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A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE)

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Received: 17 May 2014 – Accepted: 22 June 2014 – Published: 17 July 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

A variety of methods are used to measure the capability of particulate matter (PM) to catalytically generate reactive oxygen species (ROS) in vivo, also defined as the aerosol oxidative potential. A widely used measure of aerosol oxidative potential is the dithiothreitol (DTT) assay, which monitors the depletion of DTT (a surrogate for cellular antioxidants) as catalyzed by the redox-active species in PM. However, a major constraint in the routine use of the DTT assay for integrating it with the large-scale health studies is its labor-intensive and time-consuming protocol. To specifically address this concern, we have developed a semi-automated system for quantifying the oxidative potential of aerosol liquid extracts using the DTT assay. The system, capable of unattended analysis at one sample per hour, has a high analytical precision (Coefficient of Variation of 12% for standards, 4% for ambient samples), and reasonably low limit of detection ($0.31 \text{ nmol min}^{-1}$). Comparison of the automated approach with the manual method conducted on ambient samples yielded good agreement (slope = 1.08 ± 0.12 , $r^2 = 0.92$, $N = 9$). The system was utilized for the Southeastern Center for Air Pollution and Epidemiology (SCAPE) to generate an extensive data set on DTT activity of ambient particles collected from contrasting environments (urban, road-side, and rural) in the southeastern US. We find that water-soluble $\text{PM}_{2.5}$ DTT activity on a per air volume basis was spatially uniform and often well correlated with $\text{PM}_{2.5}$ mass ($r = 0.49$ to 0.88), suggesting regional sources contributing to the PM oxidative potential in southeast US. However, the greater heterogeneity in the intrinsic DTT activity (per PM mass basis) across seasons indicates variability in the DTT activity associated with aerosols from sources that vary with season. Although developed for the DTT assay, the instrument can also be used to determine oxidative potential with other acellular assays.

AMTD

7, 7245–7279, 2014

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1 Introduction

Epidemiological studies have associated increases in particulate matter (PM) levels with exacerbation of cardiovascular diseases (Zanobetti et al., 2014; Sun et al., 2010; Pope et al., 2004; Samet et al., 2000) and elevated incidence of respiratory disorders such as airway inflammation, bronchial muscle contraction, and asthma (Harkema et al., 2004; Schaumann et al., 2004; Aust et al., 2002; Norris et al., 1999). The mechanisms underlying these associations are not entirely clear but reactive oxygen species (ROS), either adsorbed on inhaled particles or generated in vivo, have been identified as signaling molecules that induce oxidative stress, causing cell damage (Nel, 2005; Gurgueira et al., 2002). These findings imply that aerosol oxidative potential, i.e. the ability of ambient particles to generate ROS, may be a more relevant measurement than PM mass concentration, or concentrations of specific aerosol chemical components, when attempting to link aerosols and health endpoints.

Both cellular (Xia et al., 2006; Kubátová et al., 2006; Bonvallot et al., 2001; Hiura et al., 1999; Antonini et al., 1998) and acellular methods (Zomer et al., 2011; Mudway et al., 2011; Jung et al., 2006; Cho et al., 2005; Venkatachari et al., 2005; Frampton et al., 1999) have been developed to measure the oxidative potential of PM. Both types of methods have advantages and disadvantages. Acellular methods require less controlled environments and provide faster readouts of PM oxidative potential. One of the most widely used cell-free measures of particles oxidative potential is the DTT (dithiothreitol, $\text{HSCH}_2(\text{CH}(\text{OH}))_2\text{CH}_2\text{SH}$) assay (Charrier and Anastasio, 2012; Verma et al., 2012, 2009a; Cho et al., 2005; Kumagai et al., 2002; Delfino et al., 2013). Typically, ROS in vivo are mainly produced in mitochondria and endoplasmic reticulum (ER) where molecular oxygen (O_2) are reduced to superoxide anion (O_2^-) by accepting electrons from cellular reductants, such as NADPH, or during ER protein folding process (Alfadda and Sallam, 2012). The DTT assay simulates this electron-transfer mechanism based on the catalytic ability of redox-active species to transfer electrons from DTT to oxygen, and thus can be considered a surrogate measure of the in-vivo capacity

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of PM to induce ROS. The rate of the reaction, commonly called DTT activity, is determined by measuring the consumption of DTT over time, which is proportional to the concentration of redox-active species in PM extracts. Researchers have identified various chemical components that may participate in the reaction, including polycyclic aromatic hydrocarbons (PAHs) (Li et al., 2003), quinones (Chung et al., 2006; Kumagai et al., 2002), transition metals (Charrier and Anastasio, 2012), water soluble organic carbon (WSOC) (Verma et al., 2009a; Cho et al., 2005), and HUmic-Like Substances (HULIS) (Verma et al., 2012; Lin and Yu, 2011). However, a consensus on the relative contributions of these species in the overall DTT activity of ambient particles is currently lacking.

Studies have also reported the association between DTT activity of ambient particles and cellular biomarkers such as fractional exhaled nitric oxide (FE_{NO}) – a marker of airway inflammation (Delfino et al., 2013), hemeoxygenase (HO-1) – an enzyme responsive to oxidative stress (Li et al., 2003), and 3-(4,5-Dimethylthiazol-2-yl)-2,5-Diphenyltetrazolium Bromide (MTT)-reduction activity (Steenhof et al., 2011). These studies suggest a plausible mechanistic link between DTT-assessed oxidative potential and adverse health effects of ambient particles. Routine DTT analysis as part of large-scale toxicological and health studies involving aerosol exposure is needed to further establish the health relevance of the DTT assay (and other chemical assays in general).

One major limitation in conducting the DTT assay on a large scale is its laborious and time-intensive analytical protocol, which requires precise handling practices at each step of the reaction for an accurate determination of the rate of DTT oxidation. Researchers have also developed alternative approaches to conduct the DTT assay other than the traditional protocol (Cho et al., 2005) for new applications. For example, a paper-based analytical device (μ PAD) DTT assay was developed for personal exposure studies (Sameenoi et al., 2012b) and a microfluidic electrochemical sensor coupled with a particle-into-liquid-sampler (PILS) was developed for real-time measurement of aerosol DTT activity (Koehler et al., 2014; Sameenoi et al., 2012a). We have

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developed a semi-automated system using programmable syringe pumps with selector valves for conducting the DTT assay on various extracts. The system is based on a simplified protocol in which the aerosol extract oxidizes DTT in a single vial. A small aliquot is withdrawn at various time intervals to determine the remaining DTT concentration and calculate the rate of DTT consumption. Particulate samples are extracted to an aqueous state and analyzed in batches using an auto-sampler, at roughly one hour per sample. Extraction liquids can be either deionized water or organic solvents, in the latter case the solvent is evaporated and reconstituted in deionized water. The system was validated against the manual protocol using both standards and ambient filter samples. The DTT activity of more than 500 samples collected from the southeastern United States as part of the Southeastern Center for Air Pollution and Epidemiology (SCAPE) were analyzed for this study. Here we provide a detailed description and characterization of the automated system and an overview of aerosol oxidative potential in the southeastern United States. Sources and components of PM_{2.5} that produce the DTT activity are presented in other papers.

2 Methods

2.1 Chemicals

Dithiothreitol (DTT), Tris base, dimethyl sulfoxide (DMSO), 5,5'-dithiobis-(2-nitrobenzoic acid) (DTNB) and 9,10-phenanthraquinone (PQN) were obtained from Sigma Aldrich (St. Louis, MO, USA). Trichloroacetic acid (TCA, 10 % w/v) was obtained from LabChem Inc. (Pittsburgh, PA, USA). Monopotassium phosphate (KH₂PO₄), dipotassium phosphate (K₂HPO₄), and ethylenediaminetetraacetate (EDTA) were obtained from VWR International LLC (West Chester, PA, USA). Details of the chemical preparation and storage are provided in the Supplement (SI).

