic. PM<sub>2.5</sub> mass concentrations, however, were ~3 times higher ( $17.4 \pm 8.4 \,\mu g \,m^{-3}$  in-vehicle;  $5.9 \pm 3.7 \,\mu g \,m^{-3}$  in the clinic), and OC concentrations only ~1.5 times higher ( $7.7 \pm 3.2 \,\mu g \,m^{-3}$  in-vehicle;  $5.2 \pm 1.3 \,\mu g \,m^{-3}$  in the clinic). Results indicate that OC mass concentrations were dominated by the semivolatile/gas-phase OC components removed by the denuder. For the clinic, 65% of OC mass is comprised of these SVOC artifacts, while SVOC artifacts are 59% of side street OC and 47% of highway OC. SVOCs from indoor sources have previously been observed to preferentially adsorb to quartz filters, which is a possible explanation for the observed differences (Polidori et al., 2006; Turpin et al., 2007). A more thorough examination of potential sources of SVOCs during sampling within the clinic was beyond the scope of the current analysis.

# 3.2. Denuder impacts on EC, OC, WSOC concentrations

Differences between denuded and non-denuded filter streams have been shown to be particularly significant in urban areas (Watson et al., 2009) and, as previously mentioned, the ACE-1 study reported high levels of OC attributed to positive artifacts from semivolatile organic carbon species (Greenwald et al., 2014). The ACE-2 study used parallel denuded and non-denuded sampling lines in order to elucidate this semivolatile contribution from OC artifacts. The substantial difference between non-denuded and denuded OC (Table 2) indicates significant semivolatile contributions to the non-denuded quartz filters. Various aspects of the ACE protocol make it susceptible to OC sampling artifacts, including positive artifacts involved with low-volume sampling (Olson and Norris, 2005) and short sampling durations (Turpin et al., 2000). Less photo-chemically oxidized, fresh emissions have also been associated with positive artifacts (Baumann, 2003), which clearly has relevant implications for samples collected during morning

Table 2

The means and standard deviations of  $PM_{2.5}$  parameters are shown for three microenvironments: an indoor space at Emory University (clinic), and two in-vehicle commuter routes—one on the highway and another on non-highway surface roads (side street). Nonvolatile components of OC, EC, and WSOC were measured by sampling air downstream of a carbon monolith denuder (these denuded samples are abbreviated "den."). Particle number concentrations (PNC) were measured by two devices, P-Trak and CPC (TSI Inc.), which detect the number of particles for  $D_P > 20$  nm and  $D_P > 10$  nm, respectively.

	-						
Parameter	Clinic	Clinic		Side street		Highway	
	Indoor		In-vehicle		In-vehicle		
DTTv <sup>a</sup>	_	_	0.78 (0.6)	n = 18	1.08 (0.8)	n = 32	
$PM_{2.5}^{b}$	5.9 (3.7)	n = 26	15.6 (7.2)	n = 29	18.3 (8.9)	n = 58	
OC <sup>b</sup>	5.2 (1.3)	n = 25	7.1 (1.4)	n = 25	8.1 (3.7)	n = 47	
OC den. <sup>b</sup>	1.6 (1.1)	n = 20	3.2 (2.0)	n = 28	4.7 (3.7)	n = 48	
EC <sup>b</sup>	0.2 (0.2)	n = 4	0.9 (0.8)	n = 17	2.6 (1.7)	n = 44	
EC den. <sup>b</sup>	0.1 (0.1)	n = 6	1.0 (1.1)	n = 17	2.2 (1.7)	n = 44	
WSOC <sup>b</sup>	6.1 (2.4)	n = 20	6.5 (3.8)	n = 17	7.3 (3.7)	n = 38	
WSOC den. <sup>b</sup>	3.7 (1.4)	n = 10	3.9 (1.8)	n = 10	4.6 (2.8)	n = 22	
PNC (P-Trak) <sup>c</sup>	1300 (440)	n = 27	1.1  imes 104 (4900)	n = 26	$2.1 \times 104 (1.0 \times 104)$	n = 53	
PNC (CPC) <sup>c</sup>	1600 (510)	n = 28	$1.6 \times 104 (7100)$	n = 29	3.6  imes 104 (1.4  imes 104)	n = 57	
p-PAH <sup>d</sup>	6.0 (3.6)	n = 19	89.1 (10.9)	n = 22	119.8 (32.1)	n = 47	

<sup>a</sup> nmol min<sup>-1</sup> m<sup>-3</sup>.

 $^{b}$  µg m $^{-3}$ .

