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The relative importance of tailpipe and non-tailpipe emissions on the oxidative potential of ambient particles in Los Angeles, CA

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Abstract

This study examines the associations between the oxidative potential of ambient PM_{2.5} and PM_{0.18}, measured by means of the dithiothreitol (DTT) assay, and their chemical constituents and modeled sources. Particulate matter (PM) samples were collected during 2012–2013 in Central Los Angeles (LA) and 2013–2014 in Anaheim, California, USA. Detailed chemical analyses of the PM samples, including carbonaceous species, inorganic elements and water-soluble ions were conducted. Univariate analysis indicated high correlation ($R > 0.60$) between the DTT activity and the concentrations of carbonaceous species at both sites. The strongest correlations were observed between DTT and organic tracers of primary vehicle tailpipe emissions including polycyclic aromatic hydrocarbons (PAHs) and hopanes as well as EC, with higher correlations for PM_{0.18} versus PM_{2.5} components. Moreover, metals and trace elements (e.g., Ba, Cu, Fe, Mn, Pb and Sb) in both size ranges were also associated with DTT activity. Multiple linear regression (MLR) analysis was performed on DTT activity and PM sources identified by a Molecular Marker-Chemical Mass Balance (MM-CMB) model (i.e. major carbonaceous sources: vehicle tailpipe emissions, wood smoke, primary biogenic, secondary organic carbon) together with other typical sources of ambient PM (i.e. crustal material, vehicular abrasion, secondary ions and sea salt). Overall, our findings illustrate the relative importance of different traffic sources on the oxidative potential of ambient PM. Despite major reductions of tailpipe emissions, the lack of similar reductions (and possibly an increase) in non-tailpipe emissions makes them an important source of traffic-related PM in Los Angeles and their increasing role in the overall PM toxicity raises concerns for public health.

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1. Introduction

A large body of epidemiological and toxicological studies have investigated linkages between aerosol chemistry and health effects associated with exposure to particulate matter (PM) ^{1–5}. In many of these studies, several adverse health outcomes have been attributed to the oxidative potential of ambient PM ^{6–9}. It has been hypothesized that these effects are caused by direct exposure to oxidants in PM, or the catalytic generation of reactive oxygen species (ROS) driven by certain PM components in human cells ^{10–12}. PM size also plays an important role in the severity of the health effects caused. Smaller particles have higher pulmonary deposition fraction and higher surface area compared to larger particles, therefore, they are considered major vectors for transport of toxic chemicals to the respiratory system ^{13,14}. Furthermore, studies have shown an increase in morbidity and mortality due to exposure to ambient fine particles (PM_{2.5}, particles with an aerodynamic diameter smaller than 2.5 µm) ⁷. Ultrafine particles (UFPs, traditionally defined as particles with an aerodynamic diameter smaller than approximately 0.1–0.2 µm), as a sub-fraction of PM_{2.5}, are strongly linked to systemic oxidative stress, inflammation, and platelet activation as well as cardiovascular effects in human and animal studies ^{15–17}.

Numerous studies have implemented biological ^{18,19} and chemical assays ^{20,21} to measure PM-induced toxicities with respect to PM oxidative potential. A widely used chemical assay is the dithiothreitol (DTT) assay in which DTT acts as a surrogate biological reducing agent ^{22,23}, with the rate of DTT consumption a proxy for the oxidative potential of a PM sample. Organic compounds such as quinones, which are believed to catalyze the electron transfer from DTT to oxygen, have been demonstrated to be associated with DTT activity ^{23,24}. In addition, certain metals such as Fe, Cu and Mn have been shown to be associated with DTT activity as well ^{22,25–27}. Furthermore, recent studies have shown that PM generated by specific sources such as vehicle tailpipe emissions, food cooking and secondary aerosols formation have different contributions to the overall oxidative potential of ambient PM and are strongly associated with health outcomes ^{28–30}. Therefore, how to target and apportion the toxicity of PM to specific sources remains a heated topic in current aerosol research.

As part of the Cardiovascular Health and Air Pollution Study (CHAPS) funded by the US National Institute of Health (NIH), ambient PM_{2.5} and PM_{0.18} (particles with an aerodynamic diameter smaller than 0.18 µm) were collected at two different locations of the Los Angeles (LA) Basin (i.e. Central LA, an urban area near Downtown Los Angeles and Anaheim, a residential area in Orange County, CA, USA). Chemical components along with the oxidative potential of the PM samples determined by DTT assay were quantified. In this paper, the temporal and spatial variations of DTT activity associated with PM in these two size ranges were investigated. In addition, major source contributions to ambient PM_{2.5} and PM_{0.18}-bound organic carbon (OC) were determined using a novel hybrid Molecular Marker-Chemical Mass Balance (MM-CMB) model described in a companion paper by Shirmohammadi et al.³¹. To provide more comprehensive insight into the dominant sources driving the DTT activity of PM_{2.5} and PM_{0.18}, both primary and secondary CMB-derived sources contributing to ambient PM_{2.5} and PM_{0.18}, along with some other sources not included by the CMB model (e.g. vehicular abrasion, crustal material, etc.), were included in

a multiple linear regression (MLR) analysis to identify possible predictors of the DTT activity. Vehicular abrasion has been estimated based on the source profile of brake wear particles reported by Schauer et al.³², crustal material was estimated by summing up the oxides of Al, K, Fe, Ca, Mg, Ti and Si, as suggested by Heuglin et al. and Marcazzan et al.^{33,34}. Moreover, secondary ions were estimated as the sum of NO_3^- , NH_4^+ and SO_4^{2-} , while sea salt was also estimated by the concentration of soluble Na^+ and the sea salt fraction of typical sea water components such as Cl^- , Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} suggested by Murphy et al.³⁵. The aforementioned source contribution estimations are discussed in more details in the Experimental section. Furthermore, the DTT activity levels measured in this study were compared to several previous studies conducted at the same sampling site in Central LA. The analysis of historical trends in ambient PM toxicity enabled us to assess the relative importance of tailpipe and non-tailpipe emissions on DTT activity in this area.