2.2 Automated DTT assay system development

Automated DTT assay system. Illustrated protocol and setup schematic of the semi-automated DTT assay system are shown in Figs. 1 and 2, respectively. There are three steps in the automated DTT method. In the first step (DTT oxidation step), 3.5 mL of the aerosol extract sample and 1 mL potassium phosphate buffer (0.5 mM) are loaded into an incubation vial (Figs. 1 and 2) (sterile polypropylene centrifuge tube, VWR International LLC, Suwanee, GA, USA) using a programmable syringe pump (A) (Fig. 2) (Kloehn, Inc., Las Vegas, NV, USA). 0.5 mL of DTT (1 mM) is then added to the incubation vial using another programmable syringe pump (B) (Fig. 2). The DTT-buffer-sample mixture is incubated at 37 °C and continuously shaken at a rotational frequency of 400 rpm via a ThermoMixer (incubating accuracy: ± 0.5 °C, Eppendorf North America, Inc., Hauppauge, NY, USA). DTT in the mixture is consumed over time in the incubation vial due to catalytic reaction of DTT-active components of the aerosol extract.

In the second step (DTT determination step), at a specified time (4 min) following the completion of step one, a small aliquot (100 μ L) of the incubated mixture is withdrawn and transferred to another centrifuge tube (referred to as, reaction vial), wrapped in aluminum foil to prevent possible light interference, using Pump B. This is mixed with 1 mL TCA (1 % w/v; the quenching agent), which had previously been added to the reaction vial by pump A. The quenched mixture with residual DTT is further mixed with 2 mL of Tris buffer (0.08 M with 4 mM EDTA) and 0.5 mL DTNB (0.2 mM) added by pump A. Reaction between the residual DTT and DTNB forms a light absorbing product, 2-nitro-5-thiobenzoic acid (TNB), which has a high extinction coefficient of $14\ 150\ \text{M}^{-1}\ \text{cm}^{-1}$ at 412 nm wavelength. Pump A then withdraws the final mixture from the reaction vial and pushes it through a Liquid Wave-guide Capillary Cell (LWCC-M-100; World Precision Instruments, Inc., FL, USA) with an optical path length of 100 mm. The waveguide is coupled to an online spectrophotometer (Ocean Optics, Inc., Dunedin, FL, USA), which included a UV-VIS light source (Ocean Optics DT-Mini-2), and a multi-wavelength light detector (USB4000 Miniature Fiber Optic Spectrometer). Absorbance intensity at

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412 nm and 700 nm (chosen as the baseline absorbance for TNB) are recorded every 2 s using data acquisition software (SpectraSuite). The system then performs a self-cleaning using deionized water (DI water, $> 18 \text{ M}\Omega \text{ cm}^{-1}$) to eliminate any residual liquid in the reaction vial, tubing, syringes and LWCC. This second step is repeated four more times, at specific time intervals (13, 23, 30 and 41 min), generating a total of 5 data points of remaining DTT concentration with time. Following this, the automated system again performs a self-cleaning routine (third step) to ensure no carry-over in the incubation vial, tubing, syringes, and LWCC, before analyzing the next aerosol sample. A 14-port Multi-position Valve (VICI Valco Instrument Co. Inc., USA) is used to consecutively select individual aerosol samples for analysis. The Kloehn control program code written for conducting the DTT assay, including hardware and software details are included in the SI. The automated system is cleaned periodically (about every 15 days) by flushing at least 3 times with methanol, followed by 6 times with DI water.

DTT activity determination. Figure 3 shows an example of the absorbance intensity plot measured over time for a filter blank (Fig. 3a) and sample (Fig. 3b), obtained from the data acquisition software. The time intervals (4, 13, 23, 30 and 41 min) represent the incubation duration of DTT and sample in potassium phosphate buffer for each measurement. Withdrawal of the mixture containing TNB and pushing it through the LWCC (DTT determination step) causes the corresponding jumps in light absorbance at 412 nm (A_1, A_2, A_3, A_4, A_5 in Fig. 3a). After the absorbance measurement, pump A pushes DI water through the LWCC, which returns the absorbance back to the baseline value (i.e. absorbance at 412 nm equals absorbance at 700 nm; B_1, B_2, B_3, B_4, B_5 in Fig. 3a), thus generating a series of roughly square bars. A decreasing absorption intensity between successive measurements ($A_1 > A_2 > A_3 > A_4 > A_5$) for a sample reflects the DTT oxidation over time. During each specified DTT measurement time interval, absorbance decreases (angled top of square wave in Fig. 3); the average of the initial five absorbance data is taken as characteristic absorption for each interval. The rate of DTT consumption (σ_{DTT} , nmol min^{-1}) was determined from the slope and intercept of linear regression of measured absorbance vs. time as follows:

$$\sigma_{\text{DTT}} = -\sigma_{\text{Abs}} \times \frac{N_0}{\text{Abs}_0}, \quad (1)$$

where σ_{Abs} is the slope of absorbance vs. time; Abs_0 is the initial absorbance calculated from the intercept of the linear regression of absorbance vs. time; and N_0 is the initial nmoles of DTT added in the reaction vial. A steeper slope corresponds to a higher rate of DTT consumption. The final DTT activity for a sample was calculated by subtracting a blank value from the sample and normalized by sample air volume or particle overall mass (or mass of a specific component) represented by the sample in the incubation vial, expressed in the units of $\text{nmol min}^{-1} \text{m}^{-3}$ for volume normalized DTT activity (DTTv), or $\text{nmol min}^{-1} \mu\text{g}^{-1}$ for mass normalized DTT activity (DTTm). DTTm represents the intrinsic property of particles linked to sources, while DTTv accounts for the emission rate, dilution, etc., and characterizes exposure to the aerosol. Thus,

$$\text{DTT activity} = \frac{\sigma_{\text{DTT}}_{\text{sample}} - \sigma_{\text{DTT}}_{\text{blank}}}{V_{\text{air}} \text{ (or } M_{\text{particle}})}, \quad (2)$$

where V_{air} and M_{particle} are the ambient air volume (m^3) and total PM mass (μg) represented by the sample in the incubation vial, respectively. For example, a 3.5 mL sample of concentration $40 \mu\text{g mL}^{-1}$ would represent a total PM mass of $140 \mu\text{g}$ (3.5×40) in the incubation vial.

2.3 Ambient samples collection and preparation

2.3.1 Sampling

For this study, ambient $\text{PM}_{2.5}$ samples were collected over 23 h on pre-baked quartz filters (Pallflex TissuquartzTM, 8 inch \times 10 inch) using high-volume (Hi-Vol) samplers

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(Thermo Anderson, flow rate normally $1.13 \text{ m}^3 \text{ min}^{-1}$) as part of SCAPE. One sampler was fixed at a stationary site, Jefferson Street (JST), a central site representative of the Atlanta urban environment, while the other sampler (Trailer) was rotated among a road-side (RS), a near-road (Georgia Tech – GT), and a rural site (Yorkville – YRK), sampling in parallel with the fixed monitoring station (JST). Site characteristics are:

1. RS site was situated within 5 m distance from the interstate highway (I75/85) in Midtown Atlanta and was chosen for capturing immediate traffic emissions;
2. GT site was located on the rooftop of the Ford Environmental Science and Technology building at Georgia Tech, Atlanta, roughly 30 m a.g.l., 840 m from the RS site, providing an intermediate location between RS and the central urban site (JST);
3. YRK site is situated in an agricultural region located approximately 70 km west of JST, representative of a rural environment.

Other sites also include an urban site in Birmingham (BHM), Alabama and its paired rural site, Centerville (CTR), Alabama. JST, YRK, BHM, and CTR are all part of the Southeastern Aerosol Research and Characterization Study (SEARCH) network sites (Hansen et al., 2003). Ambient particles were collected from June 2012 to September 2013. For two periods (November 2012 and April 2013), the trailer was located at the stationary JST site for side-by-side comparisons. Table 1 provides the sampling schedule and number of filters collected at each site. In total, 503 Hi-Vol filters were collected over 15 months. Three seasons are defined based on the temperature profile throughout sampling period (see SI, Fig. S1) – summer, fall and winter, as shown in Table 1. Collected samples were immediately wrapped in pre-baked aluminum foil and stored at -18°C until analyzed.