<sup>c</sup> # cm<sup>-3</sup>.

 $^{d}$  ng m $^{-3}$ .

rush hour, which is dominated by primary traffic sources. The semivolatile contribution is evident in Fig. 2, which shows box plots of EC, OC, and WSOC mass concentrations measured in all micro-environments on both the denuded and non-denuded filters.

Boxplots in Fig. 2 show that corresponding non-denuded and denuded EC measurements are similar, as expected for this nonvolatile PM component. It should be noted that the measured clinic EC was not considered reliable due to the small number of filters with loadings above detection (n = 4 for non-denuded; n = 6for denuded). A paired t-test did not indicate significant differences at 95% CI for side street filters between denuded and non-denuded samples (p = 0.38). Highway filters, however, suggest a slight decrease in mean EC in the denuded filters (mean difference of 0.31  $\mu$ g m<sup>-3</sup>; p = 0.02), indicating a statistically significant difference in means (although this difference becomes insignificant when 3 influential observations were removed from the analysis). It is possible for the denuded EC filters to experience particle loss to the denuder walls by diffusion (Cheng et al., 2009), but the variability from the denuder was small and is not expected to significantly impact the overall analysis.

The largest difference between denuded and non-denuded filters was observed for OC. WSOC, which represents a more oxygenated (and generally less-volatile (Hallquist et al., 2009)) component of OC, also shows difference between denuded and non-denuded samples, but to a lesser extent than that of the OC components. For combined in-vehicle commutes, results suggest that  $73\% \pm 21\%$  of WSOC samples are nonvolatile and  $49\% \pm 21\%$  of OC samples are nonvolatile.

Since non-denuded quartz filters were impacted by semivolatile positive artifacts, comparisons with gravimetric PM<sub>2.5</sub> mass and elements (both measured on Teflon filters, which are not susceptible to the same positive artifacts as quartz filters) should be viewed cautiously. The denuded quartz filters, which should have a significantly less positive artifact, therefore can be interpreted as a conservative estimate of the true PM<sub>2.5</sub> components.

# 3.3. DTT correlations with PM components

Fang et al. (2015a,b,c) recently measured 23-h average DTT activity from  $PM_{2.5}$  collected with a Hi-Vol sampler stationed along a main Atlanta roadway (Fang et al., 2015a). Fig. 3 shows the volumeand mass-normalized DTT activities measured in both studies and suggests that compared to PM collected by stationary roadside

#### Table 3

Pearson's correlation coefficient, sample size (n), and significance level (*p*-value) are listed for highway commutes (shaded values above diagonal) and side street commutes (below diagonal). For example: in the first row, second column, r = 0.82 is the correlation between highway OC and highway PM; similarly, in the second row, first column, r = 0.53 is the correlation between side street PM and side street OC. Grayed-out values indicates *p*-values > 0.1. Highway median (IQR) are listed along the first row; side street median (IQR) are listed down the first column. The box plots along the diagonal permit quick visual comparisons between the distributions of side street (left) and highway (right) commutes.

HW <b>→</b> ss <b></b>	PM 16.1 (8.9)ª	OC 7.4 (3.3)ª	EC 2.4 (2.5)ª	WSOC den 3.5 (2.6)ª	WSOC 6.7 (4.9) <sup>a</sup>	SV-OC* 3.8 (1.4) <sup>a</sup>	SV-WSOC* 2.3 (1.7)ª	DTT∨ 0.9 (0.9) <sup>b</sup>
PM 14.2 (5.2)ª	<b>↓ ↓</b>	<b>0.82</b> n=47 <0.0001	0.24 n=44 0.12	0.01 n=22 0.95	0.14 n=38 0.39	0.37 n=42 0.0168	-0.38 n=18 0.12	-0.04 n=32 0.84
OC 7.1 (2.4)ª	0.53 n=25 0.0070	_ ↓	0.34 n=43 0.0254	-0.09 n=17 0.74	0.20 n=32 0.28	0.49 n=42 0.0011	-0.29 n=14 0.31	-0.15 n=28 0.44
EC 0.8 (1.0)ª	0.67 n=17 0.0031	0.59 n=17 0.0122	<b>₽</b>	-0.15 n=15 0.58	-0.16 n=31 0.38	0.23 n=38 0.17	-0.48 n=13 0.10	-0.21 n=26 0.31
WSOC den 3.1 (1.5)ª	0.09 n=10 0.80	0.10 n=9 0.80	-0.03 n=6 0.95	⊾ ⊨	0.52 n=20 0.0190	-0.02 n=15 0.95	-0.06 n=18 0.83	0.40 n=14 0.16
WSOC 5.4 (4.1) <sup>a</sup>	0.26 n=17 0.32	0.37 n=15 0.18	0.47 n=9 0.20	0.54 n=7 0.21	⊨ ⊨	0.17 n=29 0.38	<b>0.79</b> n=18 <0.0001	<b>0.70</b> n=22 0.0003
SV-OC* 4.22 (1.25)ª	0.31 n=24 0.14	0.41 n=24 0.0457	-0.20 n=16 0.45	0.17 n=8 0.69	0.14 n=14 0.62	<b>+ +</b>	-0.03 n=12 0.92	0.03 n=27 0.89
SV-WSOC* 1.13 (2.79)ª	0.24 n=8 0.57	0.24 n=8 0.57	-0.37 n=6 0.47	0.37 n=7 0.41	<b>0.98</b> n=8 <0.0001	0.17 n=7 0.72	┟	<b>0.75</b> n=14 0.0021
DTTv 0.6 (0.6)⁵	0.33 n=18 0.18	0.44 n=15 0.0976	0.07 n=8 0.87	0.28 n=8 0.51	<b>0.84</b> n=12 <0.0001	0.56 n=15 0.0296	<b>0.92</b> n=6 0.0097	⊾ ⊨

