Oxidative potential of particulate matter collected at sites with different source characteristics

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HIGHLIGHTS

- The oxidative potential (OP) of PM was highly elevated at an underground station.
- Outdoors, PM along a highway with continuous traffic showed the highest activity.
- Contrasts in OP between sites depended on the specific OP assay used.
- The OP methods studied also differed in respect to correlation with PM composition.
- Different OP assays can provide complementary data about the oxidative properties of PM.

ABSTRACT

Background: The oxidative potential (OP) of particulate matter (PM) has been proposed as a more health relevant metric than PM mass. Different assays exist for measuring OP and little is known about how the different assays compare.
Aim: To assess the OP of PM collected at different site types and to evaluate differences between locations, size fractions and correlation with PM mass and PM composition for different measurement methods for OP.
Methods: $PM_{2.5}$ and PM_{10} was sampled at 5 sites: an underground station, a farm, 2 traffic sites and an urban background site. Three a-cellular assays; dithiothreitol (OP^{DTT}), electron spin resonance (OP^{ESR}) and ascorbate depletion (OP^{AA}) were used to characterize the OP of PM.
Results: The highest OP was observed at the underground, where OP of PM_{10} was 30 (OP^{DTT}) to >600 (OP^{ESR}) times higher compared to the urban background when expressed as OP/m^3 and 2–40 times when expressed as $OP/\mu g$. For the outdoor sites, samples from the farm showed significantly lower OP^{ESR} and OP^{AA}, whereas samples from the continuous traffic site showed the highest OP for all assays. Contrasts in OP between sites were generally larger than for PM mass and were lower for OP^{DTT} compared to OP^{ESR} and OP^{AA}. Furthermore, $OP^{DTT}/\mu g$ was significantly higher in $PM_{2.5}$ compared to PM_{10}, whereas the reverse was the case for OP^{ESR}. OP^{ESR} and OP^{AA} were highly correlated with traffic-related PM components (i.e. EC, Fe, Cu, PAHs), whereas OP^{DTT} showed the highest correlation with PM mass and OC.

Conclusions: Contrasts in OP between sites, differences in size fractions and correlation with PM composition depended on the specific OP assay used, with OP^{ESR} and OP^{AA} showing the most similar results. This suggests that either OP^{ESR} or OP^{AA} and OP^{DTT} can complement each other in providing information regarding the oxidative properties of PM, which can subsequently be used to study its health effects.

1. Introduction

Numerous studies have shown health effects related to exposure to ambient particulate matter (PM) (Brunekreef and Holgate, 2002; Pope and Dockery, 2006). In most studies effects were linked to PM_{10} or $PM_{2.5}$ mass concentrations. However, PM is a heterogeneous mixture varying in physical properties and chemical composition depending on meteorological conditions and emission sources (WHO, 2006). Current knowledge does not allow precise quantification of the health effects of individual PM components or of PM emissions from different sources (Brunekreef, 2010; WHO, 2007), although various PM characteristics, such as surface area of particles, transition metal content, surface absorbed organics components, and biological components have been proposed.

Oxidative stress has been suggested as an important underlying mechanism of action by which exposure to PM may lead to adverse health effects (Nel, 2005). Oxidative stress results when the generation of reactive oxygen species (ROS), or free radicals, exceeds the available antioxidant defenses.

The oxidative potential (OP), defined as a measure of the capacity of PM to oxidize target molecules, has been proposed as a metric that is more closely related to biological responses to PM exposures and thus could be more informative than PM mass alone (Borm et al., 2007). Oxidative potential is an attractive measure because it integrates various biologically relevant properties, including size, surface and chemical composition. Several methods for measuring OP have been developed, but no consensus has been reached yet as to which assay is most appropriate (Ayres et al., 2008). The various assays used to assess OP, each with different sensitivities to the ROS generating compounds, include Electron spin resonance (ESR) with 5,5-dimethylpyrroline-N-oxide (DMPO) as a spin trap which measures the ability of PM to induce hydroxyl radicals ($•OH$) in the presence of H_2O_2 (Shi et al., 2003a,b), the ability of PM to deplete antioxidants such as ascorbic acid (AA) and glutathione (GSH) (Mudway et al., 2004), and the consumption of dithiothreitol (DTT) which is based on the ability of redox active compounds to transfer electrons from DTT to oxygen (Cho et al., 2005). In this paper, these methods will be referred to as OP^{ESR}, OP^{DTT}, and OP^{AA} respectively. In addition, fluorescent-based probes have been used to quantify PM-related ROS. The most common used probe is 2,7-dichlorofluorescein (DCFH) (Landreman et al., 2008).