2.3.2 Extraction of PM filters

All filters extracted in DI water via the following method were also extracted in methanol, dried and reconstituted in DI water for DTT analysis. Both water and methanol extracts were separated by solid phase extraction (C-18 resin). DTT activity was analyzed with this system in order to explore the oxidative potential of chemical sub-fractions of the ambient aerosol. Thus, not including blanks and standards, for this project on the order of 2000 extracts were analyzed for DTT activity. For the water extraction procedure, portions of the filters (about 1/28 area of the Hi-Vol filter, three one-inch diameter punches) were punched and extracted in 15 mL of DI water in sterile polypropylene centrifuge tubes (VWR International LLC, Suwanee, GA, USA) by sonication for 30 min. Extracts were then filtered using PTFE 0.45 μm syringe filters (Fisherbrand™, Fisher Scientific, PA, USA) to remove insoluble components, and divided into two fractions. One fraction of at least 5 mL was analyzed for DTT activity using the automated system. The other fraction was reserved for other chemical analysis. Here we focus only on the discussion of DTT analysis of the direct water extracts.

2.4 $\text{PM}_{2.5}$ mass concentration

$\text{PM}_{2.5}$ mass concentration were measured by a Tapered Element Oscillating Microbalance (TEOM) at the SEARCH sites, i.e. JST, YRK, BHM and CTR by Atmospheric Research Analysis (ARA, Inc.) and retrieved from the data archive. For the RS and GT sites, the PM mass concentrations were estimated from the sum of chemical components analyzed on the Hi-Vol filters and the summation method was calibrated with ARA TEOM at the JST site (slope = 1.34 ± 0.06 , intercept = $-2.46 \pm 0.59 \mu\text{g m}^{-3}$, $r^2 = 0.72$, $N = 162$, see SI, Fig. S2). The measured components include EC (Sunset Laboratory OCEC analyzer), organic mass (OC \times 1.6, Turpin and Lim, 2001), water soluble metals (measured by X-ray fluorescence method (XRF)), and ammonium sulfate (assuming sulfate and ammonium are all $(\text{NH}_4)_2\text{SO}_4$ (Zhang et al., 2010), where sulfate was calculated from sulfur measured by XRF). Further description of the analytical procedure for

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each method will be reported in subsequent publications on the chemical data (Verma et al., 2014; Fang et al., 2014).

3 Results and discussion

3.1 Automated system performance

5 Performance of the automated system was assessed by conducting tests to determine instrument response, limit of detection (LOD), precision and accuracy using both standards and ambient particles.

3.1.1 Automated system response to individual compound

9,10-phenanthraquinone (PQN) has been shown to be capable of catalyzing the oxidation of DTT (Li et al., 2009; Kumagai et al., 2002), although it is not highly water-soluble. The automated system was assessed for linearity with PQN (Fig. 4). The x axis intercept ($0.11 \text{ nmol mL}^{-1}$ in the incubation vial) represents the minimum concentration of PQN required to produce a measurable signal on the system, pure water with blank subtracted. As shown, the response of the system to PQN is highly linear with a correlation coefficient (r^2) of 0.98. At least one PQN per ambient sample batch (typically 12 samples) is used as a positive control to ensure the consistency of the system.

3.1.2 Limit of detection

The limit of detection (LOD) of the system, defined as three times the standard deviation of DI water-blanks ($N = 37$), is $0.31 \text{ nmol min}^{-1}$. Expressing the LOD in terms of the PM concentration of the sample extract ($\mu\text{g mL}^{-1}$) is not straightforward as it depends on many factors, including extraction efficiency and the relative fractions of DTT active components in ambient particles. Based on the analysis of 503 Hi-Vol samples in the present study from different sites (urban, rural and roadside), approximately $100 \mu\text{g}$ of

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PM_{2.5} mass loading on the filter, extracted in 5 mL of DI water was sufficient to have reliable results above LOD. The upper limit of the PM concentration is also constrained such that the DTT consumption remains less than 50 % of the initial concentration to ensure the pseudo-1st-order reaction of the DTT oxidation. For most of the PM samples collected, roughly 1/28th area (typical PM_{2.5} mass loading = 0.2–1 mg) of a Hi-Vol filter, extracted in 15 mL of DI water, yielded a DTT consumption rate within these limits (0.8–2.6 nmol min⁻¹). In rare cases (< 10 %) when the DTT consumption exceeds 50 %, only the initial consumption data points (at least 3) were used for the rate calculation.

3.1.3 Precision

The precision of the automated system for ambient samples was assessed by separately extracting seven different equal sections (1/28th each) of the same Hi-Vol filter in 15 mL of DI water and analyzed for DTT activity. A low standard deviation of 0.081 nmol min⁻¹ (Coefficient of Variation (CV) = 4 %) indicates sufficiently high precision of the system for ambient samples.

3.1.4 Accuracy

The system was validated for accuracy by comparing the DTT activity of both standards and ambient PM samples obtained from the automated approach with that from the same experimental protocol performed manually.

Five replicates of the PQN standard (0.21 nmol mL⁻¹ in the incubation vial) were run both on the automated system and manually. The DTT consumption rate obtained from the automated system (mean ± stdev of 0.77 ± 0.03 nmol min⁻¹, CV = 4.24 %) was very close to that from the manual operation (0.74 ± 0.03 nmol min⁻¹, CV = 3.97 %). As further validation, nine ambient PM samples were analyzed for DTT activity by both manual and automated approach. As shown in Fig. 5, an orthogonal fit yielded a slope (automated/manual) of 1.08 ± 0.12, intercept close to zero (−0.02 ± 0.03 nmol min⁻¹ m⁻³),

and correlation coefficient (r^2) of 0.92. Further, a paired t test shows no significant difference between the results obtained by two methods ($t(8) < t_{\text{critical}}$, $p = 0.05$).

These tests demonstrate the robustness of the instrument as a viable alternative of the manual DTT assay making it useful for rapid and high throughput sample analysis for large-scale studies.

3.2 Field evaluation of the automated system

The Southeastern Center for Air Pollution and Epidemiology (SCAPE) was a coordinated multi-investigator effort to characterize ambient gas/particle mixtures in southeastern US, to elucidate their sources and to assess their impacts on human health. The automated system was used to measure DTT activity on the set of samples ($N = 503$) collected from multiple sites during SCAPE. Multiple DI water blanks ($N = 37$), PQN standards ($N = 55$), in addition to field blanks ($N = 63$) collected during the sampling were analyzed along with the PM samples. This project provided an ideal opportunity for the field evaluation of the semi-automated DTT assay instrument. Table 2 summarizes the performance of the system as evaluated by stability of the results from both standards and blanks. The system remained fairly consistent throughout the analysis with reasonably small variability for both standards ($CV = 15\%$) and blanks (DI blanks: $CV = 28.1\%$; field blanks: $CV = 26.7\%$).

3.2.1 Overall method precision

The overall precision of the paired ambient sampling method utilized in this study was further assessed by comparing the DTT activity of $PM_{2.5}$ samples collected simultaneously at JST using two Hi-Vols in November 2012 and April 2013 (shown in Fig. 6). The orthogonal regression yields a slope of 1.03 ± 0.05 , with an intercept of $0.02 \pm 0.01 \text{ nmol min}^{-1} \text{ m}^{-3}$, and $r^2 = 0.96$. Considering the combined uncertainties from sample collection, pretreatment, and extraction, the good agreement between the

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two sampling systems demonstrates a high overall precision of DTT measurement for ambient samples.

3.2.2 DTT activity of ambient samples

The time series of both water-soluble volume-normalized (DTTv) and mass-normalized (DTTm) DTT activity are shown in Fig. 7a and b, respectively. Comparing the time series of DTTv (Fig. 7a) between paired sites shows that there is generally little divergence between sites, with the exception of the JST-YRK (urban-rural) pair in winter. Some of this uniformity is due to the 23 h integrated sampling time of the Hi-Vol filters, which dampens any diurnal variability in the emission sources contributing to PM oxidative potential. Figure 8 shows the distribution of water-soluble DTTv and DTTm data of ambient PM_{2.5} obtained in our study in comparison with those from other studies (Charrier and Anastasio, 2012; Verma et al., 2009b; Hu et al., 2008; Ntziachristos et al., 2007; Cho et al., 2005). Our DTTv data (Fig. 8a) are in the range reported in other studies, with exception for RS (measurements made adjacent to a high-traffic highway), which is lower in the present study. However, comparing the DTTm levels, RS DTTm are well within the typical range of other studies and thus our lower DTTv levels are most probably attributed to higher PM_{2.5} concentrations reported in other studies sampling by roadways. Our study generally shows a broader span for urban and rural sites than reported previously, which is likely due to the much larger dataset collected over a yearlong period that captured a wider range of sources and ambient conditions. Overall, these results show the utility of the automated system for providing a comprehensive assessment of the aerosol oxidative properties.