\*component removed by denuder (i.e., "semivolatiles")

<sup>a</sup> median (IQR) concentration in µg m<sup>-3</sup>

<sup>b</sup> median (IOR) concentration in nmol min<sup>-1</sup> m<sup>-3</sup>



Fig. 2. Box plots display non-denuded and denuded carbonaceous PM<sub>2.5</sub> mass concentrations for elemental carbon (EC), organic carbon (OC), and water-soluble organic carbon (WSOC) measured in an indoor environment (clinic) and during two in-vehicle commutes (side street, highway).

monitors, in-vehicle filters collected during morning rush hour with a non-denuded system (shown to be susceptible to large positive artifacts based on the OC and WSOC discussion above) is on average ~2 to 3 times more DTT active per volume and ~1.5 to 2 times more DTT active per mass. Notably, the current ACE-2 DTTm concentrations were slightly higher than other comparable urban studies that also measured intrinsic DTT activity from PM<sub>2.5</sub> (Charrier and Anastasio, 2012; De Vizcaya-Ruiz et al., 2006; Hu et al., 2008; Ntziachristos et al., 2007; Verma et al., 2009), which may reflect the high levels of positive artifacts affecting the PM<sub>2.5</sub>

DTT measurements in this study. Compared to day-long Hi-Vol sampling, we would expect to see more positive artifacts due to short sampling times and lower sampling volumes, as previously mentioned (Olson and Norris, 2005; Turpin et al., 2000). We would also naturally expect to see a higher portion of PM coming from vehicular sources while conducting on-road sampling during rush hour periods, particularly from light-duty gasoline vehicles (LDGV), which according to Bates et al. (2015) is the most intrinsically DTT-active source contributing to ambient air in Atlanta (Bates et al., 2015). Another possible factor that may have influenced the



**Fig. 3.** Plots show volume- and mass-normalized DTT consumption rates for in-vehicle filters that were collected during 2-h commutes in Atlanta (light blue and dark blue data points) and 23-h roadside data from Fang et al. (2015a,b,c) measured in Atlanta during the same time period (red data points). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

elevated DTT levels observed in this study (in addition to the increase in DTT-active artifacts, which is expected to be the dominating factor), is the influence of "stop and go" traffic and idling behaviors, which are more prevalent during rush hour, and have been associated with high intrinsic DTT activity (Biswas et al., 2009; Steenhof et al., 2011). An important consideration in comparing invehicle and roadside sampling is that the in-vehicle data was sampled directly in the traffic plume, whereas roadside data may be more subject to variable transport of the traffic plume due to local wind direction that may have varied over the 23-h roadside sampling period.