2. Experimental

2.1 Sampling plan and sites

Time-integrated sampling was conducted every week from Monday to Friday, between July 2012 and February 2013 in Central LA, and from Sunday to Thursday, between July 2013 and February 2014 in Anaheim. PM sampling in Anaheim was discontinued in December 2013 and resumed in January 2014. Throughout this manuscript, “warmer months” refer to July to September period, while “colder months” refer to October to February.

The Central LA site (referred to as an urban site) was located approximately 150 m to the east and downwind of a major freeway (I-110) at the Particle Instrumentation Unit (PIU) of the University of Southern California, about 3 km south of downtown Los Angeles. The other site in Anaheim (referred to as a suburban site), was situated in a residential area and about 500 m upwind of freeway I-5.

Ambient $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$ were collected using two collocated Micro-Orifice Uniform Deposit Impactors (MOUDIs, Model 110 MSP Corporation, Minneapolis, Minnesota, USA), each operating at 30 L/min collecting particles in three stages: $<0.18\ \mu\text{m}$ (ultrafine), $0.18\text{--}2.5\ \mu\text{m}$ (accumulation), and $2.5\text{--}10\ \mu\text{m}$ (coarse). In this study we focused on ultrafine and fine (ultrafine + accumulation) PM only. For the purpose of chemical speciation, one MOUDI was loaded with Teflon filters (Teflon, 47mm, pore size $2\ \mu\text{m}$, Pall Life Sciences, Ann Arbor, MI, USA) only, while the other one with aluminum-foil substrates in the coarse and accumulation stages and quartz microfiber filters (Whatman International Ltd, Maidstone, England) in the ultrafine stage.

2.2 Gravimetric and chemical analysis

Weekly samples were analyzed to quantify the mass concentrations of PM and its chemical constituents. The PM mass concentrations were determined by pre- and post-weighting the Teflon filters, using a microbalance (Model MT5, Mettler Toledo Inc., Columbus, OH, USA; $\pm 0.001\ \text{mg}$ readability), after equilibration under controlled temperature ($22\text{--}24\ ^\circ\text{C}$) and relative humidity within the range of 40–50%. A $1.5\ \text{cm}^2$ punch of the aluminum and quartz filters were analyzed by the National Institute for Occupational Safety and Health (NIOSH)

Thermal Optical Transmission (TOT) method in order to measure the elemental carbon (EC) and organic carbon (OC) content of the samples³⁶. Furthermore, by means of gas chromatography mass spectrometry (GC-MS), organic constituents were quantified³⁷. Total elemental composition of the samples was measured by high resolution inductively coupled plasma sector field mass spectrometry (SF-ICPMS) after microwave-aided solubilization of the PM in mixture of acids (HNO₃, HF and HCl). Ion Chromatography (IC) was applied to measure the water soluble inorganic ions³⁸ as well. Metals, PAHs, hopanes and organic acids detected in this study are listed by their names in Table S1.

2.3 Toxicological analysis

Reactive oxygen species (ROS) are produced in cells via reduction of oxygen to superoxide by biological reducing agents such as NADH (nicotinamide adenine dinucleotide) and NADPH (nicotinamide adenine dinucleotide phosphate)²⁰. This transformation is catalytically formed in presence of either electron-transfer enzymes or redox-active chemical species such as organic chemicals (e.g. quinones) and metals^{39–41}. The presence of excess ROS concentrations than the antioxidant capacity of body to neutralize them leads to further oxidation of cellular components which can eventually lead to adverse health outcomes^{14,42}. The dithiothreitol (DTT) assay was formulated to simulate the in vivo generation of ROS in which DTT acts as a surrogate of biological reducing agents (NADH and NADPH)^{22,23}. This is a commonly used cell-free approach to measure the oxidative potential of PM. The ability of a PM sample to catalyze the transfer of electrons from DTT to oxygen by generating superoxide radical anions is measured in this assay^{28,30}. The concentration of redox-active species in a given sample determines the rate of depletion of DTT (i.e. nmol/min) under a standardized set of conditions. The methodological details of this chemical assay can be found elsewhere²⁰.

2.4 Statistical analysis

Univariate analysis was performed on weekly data sets in order to investigate the correlation of DTT activity with chemical species and sources. As the variables were log-normally distributed, Spearman rank correlations were obtained. These correlations also identified important species and sources that were included in the multiple linear regression (MLR) analysis. MLR was subsequently applied to investigate which species and sources still contributed significantly to the prediction of DTT activity (which was sufficiently normally distributed). Various combinations of species and sources, especially those with high correlation values with DTT activity in the univariate analysis, were tested with stepwise selection procedure in MLR models. Statistically significant ($P < 0.05$) species/sources, which were not co-linear with each other (if Variance Inflation Factor < 2.5), were kept in the model to achieve the highest R^2 value and improve the prediction of DTT activity.