OP^{ESR} and OP^{AA} have been shown to be most sensitive to transition metals. For OP^{DTT} typically compounds which react are organic species (e.g polycyclic aromatic hydrocarbons (PAHs) and quinones), but studies have also shown that high concentrations of transition metal ions can oxidize DTT (Charrier and Anastasio, 2012).

Only a few field studies have compared OP from different locations, with different contributing sources (Boogaard et al., 2012; Hu et al., 2008; Shi et al., 2003a). These studies have generally focused on a specific method to measure OP. Shi et al. (2003a) found that PM samples from an industrial city (Hettsted, Germany) showed 4.5 times higher OP^{ESR} than its rural neighboring town Zerbst, despite similar PM_{10} mass levels in the air. In the Netherlands, Boogaard et al. (2012) found that the OP^{ESR} of PM_{10} from major streets was 3.6 times higher than simultaneously measured PM_{10} at urban background locations, and 6.5 times higher compared to PM_{10} from suburban background locations. Strak et al. (2012) found only about 50% higher OP^{AA} of PM collected at two traffic sites compared to an urban background site and no difference between the traffic sites and a farm, whereas earlier samples collected at 7 outdoor samples in the screening phase of that study

showed markedly higher OP^{DTT} at two traffic sites compared to the other outdoor sites (Steenhof et al., 2011). Conversely, Hu et al. (2008) found rather low variability in OP^{DTT} across six different sites in the Los Angeles area. Along with differences in spatial variation, findings from studies using different methods to measure OP also differ with regard to the most active PM fraction and relation to PM composition.

In the framework of the OPERA project (Oxidative Potential Exposure and Risk Assessment) we aim to evaluate to value of OP as a health relevant PM metric for air quality assessment and regulation. Given the limited comparative information on the different methods to measure OP the aim the current study is to assess the OP of PM collected at different sites types and to evaluate differences between locations, size fractions and correlation with PM mass and PM composition for different measurement methods for OP.

We therefore assessed the OP from $PM_{2.5}$ and PM_{10} samples collected from 5 different sites in the Netherlands, using three different measurement methods for OP (OP^{ESR}, OP^{DTT}, OP^{AA}). We evaluated the correlation among the different measurement methods for OP, and compare the methods for different aspects (i.e. differences between locations, size fractions and correlation with PM mass and PM composition).

2. Methods

2.1. Study design

Within the framework of the RAPTES study (Risks of Airborne Particles-a Toxicological Epidemiological hybrid Study) $PM_{2.5}$ and PM_{10} was sampled at 5 locations in the Netherlands, with different source characteristics. These locations were: an underground train station, an animal farm, a continuous traffic site (located at the exit of a tunnel of a motorway with approximately 45,000 vehicles per day) a stop&go traffic site (a major inner-city intersection with approximately 34,000 vehicles per day), and an urban background site (Strak et al., 2011). Daytime 5-hour sampling was conducted, in the period March until October 2009. On each sampling day (total 30), one site was visited and each site was visited at least 5 times.

Three a-cellular assays; dithiothreitol (OP^{DTT}), electron spin resonance (OP^{ESR}) of hydroxyl radical generation, and ascorbic acid depletion (OP^{AA}) to characterize the OP of PM were selected, based on the results of a preceeding intercomparison study (Yang et al., 2014). Composition of PM was measured in detail, including metals, EC/OC and PAHs.