3.2.3 Seasonal and spatial variability

Seasonal and spatial variability of aerosol oxidative potential (both DTTv and DTTm) in the southeast US were assessed by Analysis of Variance (ANOVA) tests and Coefficient of Divergence (COD), respectively. The ANOVA tests were used to assess

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differences between seasons at a given site (SI, Tables S1 and S2), and the COD (Wilson et al., 2005) was calculated to assess spatial variability (see Table 3). The COD is calculated as follows:

$$\text{COD} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left[\frac{c_{ij} - c_{ik}}{c_{ij} + c_{ik}} \right]^2} \quad (3)$$

where c_{ij} and c_{ik} are the 23 h averaged DTT activity ($\text{nmol min}^{-1} \text{m}^{-3}$) measured at site j and k , respectively, and N is the sample size. COD ranges from 0 to 1, with values close to 0 representing a homogenous distribution and those near 1 indicating heterogeneity.

Based on ANOVA tests, there was high heterogeneity across seasons for DTTv at JST ($p = 0.01$, see SI, Table S1) with the highest DTTv in winter (December (winter)/June (summer) = 1.51), while there was no significant seasonal variation observed at YRK, GT and the RS site ($p > 0.01$). In comparison to DTTv, there are greater seasonal variations in DTTm, for example, average DTTm at most sites showed much higher levels in winter than summer and fall (winter/summer = 1.4, 1.2, and 2.2 for YRK, GT, and JST, respectively). ANOVA tests also validated the pronounced seasonal differences for DTTv and DTTm at JST and DTTm at other sites ($p < 0.01$, see SI, Tables S1 and S2). The higher seasonal differences in DTTm may suggest that the specific chemical components that contribute to the oxidative potential of particles varies between seasons and originate from different sources.

Relatively low levels of the CODs (< 0.25) (Table 3) found for both DTTv and DTTm at paired-sites indicate spatial homogeneity of water-soluble aerosol oxidative potential in the region, suggesting dominant DTT activity sources are regional in nature. Note that JST/RS and GT/RS pairs, in both fall seasons, show slightly lower CODs (more uniformity) in DTTv than in DTTm (COD for DTTv = 0.13 and 0.18 compared to COD for DTTm = 0.23 and 0.31 for JST/RS and GT/RS, respectively). This indicates that although there may be unique local sources at the RS site, for example primary vehicle

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emissions and re-suspended dust, their overall contribution was not substantial compared to the regional DTT signal and so was not clearly resolved.

3.2.4 Oxidative potential and PM_{2.5} mass

Figure 9 shows the correlation between DTT activity (DTTv) and PM_{2.5} mass concentrations for all the sites and seasons. DTTv correlates with PM concentration in various degrees (Pearson's $r = 0.49\text{--}0.88$), but generally the correlations are high for most sites. For JST, the representative urban site, Pearson's r is particularly high ($r = 0.76\text{--}0.82$) in all seasons. Lowest DTTv – PM_{2.5} mass correlations were at the road-side site, probably due to the influence of unique RS sources that contributed to mass but not significantly to DTT activity (average PM_{2.5} concentration are 8.7 and 8.2 $\mu\text{g m}^{-3}$ at JST compared to 10.4 and 9.5 $\mu\text{g m}^{-3}$ at RS in fall and winter, respectively). It is important to note that despite the significant correlation, the slope for DTT activity vs. PM_{2.5} mass varies among different sites and seasons. Overall, we attribute the variation in degree of association between DTT activity and PM_{2.5} mass to the varying PM chemical composition. This is also supported by the spatial and seasonal variability in intrinsic DTT activity (per mass) as discussed above. This analysis suggests that DTT activity in the southeast is likely, to a significant extent, related to regional sources and not dominated by a single source or a limited number of species. Further investigation on identifying the specific sources and aerosol chemical components linked to PM oxidative potential will be discussed in subsequent publications (Verma et al., 2014).

Studies have shown a correlation between health end-points and PM_{2.5} mass (Gholampour et al., 2014; Tong et al., 2012; Peter and Steffen, 2010). The overall correlation between water-soluble DTT activity and PM_{2.5} mass concentration observed in this study may help explain, at least in part, some of these associations. However the varying degree of correlation between DTT activity and PM_{2.5} mass at different sites and seasons suggests that there might be additional advantages of including PM oxidative potential in health studies, rather than relying on PM mass alone. More work is required to identify specific compounds that are most sensitive in the DTT probe

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and test how they may contribute to the observed ambient DTT activity. Application of the DTT probe and other acellular and cellular assays in different regions that have a different mix of emission sources is also needed to better understand the possible links between aerosol oxidative potential and health endpoints. The automated DTT assay analytical instrument described here would facilitate these types of future studies. Finally, although the analytical system described here can provide new insight on aerosol oxidative properties from large data sets, it does not solve limitations associated with filter-based particle collection approaches, which entail artifacts due to losses of semi-volatile DTT-active species during sampling and handling procedures. Adapting the DTT assay to an online system could limit sampling artifacts and provide new insights into DTT sources and atmospheric processing that more highly time-resolved data can provide.

4 Conclusions

An automated analytical system for quantifying the oxidative potential of aerosol liquid extracts using the DTT assay was developed. The system follows the analytical approach developed by Cho et al. (2005) and is capable of one DTT activity measurement per hour. The system response was assessed by 9,10-phenanthraquinone (PQN), which was used as a positive control when running a series of ambient samples. The method LOD was $0.31 \text{ nmol min}^{-1}$. Analytical precision based on both PQN ($CV = 15\%$) and ambient samples ($CV = 4\%$) was high. The instrument was further validated for accuracy by comparing with the manual procedure using ambient PM samples ($r^2 = 0.92$, slope = 1.08 ± 0.12). The suitability of the system for large-scale application was assessed by analyzing more than 500 filters collected in the southeastern US as part of SCAPE, the joint Emory/Georgia Tech Clean Air Research Center. The data shows that water-soluble $\text{PM}_{2.5}$ DTT activity on a per volume of air basis was spatially uniform and generally correlated with $\text{PM}_{2.5}$ mass ($r = 0.49$ to 0.88), indicating regional sources for aerosol oxidative potential. However, the higher seasonal

heterogeneity in the intrinsic water-soluble DTT activity (per PM mass basis) may indicate that the dominant regional sources change with season. More in-depth analysis of the extensive data set generated with the instrument will be forthcoming. Finally, it is noted that the method can be altered to run smaller sample volumes, for situations involving samples of lower mass loadings. It has also been modified for ROS analysis using other assays (e.g., ascorbate depletion assay). The automated system presents a useful new tool for rapid and high throughput measurement of the DTT activity of ambient particle extracts. Its application can facilitate routine use of PM oxidative potential in toxicological, panel exposures, and epidemiological studies.

The Supplement related to this article is available online at doi:10.5194/amtd-7-7245-2014-supplement.

Acknowledgements. We wish to thank the Southeastern Aerosol Research and Characterization (SEARCH) personnel for their many contributions supporting the field deployments. We also thank R. Erik Weber, Janessa Riana Rowland and Madhusudan Kamat for assistance in lab work. This research was made possible by US EPA grant R834799. The contents are solely the responsibility of the grantee and do not necessarily represent the official views of the US EPA. Further, US EPA does not endorse the purchase of any commercial products or services mentioned in the work.

References

- Alfadda, A. A. and Sallam, R. M.: Reactive oxygen species in health and disease, *J. Biomed. Biotechnol.*, 2012, 936486, doi:10.1155/2012/936486, 2012.
- Antonini, J. M., Clarke, R. W., Krishna Murthy, G. G., Sreekanthan, P., Jenkins, N., Eagar, T. W., and Brain, J. D.: Freshly generated stainless steel welding fume induces greater lung inflammation in rats as compared to aged fume, *Toxicol. Lett.*, 98, 77–86, 1998.