2.5 Source apportionment of PM_{2.5} and PM_{0.18} mass concentrations

Sources of PM_{2.5} and PM_{0.18} OC were quantified in a companion paper by Shirmohammadi et al.³¹ using a hybrid CMB model in which the PMF-derived source profiles were combined with traditional source testing profiles. The model estimated the relative contributions from mobile sources (including gasoline, diesel, and smoking vehicles), wood smoke, primary biogenic sources (including emissions from vegetative detritus, food

cooking, and re-suspended soil dust⁴³), and anthropogenic secondary OC (SOC). The details of the CMB analysis can be found in the above companion paper³¹. OC source apportionment results from the CMB model were converted to PM_{2.5} and PM_{0.18} mass concentrations to evaluate the source contributions to total mass, using the OC-to-PM ratios for the wood smoke and mobile source profiles^{44,45}. For primary biogenic and SOC sources, which were identified by the PMF model on organic species⁴³, a PM/OC ratio of 2 was used for mass conversion of both sources. The un-apportioned OC (referred to as “other OC”) was converted to “other OM” by multiplying a factor of 1.6⁴⁶. In addition to sources quantified by the CMB model, secondary ions (i.e. sum of NO₃⁻, NH₄⁺ and SO₄⁻²), crustal material, vehicular abrasion and sea salt contributions were also considered in PM_{2.5} and PM_{0.18} mass apportionment. Crustal material was calculated by summing the oxides of Al, K, Fe, Ca, Mg, Ti and Si based on the following equation^{33,34}:

$$\text{Crustal material} = 1.89\text{Al} + 1.21\text{K} + 1.43\text{Fe} + 1.40\text{Ca} + 1.66\text{Mg} + 1.67\text{Ti} + 2.14\text{Si} \quad [1]$$

Si was not measured in this study, but was estimated as $3.14 \times \text{Al}$ ⁴⁷.

Vehicular abrasions, especially particles emitted from brake wear, have been postulated to contribute significantly to the overall ambient PM_{2.5} particle levels, especially in recent years and as tailpipe emissions have generally decreased^{48–50}. Several studies have also reported the contribution of road dust and vehicular abrasion to ultrafine size fraction as well^{51–53}. These studies have also acknowledged the importance of crustal elements such as Al, Ca, Fe and Ti in the ultrafine particles size range^{51–54}.

Metals and elements such as V, Cr, Mn, Ni, Cu, Zn, As, Se, Sr, Ba and Pb have been identified as important tracers of vehicular abrasion emissions^{32,55,56}. The contribution of tire wear to trace metal emissions from motor vehicles has been reported to be negligible compared with contributions of other sources (e.g., brake wear) and it has been considered primarily a source of organic compounds^{32,57–59}. In this study, vehicular abrasion was estimated based on a study by Schauer et al.³² in which the sources of metals associated with motor vehicle traffic were determined by a CMB analysis. Intensive sampling was conducted to construct source profiles with a relatively large number of on-road vehicles in a tunnel test in Milwaukee along with brake wear and tire wear dust from Wisconsin vehicles. Schauer et al.³² reported an averaged source profile for different compositions of brake pads. Taking Ba as our basis, with the assumption that all Ba emissions are from brake wear⁵⁴, we estimated the brake wear contribution from the atmospheric concentrations of Ba and using the average mass ratio of this specie from the re-suspended brake composition reported by Schauer et al.³². An average Ba mass fraction of 13.3 ± 0.14 mg/g PM of brake dust in PM_{2.5} was applied for this conversion and was used for both PM_{2.5} and PM_{0.18} vehicular abrasion estimations. As noted above, Schauer et al.³² indicated that tire wear may be a significant contributor to motor vehicle emissions of OC, but its contribution to metals emissions is negligible. Therefore, it should be noted that vehicular abrasion source estimation in this study is mainly associated with contribution from brake wear.

Lastly, sea salt was also estimated as the sum of soluble Na^+ and the sea salt fraction of typical sea water components such as Cl^- , Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} ³⁵ as follows:

$$\text{Sea.Salt} = [\text{Na}^+] + \text{ss} [\text{Cl}^-] + \text{ss} [\text{Mg}^{+2}] + \text{ss} [\text{K}^+] + \text{ss} [\text{Ca}^{+2}] + \text{ss} [\text{SO}_4^{-2}] \quad [2]$$

where $\text{ss Cl}^- = 1.8$, $\text{ss Mg}^{2+} = 0.12$, $\text{ss K}^+ = 0.036$, $\text{ss Ca}^{2+} = 0.038$ and $\text{ss SO}_4^{2-} = 0.252$ ³⁵. The monthly-averaged source contributions ($\pm$ standard deviation) are presented in Tables S2 and S3 for Central LA and Anaheim in both size ranges.

3. Results and discussion

3.1 $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$ chemical composition

Table 1 presents the summary of monthly-averaged concentrations of EC, OC, total elements, as well as secondary ions (as sum of NO_3^- , NH_4^+ and SO_4^{2-}) for the two PM size ranges in Central LA and Anaheim. In general, $\text{PM}_{2.5}$ EC and OC constituted 4 and 24% of PM mass concentration in Central LA, while these ratios were 3 and 31% for EC and OC in Anaheim, respectively. Percent contribution of both EC and OC in $\text{PM}_{0.18}$ size range increased to 13 and 48% in Central LA, respectively. In Anaheim, OC dominated the $\text{PM}_{0.18}$ composition with an average contribution of 55% while the contribution of EC to $\text{PM}_{0.18}$ was 10%. Inorganic elements constituted 8 and 10% of PM mass concentration in $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$ size ranges, respectively, in Central LA. Similarly, the contribution of these species to PM mass was 10% for both size ranges in Anaheim. The contribution of secondary ions to $\text{PM}_{2.5}$ mass concentration was 33 and 31% in Central LA and Anaheim, respectively, while in the $\text{PM}_{0.18}$ size fraction they accounted for 13 and 14% in Central LA and Anaheim, respectively. More details on aerosol chemical composition and mass concentrations are discussed elsewhere ³¹.