For both highway and side street commutes, the non-denuded WSOC PM<sub>2.5</sub> fraction was the most highly correlated with nondenuded water-soluble DTTv activity (Table 3). Correlations with DTT activity were strongest when denuded WSOC was subtracted from non-denuded WSOC, leaving only the WSOC that would have theoretically been removed by the denuder (i.e., the semivolatile component) (r = 0.73, p = 0.0003; combined highway and side street) suggesting that some significant fraction of the nondenuded DTT was associated with a positive artifact and not PM<sub>2.5</sub>. OC and SVOCs did not exhibit the same strong correlation pattern, which is expected since water-extracted PM was used for DTT analysis, so all results indicate the water-soluble DTT activity. Since the filter for the water-soluble DTT analysis was not denuded (i.e., containing both semivolatile and nonvolatile DTT-active components), this suggests a significant fraction of the measured DTT was associated with semivolatile components that may be an artifact and not part of the PM. Nonvolatile (denuded) WSOC was not significantly associated with DTT (r = 0.36, p = 0.10). All DTT correlations to WSOC are plotted in Fig. 4. While PM<sub>2.5</sub> is not significantly correlated with WSOC or to DTT activity, there are strong positive correlations between DTTm and mass-normalized WSOC (r = 0.71, p < 0.0001; combined highway and side street), indicating that the observed WSOC-DTT relationship is from the WSOC component rather than from a confounding correlation to PM<sub>2.5</sub>. This further suggests that positive artifacts present on the non-denuded quartz filter is a driver of the observed DTT activity, and not part of the PM.

Importantly, the semivolatile WSOC relationship shows a steeper slope than non-denuded WSOC as a function of DTTv, suggesting that the semivolatile artifact present on the filters contributed substantially to the observed DTT activity. Nondenuded WSOC intercepts the negative y-axis, identifying the previously-mentioned interference present during WSOC analysis (which presumably shifted WSOC concentrations proportionally to the right by nearly 3  $\mu$ g m<sup>-3</sup>). Though WSOC levels are artificially elevated due to a consistent analytical interference that occurred during WSOC analysis, observed correlations with DTT are not likely to be affected, since the interference was systematic and impacted the denuded and non-denuded WSOC fractions similarly. This WSOC interference can be eliminated by subtracting the denuded filter results from the non-denuded filter results, since both were subject to the same analytical interference. The SV-WSOC plot, therefore, displays the expected WSOC relationship (i.e., without the interference). This SV-WSOC plot (plot D in Fig. 4) shows a positive y-intercept, which, as described by Fang et al. (2015a,b,c), is indicative of the extrapolated lower limit of the DTT analysis (Fang et al., 2015a). PM mass-normalized semivolatiles could not be determined in this study since denuded filters were not weighed for PM<sub>2.5</sub> mass. Overall, non-denuded WSOC is clearly observed to be the most highly correlated component to both volume-normalized and mass-normalized DTT.

It is likely that the most important factor contributing to elevated DTT activity stems from the increased presence of semivolatile artifacts on the in-vehicle filters. Subramanian et al. (2004) observed that a 24-h sampling period with 16.7 lpm flowrate was sufficient for semivolatile artifacts to reach gas-particle phase equilibrium on quartz filters, but 4- to 6-h sampling durations did not achieve saturation, and instead demonstrated elevated levels of semivolatile artifacts (Subramanian et al., 2004). Existing studies have suggested that DTT activity is substantially influenced by semivolatile compounds (Biswas et al., 2009; Verma et al., 2011). By



\*shows coefficient of determination for combined (side street + highway) data

**Fig. 4.** Plots show correlation between DTT and WSOC data collected from in-vehicle commutes. Volume-normalized DTT is compared to non-denuded WSOC (plot A), denuded WSOC (plot C), and "semivolatile" WSOC (i.e., the component removed by the denuder; Plot D). PM<sub>2.5</sub> mass-normalized DTT is compared to non-denuded WSOC (plot B). The type of commute is distinguishable by colored data points—side street commutes in light blue and highway commutes in dark blue—while the overall trendlines represent the combined (highway + side street) DTT-WSOC relationships. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

heating up diesel exhaust particles (DEPs), Biswas et al. (2009) observed that semivolatile DEPs appear to be responsible for the majority of DTT activity (Biswas et al., 2009). Verma et al. (2011) also observed substantial DTT loss by heating ambient PM<sub>0.18</sub> collected along Los Angeles roadways (Verma et al., 2011). Additionally, studies have suggested that DTT activity is higher in tunnels and areas where emissions have not been diluted with background air since there are more semivolatiles bound to particles (Biswas et al., 2009; Ntziachristos et al., 2007; Verma et al., 2011), hence higher DTT levels reported in these studies may also be biased high due to positive artifacts. As pointed out by Greenwald et al. (2014), the mixing height is low during the morning rush hour, which does not allow for much dilution of emissions (Greenwald et al., 2014). This low mixing height is also evident in hourly-averaged PM<sub>2.5</sub> concentrations in Atlanta that show morning rush hour values 20-30% higher than afternoon rush hour values when midday atmospheric mixing has occurred (Carrico et al., 2003). Since there is less dilution by ambient air when the mixing height is low in the mornings, more semivolatiles would be expected to favor the condensed phase during the morning rush hour. Further, being cooler in the mornings would also favor semivolatiles being found in the condensed phase.