2.2. Concentration measurements

Details about the air pollution measurements are described elsewhere (Strak et al., 2011, 2012). Briefly, $PM_{2.5}$ and PM_{10} samples were collected using Harvard Impactors (HI) (Air Diagnostics and Engineering Inc., Naples, ME, USA). The absorbance of both the HI $PM_{2.5}$ and PM_{10} filters was measured using a smoke stain reflectometer (model M43D; Diffusion Systems, London, UK) and the endotoxin content of the HI PM_{10} samples was measured using a Limulus Amoebocyte Lisate (LAL) assay (Lonza, Basel, Switzerland). Particle number concentrations (PNC) were measured with a real-time condensation particle counter (CPC model 3022A; TSI, St Paul, MN). With a high volume sampler (model TE-6070 V equipped with TE-231 High Volume Cascade Impactor, Tisch Environmental, Cleves, OH) $PM_{2.5–10}$ and $PM_{2.5}$ samples were collected. These samples were analyzed for EC and OC using a Sunset Laboratory Thermal-Optical Carbon Aerosol Analyser, for metals

(e.g. Fe, Cu) using inductively coupled plasma mass spectrometry (ICP-MS), for PAHs using Gas chromatography–mass spectrometry (GC–MS), as well as further inorganic (nitrate, sulfate) components using a Dionex ICS-2000 ion chromatograph. (Strak et al., 2011). In addition, gaseous pollutant concentrations (O_3, NO, NO_2, NO_x) were measured using real-time monitors (U.V. Photometric O_3 Analyzer model 49; Thermo Environmental Instruments, Franklin, MA, and Chemiluminescence $NO/NO_2/NO_x$ analyser model 200E, Teledyne API, San Diego, CA).

2.3. Sample preparation

2.3.1. Extraction procedures

PM_{10} and $PM_{2.5}$ Teflon filters from the Harvard Impactors were extracted with methanol (HPLC grade, Biosolve Bv, Valkenswaard, Netherlands). Filters were immersed in 2–3 ml of methanol in a petri dish and sonicated (Branson 5510 Ultrasonic cleaner, 40 kHz) for 20–30 s. Filter extracts were then transferred to a rounded glass flask and reduced in volume using the evaporator set (RV 10 Basic Rotary Evaporators, IKA Works, VWR, USA) at 30 °C until about 1 ml was left, transferred to Eppendorf vials and dried overnight at 30 °C under a constant flow of nitrogen. Dry extracts were stored at −20 °C until OP analysis.

In the RAPTES project, all $PM_{2.5}$ and PM_{10} sampling was conducted in duplicate. For $PM_{2.5}$, duplicate filters with PM loadings less than 80 µg (16 sampling days) were extracted together. Filters from the remaining 14 sampling days were extracted and analyzed individually, resulting in 14 field duplicates for OP measurements. For PM_{10}, no duplicate filters were available, as these had already been used for endotoxin measurements. Seven field blanks were extracted.

2.3.2. Sample concentrations

All extracts were re-suspended with traceselect ultrapure water (Sigma, Zwijndrecht, Netherlands) to a fixed concentration of 500 µg/ml. Field blanks were re-suspended in 200 µl, based on the average PM loading of the outdoor samples (i.e. approximately 100 µg). 25 µl of the suspension was taken out for OP^{DTT} analysis and the remainder was diluted 4 times, to a concentration of 125 µg/ml. Next, 100 µl of this solution was sent to the Institute of Energy and Environmental Technology (IUTA) in Duisburg, Germany, where OP^{ESR} analysis was performed, and 65 µl was diluted another 10 times (to 12.5 µg/ml) for OP^{AA} analysis.

2.4. OP analyses

2.4.1. DTT

The DTT assays measures the presence of reactive oxygen species (ROS) via formation of DTT disulfide due to transfer electrons from DTT to oxygen by recycling chemicals such as quinones (Cho et al., 2005). Briefly, 10 µl of PM suspension is incubated with 100 µl of 0.5 M potassium phosphate buffer (pH 7.4) and 340 µl ultrapure water for 10 min at 37 °C. Next, 50 µl 1 mM DTT (Sigma, Zwijndrecht, Netherlands) is added to start the reaction, which is stopped at designated time points (0, 10, 20 and 30 min), adding 5,5′-Dithiobis(2-nitrobenzoic acid) (DTNB) (Sigma, Zwijndrecht). The absorbance at 412 nm is recorded on a spectrophotometer (SpectraMax 190, Molecular Devices, Sunnyvale, CA). The rate of DTT consumption is calculated using linear regression of the data as seen from a plot of absorbance against time, based on the average of 2 duplicate readings, resulting in a value expressed as nmol DTT/min per µg. Domestic oil burning furnace (DOFA, obtained from US EPA, RTP, NC) at a concentration of 500 µg/ml was used as a positive control.