3.2 Spatial and temporal variations in DTT activity

The spatial and temporal variability of the DTT activity for both size ranges were investigated. The rate of DTT consumption normalized by volume of air sampled (expressed in units of $\text{nmol}/\text{min m}^3$) is presented in Figure 1, while the DTT consumption rate normalized by PM mass data (expressed in units of $\text{nmol}/\text{min mg}$) are presented in Figure 2. Our measurements showed that the volume-normalized DTT activity, as a metric for comparison of inhalation exposures, at both sites varied across a range of 0.05–0.15 $\text{nmol}/\text{min m}^3$ and 0.2–0.6 $\text{nmol}/\text{min m}^3$ for $\text{PM}_{0.18}$ and $\text{PM}_{2.5}$, respectively. Mass-normalized DTT activity, indicative of PM intrinsic toxicity, typically ranged from 20–60 $\text{nmol}/\text{min mg}$ and 20–45 $\text{nmol}/\text{min mg}$ for $\text{PM}_{0.18}$ and $\text{PM}_{2.5}$, respectively at the two study sites. As evident from Figure 1, within the same size range DTT activity is spatially uniform. Between both sampling sites, a seasonal variability with 40 and 90% increase in volume-normalized DTT activity in colder months in comparison to warmer months was observed for $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$, respectively. This increase was also seen in mass-based DTT activity with 20 and 40% increase in colder months for $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$, respectively. These trends are in general agreement with the recent study of Saffari et al.⁶⁰, who investigated the seasonal variation of $\text{PM}_{0.25}$ in the LA Basin as well as with the study by Verma et al.³⁰,

which also demonstrated higher levels of ambient PM_{2.5} DTT activity in the southeastern USA during colder periods. The elevated levels of volume-normalized DTT activity during these months are mainly attributed to the higher atmospheric stability in addition to enhanced gas-to-particle partitioning of redox active semi-volatile organic compounds^{30,60}.

3.3 Regression analysis and source apportionment of DTT

3.3.1 Correlations between DTT activity and PM chemical species—To investigate the association of DTT activity with PM_{2.5} and PM_{0.18} chemical composition, univariate correlation analysis was performed between the weekly samples of volume-normalized DTT activity and chemical species concentrations at each sampling site separately. Univariate correlation also helped identify important chemical species that should be considered as input species for the subsequent MLR analysis. Table 2 shows the Spearman's correlation coefficients between the air volume-normalized DTT activity and concentrations of chemical species including EC, OC, PAHs, hopanes, n-alkanes, organic acids, levoglucosan and selected elements for PM_{2.5} and PM_{0.18} in Central LA and Anaheim. Most notably, organic compounds showed overall high correlation values with DTT activity in both size ranges ($R > 0.60$), especially in Central LA. Similarly high correlations between the DTT activity and organic compounds such as OC, hopanes, and PAHs have also been reported in previous studies conducted in the LA Basin^{20,60–63}. EC, which is a marker of combustion processes mainly from vehicle tailpipe emissions⁶⁴, was also highly correlated with DTT activity at both sampling sites especially in PM_{0.18} size range ($R = 0.76$ averaged over Central LA and Anaheim). Verma et al.³⁰ also demonstrated strong correlations between DTT activity and EC in southeastern United States. Overall, high correlations of these specific markers elucidate the underlining toxicity associated with the sources of these tracers. Levoglucosan, a tracer of biomass burning, showed relatively high correlation with DTT activity, with R values of 0.64 and 0.61 for PM_{2.5} and PM_{0.18}, respectively, averaged over Central LA and Anaheim. This observation is also in line with findings of Verma et al.^{65,66} who also indicated biomass burning as an important source of reactive oxygen species and observed strong correlations between DTT activity and biomass burning characterized by high concentration of levoglucosan. Some metals such as Ba, Cu, Fe, K, Mn, Pd and Pb were also significantly correlated with DTT activity in both size ranges in Central LA ($R > 0.60$) and Anaheim ($R > 0.70$). A number of previous studies have also reported strong correlations of these metals with the DTT activity^{63,67–70}. Metals such as Ba, Cu, Fe, Mn, Pb and Sr are primarily associated with vehicular abrasion and re-suspension of soil and road dust^{55,71,72}.

MLR analysis was conducted between DTT activity and chemical species for both size ranges in Central LA and Anaheim in order to investigate the compounds driving the PM redox activity. The best fitted regression models for both size ranges and sampling sites are presented in Table 3. The optimum model for Central LA in the PM_{2.5} size range included the sum of phthalic, glutaric and succinic acids as the tracers of SOC⁴³, as well as Ba, a tracer of vehicular abrasion⁵⁵, leading to an R^2 value of 0.50. EC, an important tracer of vehicular emissions⁶⁴, and Ba for PM_{0.18} were found to be the best fitted species in Central LA with R^2 value of 0.60. In Anaheim, for the PM_{2.5} size fraction, Cu and sum of organic acids, indicative of vehicular abrasion^{73,74} and SOC sources^{75,76}, respectively, best

predicted DTT activity ($R^2 = 0.86$). In the $PM_{0.18}$ size range at that site, EC and Pb (an indicator of vehicular abrasion^{55,71}), are the main driving species of the DTT activity ($R^2 = 0.71$). It should be mentioned that other tracers of the same source were also examined in the MLR models, and they all led to similar results albeit with somewhat lower R^2 values, with either statistically significant ($P < 0.05$) or approaching significance ($P < 0.08$) contribution to DTT activity. For instance, in Central LA for $PM_{2.5}$ size fraction, SOC tracers along with other tracers of vehicular abrasion such as Fe and Zn also had similar results with R^2 of 0.38 and 0.31, respectively. Other combinations of the tracers of vehicle tailpipe emissions and vehicular abrasion in $PM_{0.18}$ at this site were also examined such as Cu and EC ($R^2 = 0.37$) as well as PAHs and Mn ($R^2 = 0.59$). Similarly, in Anaheim other tracers of vehicular abrasion such as Zn and Ba with SOC tracers showed association with $PM_{2.5}$ DTT activity with R^2 of 0.81 and 0.78, respectively. PAHs and Zn as other tracers of vehicle tailpipe emissions and vehicular abrasion, respectively were associated with $PM_{0.18}$ DTT activity with R^2 of 0.73.