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- Aust, A. E., Ball, J. C., Hu, A. A., Lighty, J. S., Smith, K. R., Straccia, A. M., Veranth, J. M., and Young, W. C.: Particle characteristics responsible for effects on human lung epithelial cells, *Res. Rep. Health Eff. Inst.*, 110, 1–65, 2002.
- Bonvallot, V., Baeza-Squiban, A., Baulig, A., Brulant, S., Boland, S., Muzeau, F., Barouki, R., and Marano, F.: Organic compounds from diesel exhaust particles elicit a proinflammatory response in human airway epithelial cells and induce cytochrome p450 1A1 expression, *American Journal of Respiratory Cell and Molecular Biology*, 25, 515–521, 2001.
- Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: evidence for the importance of soluble transition metals, *Atmos. Chem. Phys.*, 12, 9321–9333, doi:10.5194/acp-12-9321-2012, 2012.
- Cho, A. K., Sioutas, C., Miguel, A. H., Kumagai, Y., Schmitz, D. A., Singh, M., Eiguren-Fernandez, A., and Froines, J. R.: Redox activity of airborne particulate matter at different sites in the Los Angeles Basin, *Environ. Res.*, 99, 40–47, 2005.
- Chung, M. Y., Lazaro, R. A., Lim, D., Jackson, J., Lyon, J., Rendulic, D., and Hasson, A. S.: Aerosol-borne quinones and reactive oxygen species generation by particulate matter extracts, *Environ. Sci. Technol.*, 40, 4880–4886, 2006.
- Delfino, R. J., Staimer, N., Tjoa, T., Gillen, D. L., Schauer, J. J., and Shafer, M. M.: Airway inflammation and oxidative potential of air pollutant particles in a pediatric asthma panel, *J. Expos. Sci. Environ. Epidemiol.*, 23, 466–473, 2013.
- Fang, T., Verma, V., Peltier, R. E., Guo, H. Y., King, L. E., Edgerton, E. S., and Weber, R. J.: Distribution of ambient atmospheric water-soluble metals in the southeastern United States and insights into their complexation states, in preparation, 2014.
- Frampton, M. W., Ghio, A. J., Samet, J. M., Carson, J. L., Carter, J. D., and Devlin, R. B.: Effects of aqueous extracts of PM₁₀ filters from the Utah Valley on human airway epithelial cells, *Am. J. Physiol.-Lung. C.*, 277, L960–L967, 1999.
- Gholampour, A., Nabizadeh, R., Naseri, S., Yunesian, M., Taghipour, H., Rastkari, N., Nazmara, S., Faridi, S., and Mahvi, A. H.: Exposure and health impacts of outdoor particulate matter in two urban and industrialized area of Tabriz, Iran, *Journal of Environmental Health Science and Engineering*, 12, 27, doi:10.1186/2052-336X-12-27, 2014.
- Gurgueira, S. A., Lawrence, J., Coull, B., Murthy, G. G., and Gonzalez-Flecha, B.: Rapid increases in the steady-state concentration of reactive oxygen species in the lungs and heart after particulate air pollution inhalation, *Environ. Health Persp.*, 110, 749–755, 2002.

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- Hansen, D. A., Edgerton, E. S., Hartsell, B. E., Jansen, J. J., Kandasamy, N., Hidy, G. M., and Blanchard, C. L.: The Southeastern Aerosol Research and Characterization Study: Part 1 – overview, *J. Air Waste Manage.*, 53, 1460–1471, 2003.
- Harkema, J. R., Keeler, G., Wagner, J., Morishita, M., Timm, E., Hotchkiss, J., Marsik, F., Dvonch, T., Kaminski, N., and Barr, E.: Effects of concentrated ambient particles on normal and hypersecretory airways in rats, *Res. Rep. Health Eff. Inst.*, 120, 1–68, 2004.
- Hiura, T. S., Kaszubowski, M. P., Li, N., and Nel, A. E.: Chemicals in diesel exhaust particles generate reactive oxygen radicals and induce apoptosis in macrophages, *J. Immunol.*, 163, 5582–5591, 1999.
- Hu, S., Polidori, A., Arhami, M., Shafer, M. M., Schauer, J. J., Cho, A., and Sioutas, C.: Redox activity and chemical speciation of size fractioned PM in the communities of the Los Angeles-Long Beach harbor, *Atmos. Chem. Phys.*, 8, 6439–6451, doi:10.5194/acp-8-6439-2008, 2008.
- Jung, H., Guo, B., Anastasio, C., and Kennedy, I. M.: Quantitative measurements of the generation of hydroxyl radicals by soot particles in a surrogate lung fluid, *Atmos. Environ.*, 40, 1043–1052, 2006.
- Koehler, K. A., Shapiro, J., Sameenoi, Y., Henry, C., and Volckens, J.: Laboratory evaluation of a microfluidic electrochemical sensor for aerosol oxidative load, *Aerosol Sci. Tech.*, 48, 489–497, 2014.
- Kubátová, A., Dronen, L. C., Picklo, M. J., and Hawthorne, S. B.: Midpolarity and nonpolar wood smoke particulate matter fractions deplete glutathione in RAW 264.7 macrophages, *Chem. Res. Toxicol.*, 19, 255–261, 2006.
- Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T., and Shimojo, N.: Oxidation of proximal protein sulfhydryls by phenanthraquinone, a component of diesel exhaust particles, *Chem. Res. Toxicol.*, 15, 483–489, 2002.
- Li, N., Sioutas, C., Cho, A. K., Schmitz, D., Misra, C., Sempf, J., Wang, M., Oberley, T., Froines, J., and Nel, A.: Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage, *Environ. Health Persp.*, 111, 455–460, 2003.
- Li, Q. F., Wyatt, A., and Kamens, R. M.: Oxidant generation and toxicity enhancement of aged-diesel exhaust, *Atmos. Environ.*, 43, 1037–1042, 2009.
- Lin, P. and Yu, J. Z.: Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols, *Environ. Sci. Technol.*, 45, 10362–10368, 2011.

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- Mudway, I. S., Fuller, G., Green, D., Dunster, C., and Kelly, F. J.: Report: Quantifying the London Specific Component of PM₁₀ Oxidative Activity, University of London, Defra, UK, 2011.
- Nel, A.: Air pollution-related illness: effects of particles, *Science*, 308, 804–806, 2005.
- Norris, G., YoungPong, S. N., Koenig, J. Q., Larson, T. V., Sheppard, L., and Stout, J. W.: An association between fine particles and asthma emergency department visits for children in Seattle, *Environ. Health Persp.*, 107, 489–493, 1999.
- Ntziachristos, L., Froines, J. R., Cho, A. K., and Sioutas, C.: Relationship between redox activity and chemical speciation of size-fractionated particulate matter, *Particle and Fibre Toxicology*, 4, 5, doi:10.1186/1743-8977-4-5, 2007.
- Peter, M. and Steffen, L.: Oxidative damage to DNA and Lipids as biomarkers of exposure to air pollution, *Environ. Health Persp.*, 118, 1126–1136, 2010.
- Pope, C. A., Burnett, R. T., Thurston, G. D., Thun, M. J., Calle, E. E., Krewski, D., and Godleski, J. J.: Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease, *Circulation*, 109, 71–77, 2004.
- Sameenoi, Y., Koehler, K., Shapiro, J., Boonsong, K., Sun, Y., Collett, J., Volckens, J., and Henry, C. S.: Microfluidic electrochemical sensor for on-line monitoring of aerosol oxidative activity, *J. Am. Chem. Soc.*, 134, 10562–10568, 2012a.
- Sameenoi, Y., Panymeesamer, P., Supalakorn, N., Koehler, K., Chailapakul, O., Henry, C. S., and Volckens, J.: Microfluidic paper-based analytical device for aerosol oxidative activity, *Environ. Sci. Technol.*, 47, 932–940, 2012b.
- Samet, J. M., Dominici, F., Curriero, F. C., Coursac, I., and Zeger, S. L.: Fine particulate air pollution and mortality in 20 US cities, 1987–1994, *New Engl. J. Med.*, 343, 1742–1749, 2000.
- Schaumann, F., Borm, P. J. A., Herbrich, A., Knoch, J., Pitz, M., Schins, R. P. F., Luettig, B., Hohlfeld, J. M., Heinrich, J., and Krug, N.: Metal-rich ambientparticles (particulate matter_{2.5}) cause airway inflammation in healthy subjects, *American Journal of Respiratory and Critical Care Medicine*, 170, 898–903, 2004.
- Steenhof, M., Gosens, I., Strak, M., Godri, K. J., Hoek, G., Cassee, F. R., Mudway, I. S., Kelly, F. J., Harrison, R. M., Lebret, E., Brunekreef, B., Janssen, N. A. H., and Pieters, R. H. H.: In vitro toxicity of particulate matter (PM) collected at different sites in the Netherlands is associated with PM composition, size fraction and oxidative potential-the RAPTES project, *Particle and Fibre Toxicology*, 8, 26, doi:10.1186/1743-8977-8-26, 2011.