2.4.2. Ascorbic acid (AA) depletion

For the measurement of AA depletion, briefly, PM extracts are incubated in a spectrophotometer (SpectraMAX 190: Molecular Devices, Sunnyvale, CA) for 10 min at 37 °C. After adding ascorbic acid, the absorption at 265 nm is measured every 2 min for 2 h. The 96-well plate is auto shaken for 3 s before each measurement. The maximum depletion rate of AA is determined by performing a linear regression of the linear section data, which is plotted as absorbance against time. All measurements were done in duplicate. The results are expressed as nmol/s of max AA depletion per µg PM. Domestic oil burning furnace (DOFA, obtained from US EPA, RTP, NC) at a concentration of 12.5 µg/ml was used as a positive control.

2.4.3. ESR

The ESR assay measures oxidative potential based on the ability of PM to generate hydroxyl radicals (·OH) in the presence of hydrogen peroxide (H_2O_2), and the spin trap 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) (Shi et al., 2003a). Briefly, PM suspensions are mixed with H_2O_2 and DMPO, followed by incubation for 15 min at 37 °C in a heated shaking water bath. After incubation, the suspension is vortexed for 15 s and transferred into a 50 µl glass capillary without any filtration. The DMPO–OH quartet signal is measured with a MiniScope MS-400 spectrometer (Magnettech, Berlin, Germany). Measurements are conducted in triplicate. OP^{ESR} is calculated as the average of the total amplitudes of the DMPO–OH quartet in arbitrary units (A.U.) per µg PM. Road dust (Certified Reference Material BCR 723) at a concentration of 125 µg/ml and $CuSO_4$ (2.5 µM) were used a positive controls.

2.4.4. Calculations

For all assays, the results were initially expressed as OP/µg. Mean field blank values (in OP/µg; see Supplemental Material, Table S1.1) were subtracted from all sample values. 88% (OP^{DTT}) to 97% (OP^{AA}) of the samples were above the detection limit. Field blank corrected OP values in OP/µg were multiplied with the PM mass concentration (µg/m^3) to calculate OP/m^3. We use OP/m^3 as the primary metric of interest as this is the most relevant metric for human exposure and epidemiological studies. Variation in positive control values between different runs was calculated as the %RSD and was less than 10% for all three OP assays. The coefficients of variation (CV) value, as a measure for the precision of duplicate measurements, ranged from 8% for OP^{AA} to 18% for OP^{DTT} (Supplemental Material, Table S1.1) compared to 5% for $PM_{2.5}$ mass concentrations, as reported by Strak et al. (2011). CV values were calculated as the sum of the squared absolute differences of the duplicates, divided by two times the number of duplicates. The square root of this value was then divided by the mean and multiplied by 100 to get the percentage (Eeftens et al., 2012).

2.5. Data analysis

Differences between sites were analyzed using general linear models (proc GLM in SAS; version 9.3). OP concentrations were log-transformed to normalize distributions. Measurements were not conducted simultaneously at all sites for logistical reasons, thus some of the differences between the sites could be due to temporal variation in general background air pollution concentrations. As no information on background OP concentrations was available, we used PM_{10} and black carbon data from the Dutch National Air Quality Monitoring Network to characterize the temporal variation, as described by Strak et al. (2011). Site-specific geometric mean (GM) OP, adjusted for background PM_{10} and background BC concentrations, were calculated using the LSMEANS option in proc GLM (i.e. background concentrations and site were included as independent variables in a model with OP as the dependent variable). We further report the test for statistical significance of the differences between each site and the urban background site. For comparison, GMs per site were also calculated for other PM characteristics, as reported by Strak et al. (2011, 2012) with additional data for PAHs. Out of the 16 PAHs analyzed for the RAPTES project, we selected pyrene and benzo(ghi)perylene as a low and high molecular weight traffic-related PAH respectively, and benzo(a)pyrene and benzo(e)pyrene as markers for the entire mixture. In addition, benzo(a)anthracene is included as it is prominent in the traffic profile of PAH, and the

benzo(a)anthracene quinone showed up most strongly amongst the quinones of particulate PAH in the traffic profile in recent studies conducted by the University of Birmingham (Alam et al., 2013).