3.3.2 Correlations between DTT activity and sources—Univariate analysis was performed to assess how individual sources (i.e., the CMB-derived sources along with secondary ions, crustal material, vehicular abrasion and sea salt) correlate with the DTT activity (Table 4). Wood smoke showed positive significant correlations with DTT activity with R values of 0.56 and 0.61 in Central LA for $PM_{2.5}$ and $PM_{0.18}$, respectively, and similarly, in Anaheim with R values of 0.55 and 0.57 for $PM_{2.5}$ and $PM_{0.18}$, respectively. Vehicle tailpipe emissions also exhibited positive and significant correlations with DTT activity with R values of 0.69 and 0.72 for $PM_{2.5}$ in Central LA and Anaheim, respectively. For $PM_{0.18}$, stronger correlations between DTT activity and vehicle tailpipe emissions were observed in comparison to $PM_{2.5}$ in both Central LA ($R = 0.77$) and Anaheim ($R = 0.88$), underscoring the greater impact of vehicle tailpipe emissions on the DTT activity in this size range. Primary biogenic sources, which include emissions from vegetative detritus, food cooking and re-suspended soil dust⁴³ significantly correlated with DTT activity in both size ranges in Central LA with an average R value of 0.71. SOC also showed positive association with the DTT activity in $PM_{2.5}$ size range with higher correlation in Anaheim ($R = 0.58$). Secondary ions showed low or negative correlations except for $PM_{2.5}$ in Anaheim. Crustal materials in $PM_{0.18}$ ($R = 0.58$) and vehicular abrasion emissions in both size ranges ($R = 0.73$) also showed statistically significant correlations in both size ranges in Central LA. In Anaheim, remarkably higher R values of 0.77 and 0.82 for crustal materials and vehicular abrasion, respectively, were observed for both size fractions on average. Sea salt, on the other hand, showed low or negative correlations with DTT activity in both size ranges at both sampling sites.

Furthermore, MLR analysis was also performed on DTT activity and the PM sources mentioned above to identify the best and statistically significant ($P < 0.05$) predictors of the DTT activity. The details of the output models are presented in Table 5. In Central LA, primary biogenic, SOC and vehicular abrasion sources contributed significantly to $PM_{2.5}$ DTT activity with R^2 value of 0.71, while in $PM_{0.18}$ size range, vehicle tailpipe emissions as well as vehicular abrasion were the main drivers of the DTT activity ($R^2 = 0.72$). Similarly, in Anaheim, SOC and vehicular abrasion in $PM_{2.5}$ size range ($R^2 = 0.81$) and vehicle

tailpipe emissions as well as vehicular abrasion in $PM_{0.18}$ ($R^2 = 0.75$) were identified to be the significant contributors of DTT activity.

3.4 Comparison with previous studies in Los Angeles

Table 6(a–b) presents a comparison of DTT activity measured in the current study with previous studies conducted in Central LA, all at the same sampling site, over the past decade for fine and ultrafine particles. Overall a small increase in the per PM mass-normalized DTT activity of ambient $PM_{2.5}$ can be seen from 2002 to 2012. The DTT activity normalized per m^3 of air volume has been more stable over time in Central LA, which may be attributed to an increase in intrinsic DTT activity, combined with the documented decrease in $PM_{2.5}$ mass concentration over time in Central LA, as discussed in following sections. Unlike $PM_{2.5}$, in the ultrafine size range, the cut point was not consistent among different studies.

Nonetheless, both air volume and PM mass-based DTT activity have generally decreased over the past decade in Central LA. Verma et al.⁶³ reported $PM_{0.18}$ DTT activity of 0.07 ± 0.03 nmol/min μg in June–August 2009, while three years later, this value approximately decreased by 66% to 0.024 ± 0.001 nmol/min μg in July–August in Central LA. Even though Saffari et al.⁶⁰ reported $PM_{0.25}$ DTT activity levels, still a 42% decrease can be seen in comparison to $PM_{0.18}$ DTT levels measured at this study after four years.

Several studies have shown a major reduction in ambient $PM_{2.5}$ levels and its sources over the past decade in the Los Angeles Basin and demonstrated that stringent regulations on mobile sources, in particular starting 2007, have resulted in major reductions in tailpipe emissions^{48,77–80}. However, the small but consistent increase in $PM_{2.5}$ mass-based DTT activity level reveals that other factors besides tailpipe emissions may affect the $PM_{2.5}$ toxicity as well. The results discussed in the previous section revealed that vehicular abrasion, an important component of non-tailpipe emissions, together with secondary OC, were two major sources significantly contributing to $PM_{2.5}$ DTT activity, in addition to tailpipe emissions. Shirmohammadi et al.³¹ recently showed that important tracers of tailpipe emissions in $PM_{2.5}$ and $PM_{0.18}$ such as PAHs, hopanes and steranes concentrations have decreased by 40–70% and 50–70%, respectively over the past decade in Central LA. These findings, along with the comparison of ultrafine PM redox activity with previous studies, corroborate the effectiveness of stringent regulations on vehicular tailpipe emissions in reducing the overall ambient ultrafine PM toxicity. However, tailpipe emissions are not the only contributor of PM toxicity in the fine PM, as indicated and discussed above. Harrison et al.⁸¹ showed that tracers of vehicular abrasion, which are generally more prevalent in the coarse ($PM_{2.5-10}$) size fraction, also partition into the upper size range of $PM_{2.5}$. Similar findings have been reported in other studies as well^{82,83}. Recently, Shirmohammadi et al.⁸⁴ discussed the increase in metals and trace element concentrations in the coarse PM over a 3-year period in Central LA, especially those emitted from vehicular abrasion and road dust. This was attributed to the increase in the vehicle's speed and number of trucks (by 6 and 15%, respectively, which was also statistically significant (Mann-Whitney Rank Sum Test, $P < 0.001$) as the turbulence caused by the passing traffic highly contributes to substantial amount of coarse particles emissions from re-suspension of soil and road dust⁸⁵, in Central LA. Moreover, comparison with several previous studies conducted in Central LA also revealed a similar trend, with an increase in the contribution of