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- Sun, Q. H., Hong, X. R., and Wold, L. E.: Cardiovascular effects of ambient particulate air pollution exposure, *Circulation*, 121, 2755–2765, 2010.
- Tong, H., Rappold, A. G., Diaz-Sanchez, D., Steck, S. E., Berntsen, J., Cascio, W. E., Devlin, R. B., and Samet, J. M.: Omega-3 fatty acid supplementation appears to attenuate particulate air pollution-induced cardiac effects and lipid changes in healthy middle-aged adults, *Environ. Health Persp.*, 120, 952–957, 2012.
- Turpin, B. J. and Lim, H.-J.: Species contributions to PM_{2.5} mass concentrations: revisiting common assumptions for estimating organic mass, *Aerosol Sci. Tech.*, 35, 602–610, 2001.
- Venkatachari, P., Hopke, P. K., Grover, B. D., and Eatough, D. J.: Measurement of particle-bound reactive oxygen species in rubidoux aerosols, *J. Atmos. Chem.*, 50, 49–58, 2005.
- Verma, V., Ning, Z., Cho, A. K., Schauer, J. J., Shafer, M. M., and Sioutas, C.: Redox activity of urban quasi-ultrafine particles from primary and secondary sources, *Atmos. Environ.*, 43, 6360–6368, 2009a.
- Verma, V., Polidori, A., Schauer, J. J., Shafer, M. M., Cassee, F. R., and Sioutas, C.: Physicochemical and toxicological profiles of particulate matter in Los Angeles during the October 2007 southern California wildfires, *Environ. Sci. Technol.*, 43, 954–960, 2009b.
- Verma, V., Rico-Martinez, R., Kotra, N., King, L. E., Liu, J., Snell, T. W., and Weber, R. J.: Contribution of water-soluble and insoluble components and their hydrophobic/hydrophilic subfractions to the reactive oxygen species-generating potential of fine ambient aerosols, *Environ. Sci. Technol.*, 46, 11384–11392, 2012.
- Verma, V., Fang, T., Guo, H. Y., King, L. E., Edgerton, E. S., and Weber, R. J.: ROS generation potential of water-soluble PM_{2.5} in southeastern United States – spatiotemporal trends and source apportionment using Positive Matrix Factorization, in preparation, 2014.
- Wilson, J. G., Kingham, S., Pearce, J., and Sturman, A. P.: A review of intraurban variations in particulate air pollution: Implications for epidemiological research, *Atmos. Environ.*, 39, 6444–6462, 2005.
- Xia, T., Kovoichich, M., Brant, J., Hotze, M., Sempff, J., Oberley, T., Sioutas, C., Yeh, J. I., Wiesner, M. R., and Nel, A. E.: Comparison of the abilities of ambient and manufactured nanoparticles to induce cellular toxicity according to an oxidative stress paradigm, *Nano Lett.*, 6, 1794–1807, 2006.
- Zanobetti, A., Coull, B. A., Gryparis, A., Kloog, I., Sparrow, D., Vokonas, P. S., Wright, R. O., Gold, D. R., and Schwartz, J.: Associations between arrhythmia episodes and temporally and

spatially resolved black carbon and particulate matter in elderly patients, *Occup. Environ. Med.*, 71, 201–207, 2014.

Zhang, X., Hecobian, A., Zheng, M., Frank, N. H., and Weber, R. J.: Biomass burning impact on PM_{2.5} over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis, *Atmos. Chem. Phys.*, 10, 6839–6853, doi:10.5194/acp-10-6839-2010, 2010.

Zomer, B., Collé, L., Jedyńska, A., Pasterkamp, G., Kooter, I., and Bloemen, H.: Chemiluminescent reductive acridinium triggering (CRAT) – mechanism and applications, *Anal. Bioanal. Chem.*, 401, 2945–2954, 2011.

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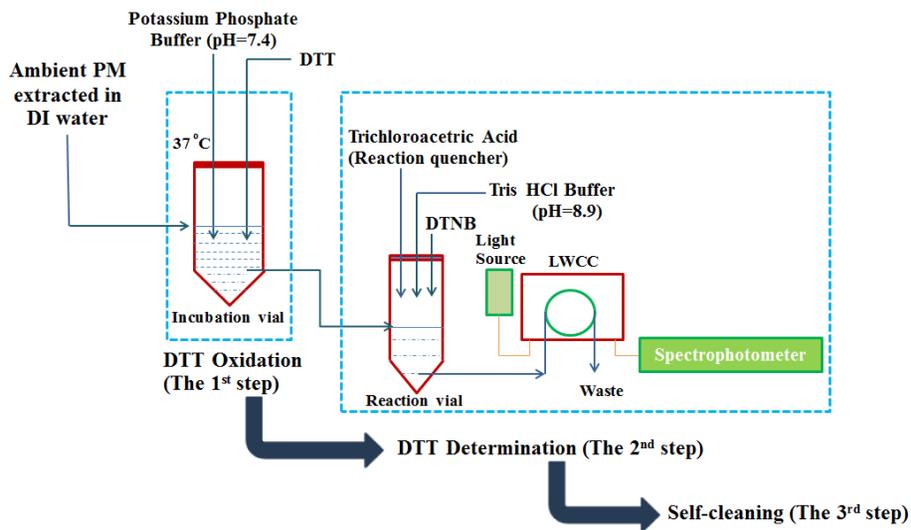


Figure 1. Automated system protocol.

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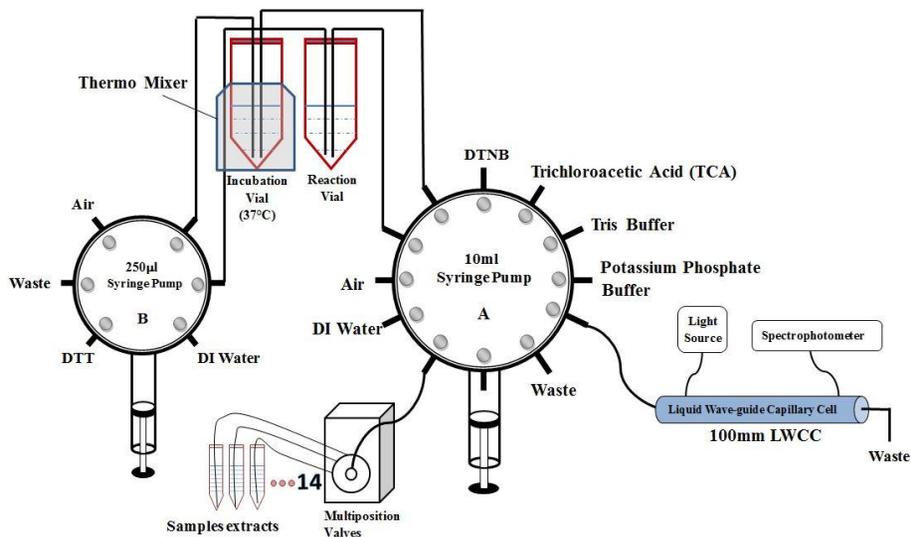


Figure 2. Automated system setup.