Correlation between different OP assays and with PM composition was primarily assessed using Spearman rank correlation. In addition, regression analysis was conducted using univariate models as well as two-pollutant models with adjustment for the PM mass concentration. For data collected with the HVS, composition of PM_{10} was calculated as the sum of $PM_{2.5}$ and $PM_{2.5-10}$. Conversely, OP of $PM_{2.5-10}$ from the HIs was calculated as OP^{PM10}–$OP^{PM2.5}$. No further modeling of the relations between OP and composition was conducted because of the high correlation among different PM components (see Supplemental Material Table S1.2) and the limited sample size.

Given the very different PM mixture at the underground train station (Strak et al., 2011) all analyses were also conducted after excluding the data from the underground.

3. Results

3.1. Contrasts in OP between sites

Table 1 presents the geometric mean (GM) OP per m^3 of $PM_{2.5}$ and PM_{10} per site, as well as PM characteristics (PM mass and PM absorbance) derived from the same filters (HI). Results are adjusted for national background concentrations of PM_{10} and BC from the National Air Quality Monitoring Network (see Section 2.5). Unadjusted results and results for OP expressed per µg PM are given in the Supplemental material (Table S1.3). Background PM_{10} and BC concentrations were significantly ($p < 0.05$) associated with OP in all models. The adjustment for background concentrations mainly affected the farm, where GMs of OP decreased by 7–28% for $PM_{2.5}$ and by 28–46% for PM_{10} compared to the unadjusted results. For the other locations, GMs generally increased by up to 10%. The difference between adjusted and unadjusted results for the farm was mainly caused by one day with high background PM_{10} concentrations (86 µg/m^3). Unadjusted results for the farm after excluding this specific day were very similar (<1% difference) to the adjusted results.

By far the highest OP/m^3 was observed at the underground, where OP was 13 ($OP^{DTT–PM2.5}$) to over 600 ($OP^{ESR–PM10}$) times higher compared to the urban background location. OP/m^3 at the underground was also significantly higher ($p < 0.001$) compared to the other outdoor sites. For the outdoor sites, samples from the farm showed significantly higher OP^{DTT} compared to the urban background for $PM_{2.5}$ and significantly lower OP^{ESR} and OP^{AA} for PM_{10}. Samples from the continuous traffic site showed significantly higher OP/m^3 compared to the urban background for all assays.

When expressed per µg, OP at the underground and continuous traffic site was significantly higher compared to the urban background for all assays, whereas PM from the farm had significantly lower OP/µg for OP^{ESR} and OP^{AA}. The stop&go traffic site did not significantly differ from the urban background site for any of the OP/µg metrics (Supplemental Material, Table S1.3). OP/µg at the underground was also significantly elevated compared to the other outdoor locations, with the exception of OP^{DTT} at the continuous traffic site.

Fig. 1 presents the ratio of the GM per site to the GM of the urban background site for OP^{PM10}/m^3 and PM_{10} mass. Ratios for $PM_{2.5}$ showed a similar pattern. Contrasts in OP between sites generally exceeded contrasts in PM mass, and were smaller for OP^{DTT} compared to OP^{ESR} and OP^{AA}.

Site-specific GMs for PM characteristics derived from the HVS (i.e. EC, OC, trace metals, PAHs, nitrate and sulfate) and continuous monitors (i.e. PNC, NO_2, O_3) are presented in Supplemental Material, Table S1.4 and S1.5 respectively. For the underground, the contrasts in OP also exceeded the contrasts in PM-absorbance, EC and PAHs. For OP^{DTT} the contrast was lower than the contrast for Fe and Cu, whereas for OP^{ESR} and OP^{AA} the contrast between the underground and the outdoor sites was similar for these components. For the farm and continuous traffic site, contrasts for OP^{ESR} and OP^{AA} were also generally similar to the contrasts observed for EC, Cu, Fe and benzo(a)anthracene. However, for the stop&go traffic site, the higher levels of traffic-related PM components were not reflected in significantly higher OP.