vehicular abrasion tracers in $PM_{2.5}$ mass over time unlike the $PM_{2.5}$ mass concentration decrease after implemented regulations on vehicle tailpipe emissions (Figure 3a–b). For instance, as can be inferred from Figure 3b, compared to a study conducted by Minguillón et al.⁸⁶ during a 13-week period between March– September 2007 (except June) in the same sampling site in Central LA, $PM_{2.5}$ mass concentration decreased by 24% in this study, while the contribution of the sum of VA tracers (i.e. Ba, Cu, Mn, Pb and Sr) to $PM_{2.5}$ mass increased by a factor of near 2.2. In line with this comparison, the annual trends of individual VA tracers from 2008 to 2012, obtained from the Speciation Trends Network (STN) data at the North Main street in downtown Los Angeles, showed that, although the per air volume concentrations of these species were relatively stable from 2008 to 2012 (Figure S1 (a–e)), an increasing trend in the contribution of these tracers to $PM_{2.5}$ mass concentration is evident from their year-to-year per mass concentrations levels (Figure S2 (a–e)). The median value of the sum of per PM mass concentrations ($\mu\text{g}/\mu\text{g PM}$) of the VA tracers (i.e. Ba, Cu, Mn, Pb and Sr) increased statistically significantly by 11% from 2008 to 2012 (Mann-Whitney Rank Sum Test, $P = 0.05$). This increase over these years can also be seen for individual species. For example, the per mass concentration of Ba (which was also used as the basis of our VA contribution's estimation in previous section) increased statistically significantly by 66% from 2008 to 2012 (Mann-Whitney Rank Sum Test, $P < 0.01$). More information regarding the STN data is provided in Supplementary Information. Therefore, it can be hypothesized that the per PM mass increase in redox active metals and other trace elements from non-tailpipe emissions may counteract the reduction in vehicular tailpipe emissions in $PM_{2.5}$, leading to a slight increase in the overall DTT activity in this size fraction of PM with time. This is in contrast to the ultrafine PM, the toxicity of which seems to be largely dominated by tailpipe emissions, and appears to be decreasing with time, as shown in Table 6b.

4. Conclusions

In this study, the oxidative potential of ambient $PM_{2.5}$ and $PM_{0.18}$, determined by the DTT assay, was linked to PM sources and chemical components in the LA Basin. Univariate analysis between chemical species and DTT activity suggested the potential influence of different sources and species on abiotic PM-induced toxicity measured by the DTT assay. MLR analysis performed on ambient PM sources in Central LA and Anaheim in both size ranges revealed the contribution from different sources to the oxidative potential of PM. Primary biogenic emissions, SOC and vehicular abrasion in the $PM_{2.5}$ size range, along with vehicular abrasion and vehicle tailpipe emissions in the $PM_{0.18}$ size range were found to be the major sources driving the DTT activity levels in Central LA. MLR yielded similar results for Anaheim, with higher contributions from vehicular abrasion and SOC in $PM_{2.5}$ size range. Vehicular abrasion, followed by vehicle tailpipe emissions, were the two significant contributors to $PM_{0.18}$ DTT activity in Anaheim.

A comparison with previous studies conducted in Central LA revealed trends in DTT activity of ambient $PM_{2.5}$ and $PM_{0.18}$ in the past decade. Ambient $PM_{0.18}$, the toxicity of which was found to be mainly dominated by tailpipe emissions, showed a consistent decrease in DTT activity levels in the past decade, likely due to major reductions in tailpipe emissions in the LA Basin, as a result of stringent regulations on mobile sources. In $PM_{2.5}$

size range, however, DTT activity levels showed overall a slight increase over the years, which is probably driven by the increase in the contribution of non-tailpipe emissions to ambient PM_{2.5}, counteracting with reductions in the tailpipe emissions in this size fraction. Our findings illustrated the relative importance of different traffic sources on the oxidative potential of ambient PM. Despite rapid reduction of tailpipe emissions, the lack of similar reductions (and possibly an increase) in non-tailpipe emissions makes them an important source of traffic-related PM emissions in Los Angeles and a concern for public health.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. (a–b). Monthly-averaged volume-normalized dithiothreitol (DTT) activity (nmol/min m^3) of ambient $PM_{2.5}$ and $PM_{0.18}$ at a) Central LA and b) Anaheim. February 2014 data corresponds to one sample. Sampling was not conducted in December 2013 at Anaheim. Error bars correspond to one standard deviation.

Figure 2.
(a–b). Monthly-averaged mass-normalized dithiothreitol (DTT) activity (nmol/min mg) of ambient $PM_{2.5}$ and $PM_{0.18}$ at a) Central LA and b) Anaheim. February 2014 data corresponds to one sample. Sampling was not conducted in December 2013 at Anaheim. Error bars correspond to one standard deviation.

Figure 3.

(a–b). Comparison of the sum of vehicular abrasion (VA) tracers' concentrations (i.e. sum of Ba, Cu, Mn, Pb and Sr) a) per volume of air ($\mu\text{g}/\text{m}^3$) and b) per mass collected ($\mu\text{g}/\mu\text{g PM}$) in PM_{2.5} size range with previous studies conducted at Central LA. Error bars correspond to one standard deviation. The dates in the parentheses refer to the pertinent sampling dates.