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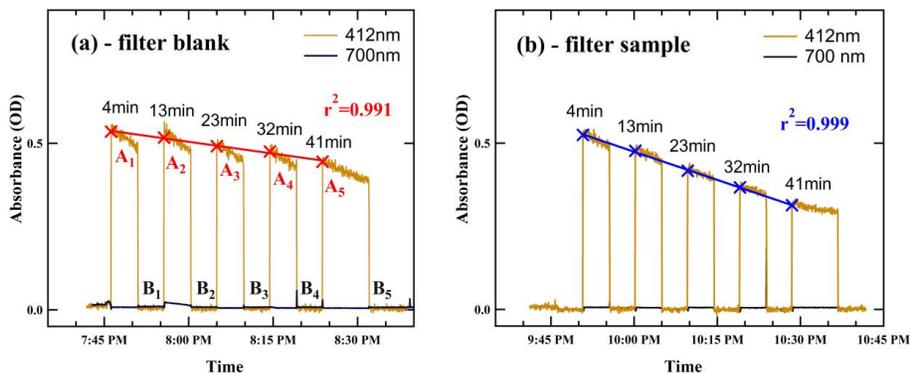


Figure 3. Example of an absorbance plot for a filter blank (a) and an ambient aerosol sample (b).

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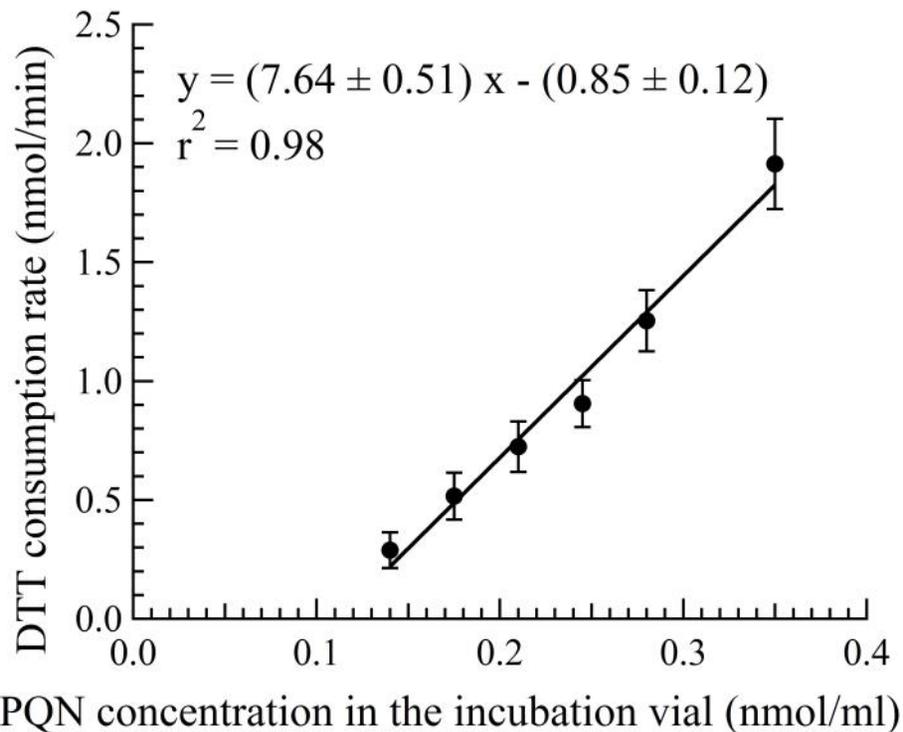


Figure 4. Blank corrected DTT consumption rate as a function of PQN (9,10-phenanthraquinone) used as a positive control. Each error bar represents the standard deviation of three independent DTT measurements on each concentration.

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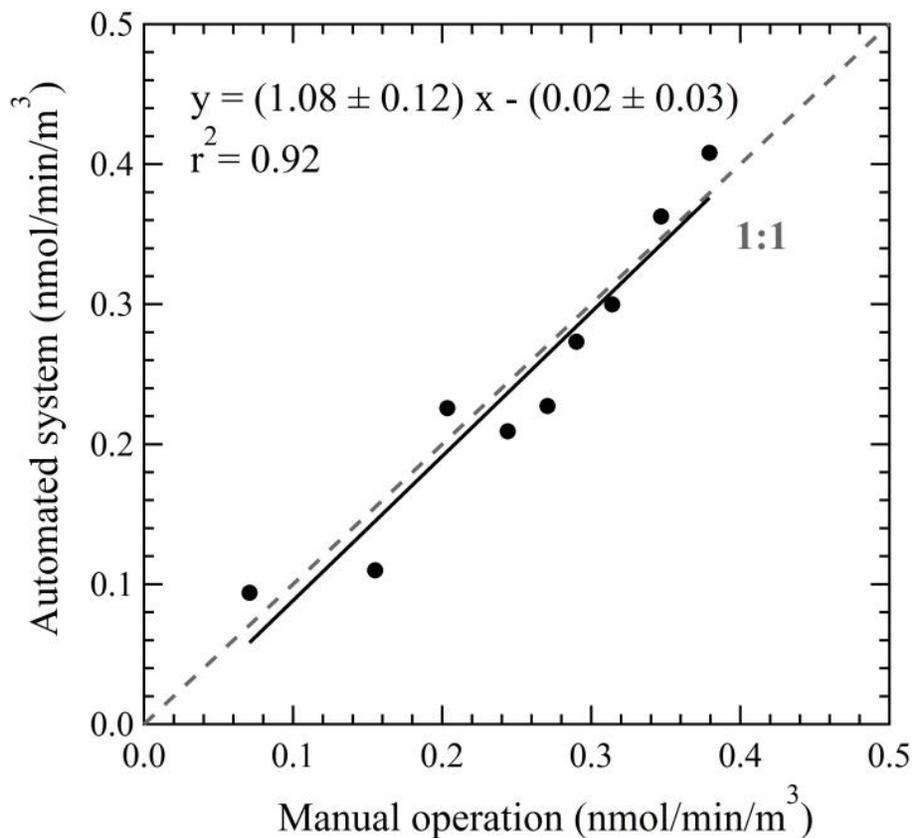


Figure 5. Comparison of the automated system with manual operation using ambient aerosol extracts (PM_{2.5} samples collected from JST site, Atlanta, in December 2012) (Regression analysis was done by orthogonal regression. The dotted line is 1 : 1).

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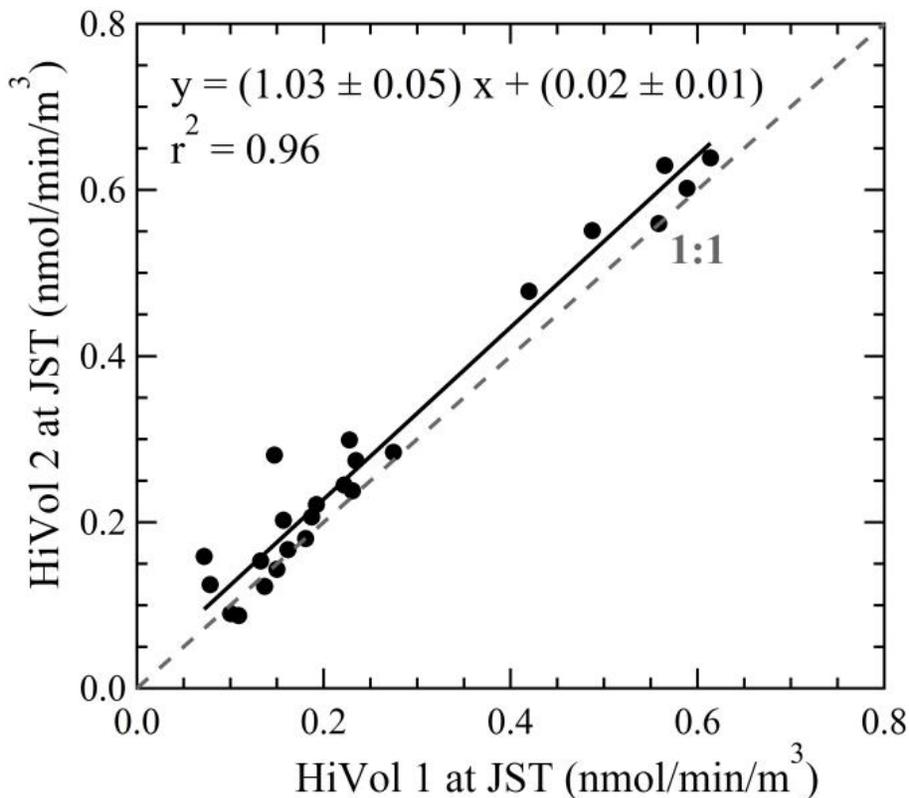


Figure 6. Overall method precision of the automated system assessed by PM_{2.5} filter samples ($N = 24$) collected simultaneously using two Hi-Vol samplers deployed side-by-side at JST during November 2012 and April 2013 (Regression analysis was done by orthogonal regression. The dotted line is 1 : 1).