3.2. OP of different PM size fractions (PM_{10}, $PM_{2.5}$)

For all sites combined, OP of PM_{10} was 1.4, 1.9 and 2.5 times higher than OP of $PM_{2.5}$ for OP^{DTT}, OP^{AA} and OP^{ESR} respectively. PM mass concentrations were 1.9 times higher for PM_{10} than for $PM_{2.5}$. For PM mass and OP^{DTT}, PM_{10}/$PM_{2.5}$ ratios differed significantly ($p < 0.05$) between locations, with significantly higher values at the underground train station compared to the outdoor locations (median ratio 2.8 for PM mass and 2.4 for OP^{DTT}). After excluding the underground location, median PM_{10}/$PM_{2.5}$ ratios were 1.3, 1.6 and 2.2 for OP^{DTT}, OP^{AA} and OP^{ESR}, respectively, compared to 1.6 for PM mass. PM_{10}/$PM_{2.5}$ ratios for OP^{ESR} and OP^{AA} were statistically different from unity at the $p < 0.01$ level (non parametric signed rank test), whereas this was only borderline significant for OP^{DTT} ($p = 0.06$). OP of $PM_{2.5}$ and PM_{10} were highly correlated for all methods (Spearman R 0.7–0.8; Table 2 and Supplemental material, Fig. S1.1).

When expressed per µg, OP^{DTT}/µg was significantly lower for PM_{10} compared to $PM_{2.5}$ (median ratio 0.8; $p < 0.01$), whereas OP^{ESR} was significantly ($p < 0.05$) higher for PM_{10} compared to $PM_{2.5}$ (median ratio 1.3; $p < 0.05$). No significant difference between OP/µg of PM_{10} and $PM_{2.5}$ were found for OP^{AA}.

Median values for OP^{PM10}–$OP^{PM2.5}$ are presented in supplemental Table S1.6.

Table 1
Geometric mean of PM mass concentrations, PM absorbance and OP per site, adjusted for background concentrations of PM_{10} and BC.

	Urban back-ground (n = 5)	Farm (n = 5)	Stop&go traffic (n = 6)	Continuous traffic (n = 5)	Under-ground (n = 9)
	GM	GM	GM	GM	GM
$PM_{2.5}$ mass (µg/m^3)	17.3	28.6[**]	20.8	24.8[*]	142.8[**]
PM_{10} mass (µg/m^3)	27.5	45.7[**]	35.3	40.9[**]	408.6[**]
$PM_{2.5}$ absorbance	1.5	0.9	3.6[**]	6.4[**]	13.5[**]
PM_{10} absorbance	1.4	1.0	3.8[**]	6.7[**]	21.2[**]
$rOP^{DTT–PM2.5}$ (nmol DTT/min/m^3)	1.4	2.7[*]	1.7	3.3[**]	18.0[**]
$OP^{DTT–PM10}$ (nmol DTT/min/m^3)	1.7	2.3	2.6[*]	3.7[**]	51.5[**]
$OP^{ESR–PM2.5}$ (A.U/1000/m^3)	1.9	1.7	2.1	9.7[**]	735.0[**]
$OP^{ESR–PM10}$ (A.U/1000/m^3)	4.1	2.2[a]	5.2	23.3[**]	2491.1[**]
$OP^{AA–PM2.5}$ (nmol AA/s/m^3)	22.8	19.0	22.8	103.5[**]	1840.3[**]
$OP^{AA–PM10}$ (nmol AA/s/m^3)	41.9	17.4[*]	39.6	172.5[*]	4793.0[**]

[*] Significantly different from the urban background $p < 0.05$.
[**] Significantly different from the urban background $p < 0.01$.
[a] Significantly different from the urban background ($p < 0.05$.) when 1 observation with very high levels was excluded (see Supplemental Material, Fig. S1.1).
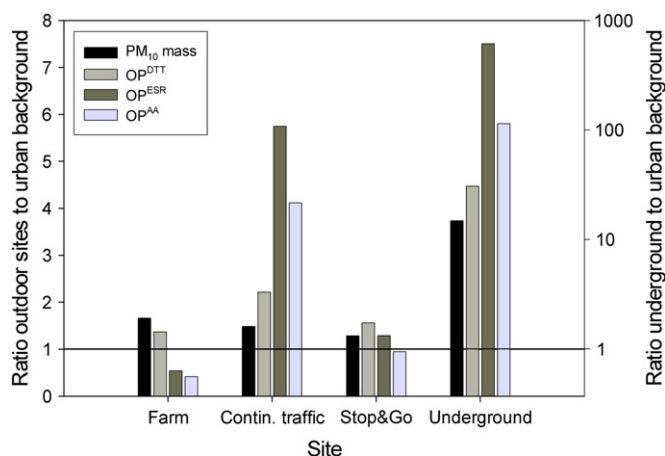
Fig. 1. Ratio of the GM per site to the GM of the urban background site for OP^{PM10}/m^3 and PM_{10} mass. Note: ratios for the underground are on a log scale.