Table 1

(a–b). Monthly-averaged mass concentrations ($\mu\text{g}/\text{m}^3$) of EC, OC, total metals and elements (i.e. sum of 50 species presented by names in Table S1.), as well as secondary ions (i.e. sum of NO_3^- , NH_4^+ and SO_4^{2-}) at a) Central LA and b) Anaheim. Sampling was not conducted at Anaheim in December 2013.

a) Central LA									
Sampling months	EC		OC		Metals and elements		Secondary ions		
	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	
Jul 2012	0.40 ± 0.12	0.23 ± 0.07	1.86 ± 0.43	0.75 ± 0.21	1.35 ± 0.01	0.14 ± 0.00	4.14 ± 1.40	0.56 ± 0.23	
Aug 2012	0.52 ± 0.18	0.31 ± 0.14	2.02 ± 0.42	0.86 ± 0.27	1.53 ± 0.01	0.19 ± 0.00	4.03 ± 1.01	0.38 ± 0.09	
Sep 2012	0.59 ± 0.08	0.25 ± 0.03	2.51 ± 0.38	0.95 ± 0.17	1.33 ± 0.01	0.16 ± 0.00	3.58 ± 0.56	0.31 ± 0.06	
Oct 2012	0.70 ± 0.30	0.37 ± 0.17	2.93 ± 0.93	1.31 ± 0.37	0.82 ± 0.01	0.25 ± 0.00	3.81 ± 2.60	0.30 ± 0.07	
Nov 2012	0.45 ± 0.12	0.25 ± 0.06	3.00 ± 0.62	1.03 ± 0.36	1.00 ± 0.01	0.26 ± 0.00	6.96 ± 2.35	0.26 ± 0.08	
Dec 2012	0.43 ± 0.10	0.26 ± 0.06	3.51 ± 1.23	1.22 ± 0.44	0.87 ± 0.01	0.39 ± 0.01	3.38 ± 1.38	0.15 ± 0.05	
Jan 2013	0.51 ± 0.05	0.32 ± 0.02	3.97 ± 0.68	1.36 ± 0.11	0.55 ± 0.00	0.25 ± 0.00	1.89 ± 0.46	0.18 ± 0.03	
Feb 2013	0.54 ± 0.32	0.30 ± 0.18	3.48 ± 1.86	1.21 ± 0.65	0.78 ± 0.01	0.20 ± 0.00	5.20 ± 1.69	0.25 ± 0.05	
b) Anaheim									
Sampling months	EC		OC		Metals and elements		Secondary ions		
	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	$\text{PM}_{2.5}$	$\text{PM}_{0.18}$	
Jul 2013	0.13 ± 0.03	0.11 ± 0.02	1.64 ± 0.35	1.01 ± 0.22	1.00 ± 0.01	0.17 ± 0.00	2.25 ± 0.48	0.40 ± 0.19	
Aug 2013	0.18 ± 0.06	0.16 ± 0.05	2.43 ± 0.14	1.22 ± 0.14	0.95 ± 0.01	0.20 ± 0.00	3.17 ± 0.43	0.48 ± 0.11	
Sep 2013	0.18 ± 0.03	0.15 ± 0.03	1.82 ± 0.15	1.12 ± 0.15	0.99 ± 0.01	0.17 ± 0.00	1.97 ± 0.34	0.44 ± 0.13	
Oct 2013	0.31 ± 0.00	0.26 ± 0.00	2.95 ± 0.00	1.68 ± 0.00	1.12 ± 0.00	0.40 ± 0.00	2.29 ± 1.1	0.40 ± 0.11	
Nov 2013	0.53 ± 0.19	0.42 ± 0.20	4.62 ± 1.71	1.85 ± 0.71	1.05 ± 0.00	0.43 ± 0.00	2.68 ± 0.67	0.32 ± 0.08	
Dec 2013									
Jan 2014	0.46 ± 0.20	0.37 ± 0.17	3.74 ± 1.13	1.57 ± 0.49	0.94 ± 0.01	0.34 ± 0.00	4.46 ± 0.69	0.23 ± 0.07	
Feb 2014	0.33 ± 0.18	0.28 ± 0.17	3.15 ± 0.99	1.54 ± 0.03	0.39 ± 0.00	0.16 ± 0.00	3.47 ± 0.22	0.31 ± 0.03	

Table 2

Spearman's correlation coefficients (R) between the dithiothreitol (DTT) activity (nmol/min m³) and selected PM_{2.5} and PM_{0.18} components at Central LA and Anaheim.

Species	Central LA		Anaheim	
	PM _{2.5} DTT	PM _{0.18} DTT	PM _{2.5} DTT	PM _{0.18} DTT
EC	0.54	0.67	0.72	0.86
OC	0.79	0.89	0.81	0.87
PAHs	0.63	0.69	0.60	0.78
Hopanes	0.62	0.68	0.84	0.81
<i>n</i> -Alkanes	0.74	0.57	0.57	0.85
Organic acids	0.66	0.69	0.38	0.13
Levogluconan	0.56	0.64	0.72	0.58
NO ₃ ⁻	0.32	0.35	0.60	0.40
SO ₄ ⁻²	-0.44	-0.11	-0.59	-0.73
NH ₄ ⁺	-0.019	-0.299	.431	.205
Al	0.21	0.65	0.69	0.76
P	0.53	0.72	0.74	0.84
S	-0.37	0.21	-0.49	0.15
K	0.55	0.83	0.73	0.86
Ca	0.36	0.70	0.62	0.83
Ti	0.48 *	0.64	0.66	0.75
V	-0.20	0.06	-0.39	0.29
Cr	0.29	0.34	0.64	0.46 *
Mn	0.46 *	0.70	0.84	0.82
Fe	0.54	0.75	0.81	0.83
Co	.26	0.45 *	0.59	0.69
Ni	-0.11	0.04	0.34	0.39
Cu	0.51	0.58	0.81	0.88
Zn	0.54	0.51	0.83	0.88
Rb	0.64	0.79	0.70	0.78
Sr	0.53	0.72	0.48 *	0.62
Pd	0.57	0.78	0.72	0.77
Cd	0.61	0.78	0.66	0.81
Sn	0.12	0.22	0.76	0.82
Sb	0.60	0.75	0.66	0.84
Ba	0.58	0.80	0.79	0.85
Pb	0.58	0.64	0.68	0.78

Bold numbers indicate values with $R > 0.50$ and $P < 0.05$.