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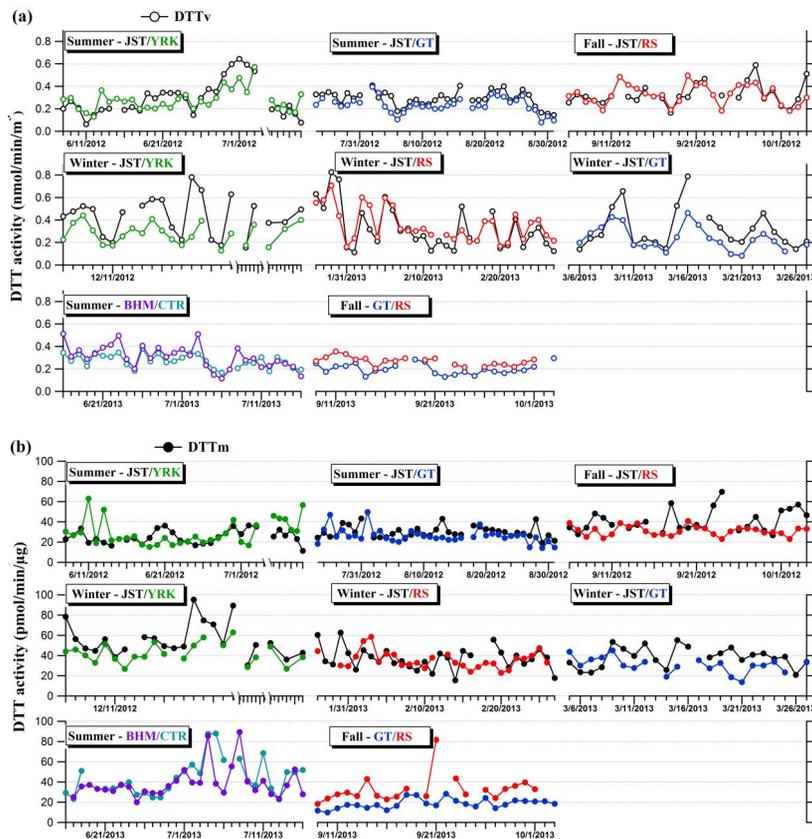


Figure 7. Water-soluble DTT activity of the ambient particles collected in paired sampling sites. The plots show **(a)** volume-normalized (DTTv) and **(b)** mass-normalized (DTTm) DTT activity at JST (urban, black) paired with YRK (rural, green), RS (roadside, red), GT (near-road, blue). Also included is the CTR (rural, cyan) – BHM (urban, purple) pair, and the GT-RS pair.

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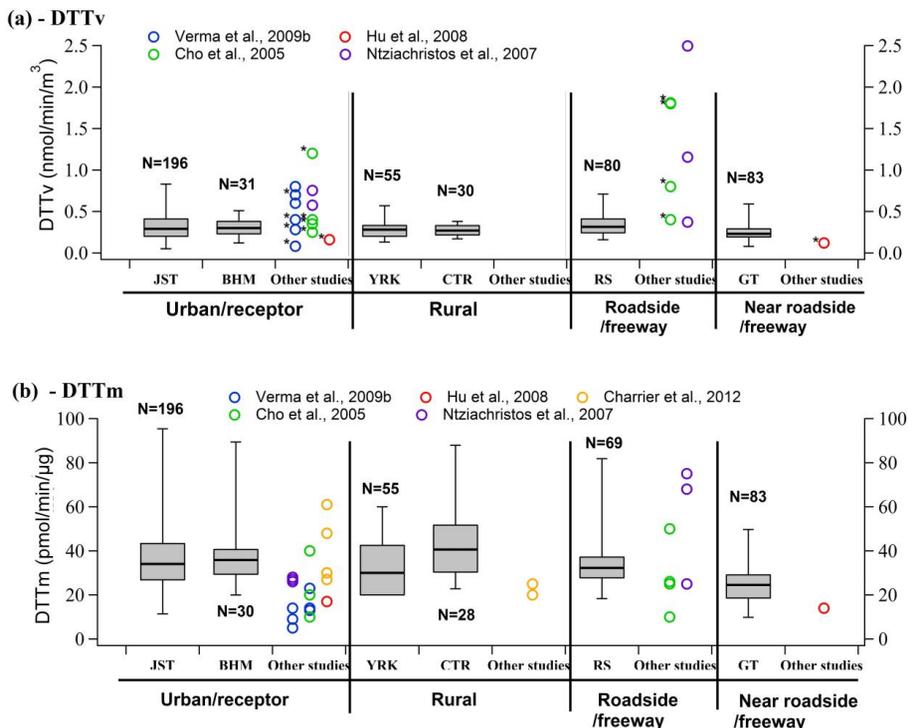



Figure 8. Distribution of water-soluble volume-normalized **(a)** and mass-normalized **(b)** DTT activity (oxidative potential) of ambient PM_{2.5} in our study compared with other studies. Data from this study are expressed as median, maximal, minimal, percentile 25 and 75. Roadside/freeway – sampling sites are located adjacent to road/highway; Near roadside/freeway – sampling sites are further away but less than 1 km from road/freeway. * – numbers not presented in the paper, thus estimated from graphs.

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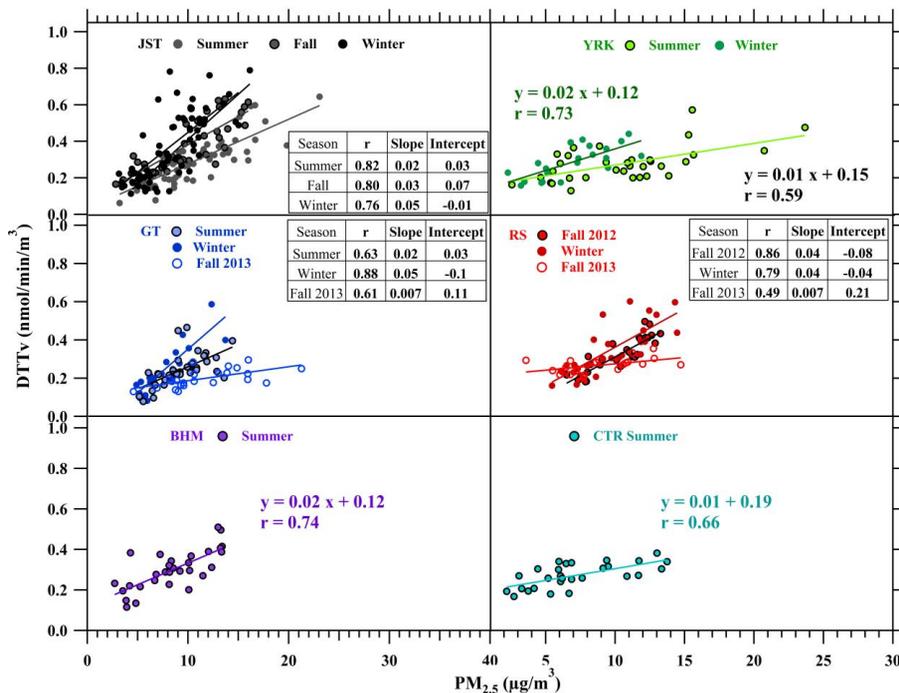


Figure 9. Correlation (Pearson's r) between water-soluble DTT activity (DTTv) and PM_{2.5} mass concentration at JST (urban), YRK (rural), RS (roadside), GT (near-road), CTR (rural), BHM (urban) sites.

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