Pearson correlation coefficients for carbonaceous PM components and water-soluble DTTv activities for highway and side street commutes are highlighted in Table 3. PM components that are not shown in Table 3 (e.g., PNC, PAHs, metals) were not correlated with DTT activity, but are listed in the Supplementary Index. Previous research offers some evidence linking DTT activity to PAHs, though the findings are inconsistent. Some studies (including the current study) do not report correlation between water-soluble DTT and PAHs (Biswas et al., 2009; Verma et al., 2009), while others note strong correlation (Cho et al., 2005; Hu et al., 2008; Li et al., 2003; Ntziachristos et al., 2007; Verma et al., 2011). PAHs are not innately DTT-active (Charrier and Anastasio, 2012), but a semivolatile ambient particle study by Verma et al. (2011) observed that PAHs were highly correlated with DTTv (r = 0.88 and r = 0.80, for low and high molecular weight PAHs) (Verma et al., 2011). The strong correlation was attributed to a postulation proposed by Ntziachristos et al. (2007) hypothesizing that PAHs may photo-oxidize into guinones and nitro-PAHs, which are both highly DTT-active compounds (Antinolo et al., 2015; Cho et al., 2005; Ntziachristos et al., 2007; Rattanavaraha et al., 2011; Verma et al., 2015b). The lack of photochemical processing (which alter PAHs into reactive quinones) could be a possible explanation for why the current results do not show associations between DTT activity and p-PAHs. Thus, the ACE-2 samples collected for brief (2-h) durations in the mornings, when sunlight was indirect, would likely not experience photochemical processing similar to samples collected as part of the previous studies. Also, since only water-soluble DTT activity was measured, particle-bound quinones (i.e., p-PAHs converted to quinones that remain bound to soot surfaces) would not be measured. Although water-soluble extracts are thought to be more relatable to the lung environment, they miss some organic DTTactive components; Verma et al. (2012) demonstrated that Hi-Vol filters collected in Atlanta, which were extracted into both water and methanol, indicated higher mass-normalized DTT activity in the methanol extracts (Verma et al., 2012). However, due to time and budget restraints, methanol extracts were not assessed for this work.

In the initial ACE-1 study, we reported that incomplete fuel combustion, road dust, and brake pad/tire wear were identified as the predominant factors contributing to in-vehicle PM, as determined by PMF analysis (Greenwald et al., 2014). Cu, Fe, Mn, and Zn are dominant components of two of these leading factors (i.e., road dust and brake pad/tire wear). The water-soluble forms are referred to as "health-related metals" in Fang et al. (2015b) due to studies that have observed associations with adverse health impacts (Akhtar et al., 2010; Gasser et al., 2009; Kodavanti et al., 2005; Riediker et al., 2004), and Mn and Cu are thought to be particularly DTT active (Charrier et al., 2015). These four watersoluble health-relevant metals (including Zn, which is not redox active) have been shown to be correlated with DTT activity onroadway or in near-road environments (Fang et al., 2015b, 2015c; Verma et al., 2014), though these correlations-on a pairwise basis-were not observed for the in-vehicle samples in this ACE-2 study. The lack of DTT correlation to water-soluble metals (which are not expected to be semivolatile) supports that a sizable contribution of in-vehicle DTT activity measured during rush hour may be coming from semivolatile organic species (i.e., substantial PM<sub>2.5</sub> positive artifact). This may explain why denuded filters did not indicate correlation to DTT activity, while the semivolatile species collected on non-denuded filters did correlate to DTT activity. Additionally, Verma et al. (2015a,b) showed that metals account for only ~40% of water-soluble DTT activity measured from Hi-Vol filters in urban Atlanta (the remaining fraction was attributed to organic aerosols), thus weak correlations between metals and DTT activity may be expected (Verma et al., 2015a). It is recommended that gas-phase DTT activity is measured for future work, and that care is taken in environments with expected high levels of fresh emissions to minimize possible PM<sub>2.5</sub> DTT sampling biases. In general, SVOCs are expected to be highly prevalent when sampling in a morning traffic environment and, although the potential for artifacts in this environment is considerable, our results suggest that SVOCs are important contributors to DTT activity in the on-road environment.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.atmosenv.2017.06.044.

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