* indicates values with $R < 0.5$ and $P < 0.05$. PAHs, hopanes, *n*-alkanes and organic acids species are presented by their names in Table S1.

Table 3

Output of multiple linear regression (MLR) analysis between the dithiothreitol (DTT) activity ($\text{nmol}/\text{min m}^3$) and chemical species for $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$ size ranges at Central LA and Anaheim.

DTT activity	Species	Unstandardized Coefficient	Units	Standard error	Partial R	P value	R ²
Central LA $\text{PM}_{2.5}$	(Constant)	0.12	$\text{nmol min}^{-1} \text{m}^{-3}$	0.057	-		
	SOC tracers *	0.01	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.004	0.432	0.022	0.50
	Ba	0.012	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.003	0.685	0.000	
Central LA $\text{PM}_{0.18}$	(Constant)	0.011	$\text{nmol min}^{-1} \text{m}^{-3}$	0.021	-		
	EC	0.155	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.076	0.37	0.053	0.60
	Ba	0.014	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.003	0.658	0.000	
Anaheim $\text{PM}_{2.5}$	(Constant)	0.121	$\text{nmol min}^{-1} \text{m}^{-3}$	0.051	-		
	Organic acids	0.002	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.001	0.490	0.033	0.83
	Cu	0.023	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.003	0.891	0.000	
Anaheim $\text{PM}_{0.18}$	(Constant)	0.032	$\text{nmol min}^{-1} \text{m}^{-3}$	0.009	-		
	EC	0.136	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.065	0.453	0.051	0.84
	Pb	0.056	$\text{nmol min}^{-1} \text{ng}^{-1}$	0.022	0.533	0.019	

* Sum of phthalic acid, glutaric acid and succinic acid ³⁹.

Table 4

Spearman's correlation coefficients (R) between the dithiothreitol (DTT) activity (nmol/min m³) and sources of PM_{2.5} and PM_{0.18} at Central LA and Anaheim.

Sources	Central LA		Anaheim	
	PM _{2.5} DTT	PM _{0.18} DTT	PM _{2.5} DTT	PM _{0.18} DTT
Wood smoke	0.56 *	0.61 *	0.55 *	0.57 *
Primary biogenic	0.68 *	0.76 *	0.32	0.21
SOC	0.28	−0.14	0.58 *	−0.08
Secondary Ions	−0.07	−0.05	0.49*	0.02
Crustal material	0.33	0.72 *	0.73 *	0.81 *
Vehicular abrasion	0.58 *	0.80 *	0.79 *	0.85 *
Sea salt	−0.46	−0.00	−0.32	0.42
Vehicle tailpipe emissions	0.69 *	0.77 *	0.72 *	0.88 *

Bold numbers indicate values with $R > 0.50$ and $P < 0.1$ and

* indicates values with $P < 0.05$.

Table 5

Output of multiple linear regression analysis between the dithiothreitol (DTT) activity ($\text{nmol}/\text{min m}^3$) and sources of $\text{PM}_{2.5}$ and $\text{PM}_{0.18}$ size ranges at Central LA and Anaheim.

DTT activity	Sources	Unstandardized Coefficient	Units	Standard error	Partial R	P value	R ²
Central LA $\text{PM}_{2.5}$	(Constant)	-0.015	$\text{nmol min}^{-1} \text{m}^{-3}$	0.056	-		
	Primary biogenic	0.081	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.025	0.582	0.004	0.71
	SOC	0.159	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.036	0.697	0.000	
	Vehicular abrasion	0.069	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.032	0.425	0.043	
Central LA $\text{PM}_{0.18}$	(Constant)	0.012	$\text{nmol min}^{-1} \text{m}^{-3}$	0.013	-		
	Vehicle tailpipe emission	0.134	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.037	0.630	0.002	0.72
	Vehicular abrasion	0.093	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.032	0.539	0.010	
Anaheim $\text{PM}_{2.5}$	(Constant)	0.175	$\text{nmol min}^{-1} \text{m}^{-3}$	0.031	-		
	SOC	0.081	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.034	0.487	0.029	0.81
	Vehicular abrasion	0.181	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.032	0.798	0.000	
Anaheim $\text{PM}_{0.18}$	(Constant)	0.046	$\text{nmol min}^{-1} \text{m}^{-3}$	0.008	-		
	Vehicle tailpipe emission	0.068	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.030	0.474	0.040	0.75
	Vehicular abrasion	0.105	$\text{nmol min}^{-1} \mu\text{g}^{-1}$	0.029	0.658	0.002	

Table 6

(a–b). Comparison of dithiothreitol (DTT) activity levels ($\pm$ standard deviation) with previous studies conducted at Central Los Angeles for: a) $\text{PM}_{2.5}$ and b) $\text{PM}_{0.18}$ size ranges.

a)				
Study	Size fraction	Sampling period	DTT activity (nmol/min μg)	DTT activity (nmol/min m^3)
Li et al. 2003	$\text{PM}_{2.5}$	Mar 2002	0.013	0.28
Hu et al. 2008	$\text{PM}_{2.5}$	Mar–May 2007	0.022	0.33
Verma et al. 2009b	$\text{PM}_{2.5}$	Nov 2007	0.007 ± 0.003	0.35 ± 0.30
Current study	$\text{PM}_{2.5}$	2012–2013	0.028 ± 0.005	0.35 ± 0.04

b)				
Study	Size fraction	Sampling period	DTT activity (nmol/min μg)	DTT activity (nmol/min m^3)
Li et al. 2003	$\text{PM}_{0.15}$	Mar 2002	0.091	0.35
Verma et al. 2009a	$\text{PM}_{0.18}$	Aug 2009	0.07 ± 0.03	0.33 ± 0.25
Saffari et al. 2014	$\text{PM}_{0.25}$	2008–2009	0.078 ± 0.007	0.82 ± 0.12
Current study	$\text{PM}_{0.18}$	2012–2013	0.045 ± 0.008	0.11 ± 0.03