3.3. Correlation among OP and PM composition

Correlations among the different OP measures for OP/m^3 are shown in Table 2. When data from all sites were considered (upper part), high correlations were observed among all OP measures (Spearman R 0.77–0.96). These high correlations were partly driven by the high OP values at the underground site (Table 1). When only the outdoor sites were considered (lower part of Table 2, Fig. 2), correlations decrease, especially for $OP^{DTT-PM25}$. Still, high correlations were observed among OP^{ESR} and OP^{AA} (Spearman R 0.89 for $PM_{2.5}$ and 0.95 for PM_{10}). These OP metrics were also significantly correlated when expressed per μg (Spearman R 0.90 for $PM_{2.5}$ and 0.93 for PM_{10}; Supplemental Material, Table S1.7).

Because the underground site showed highly elevated OP as well as highly elevated concentrations of PM mass and most of the PM components (i.e. EC, metals, pyrene), correlations between OP and these PM characteristics were also high (Supplemental Material Table S1.8). Correlations between the different OP measures and PM composition for the outdoor sites are shown in Table 3. The correlation with PM mass is further shown in Fig. 3. For $PM_{2.5}$, OP^{DTT} showed the highest correlation with $PM_{2.5}$ mass and OC (Spearman R 0.86 and 0.69), whereas for PM_{10} high (≥0.7) correlations were observed between OP^{DTT} and PM_{10} mass, PM-absorbance and NO_2. For OP^{ESR} and OP^{AA}, significant correlations at the p < 0.01 levels are observed with the traffic-related PM components (i.e. PM-absorbance/EC, Fe, Cu and PAHs). Correlations were generally higher for PM_{10} compared to $PM_{2.5}$, especially for OP^{ESR}. None of the OP metrics were highly correlated with sulfate, nitrate, Ni and V, whereas PM mass was only highly correlated with OP^{DTT}. For OP^{ESR} and OP^{AA}, all PM components that were significantly (p < 0.05) correlated with OP in the univariate models remained significant at the p < 0.05 when adjusted for PM mass (Supplemental Material Table S1.8). However, for OP^{DTT} PM mass remained the most significant

predictor of OP in all models, whereas the significant associations between $OP^{DTT-PM2.5}$ and SO_4^{2-}, NO_3^- and OC observed in the univariate models all lost significance when adjusted for $PM_{2.5}$ mass (Supplemental Material Table S1.9).

4. Discussion

4.1. Contrasts in OP between sites

4.1.1. Underground train station

We found highly elevated OP at the underground train station compared to the outdoor sites. The largest contrast was found for OP^{ESR} and the lowest for OP^{DTT}. The contrasts in OP/m^3 exceeded the contrast for PM mass concentrations ($\mu g/m^3$), reflected in significantly higher $OP/\mu g$.

Although several studies have characterized PM from underground train or subway stations (Nieuwenhuijsen et al., 2007), few studies have included measurements of the oxidative potential of PM. In earlier publications from the RAPTES project, we have reported OP^{PM10} calculated as the sum of OP from $PM_{0.18}$, $PM_{0.18-2.5}$ and $PM_{2.5-10}$ collected with a Micro-Orifice Impactor (MOI) and measured as the capacity of PM to deplete the antioxidants ascorbate and glutathione in a synthetic human respiratory tract lining fluid (RTLF). A detailed comparison between the current and previously reported data is described in the supplemental material (S2). OP^{PM10} was about 100 times higher at the underground station compared to the urban background (Strak et al., 2011, 2012), which is similar to the contrast found for $OP^{AA-PM10}$ in the present study. Using samples collected with the Versatile Aerosol Concentration Enrichment System (VACES) from 8 sites visited in the screening phase of the same study, Steenhof et al. (2011) also reported the highest OP^{DTT} at the underground train station. Seaton et al. (2005) found higher free radical activity (measured using a cell-free plasmid DNA Assay) in $PM_{2.5}$ from 3 platforms of the London Underground, compared to PM_{10} from Manchester.

Higher intracellular ROS production from subway particles, measured using the 2′7′-dichlorofluorescin diacetate (DCFH-DA) method, was found in Stockholm and Seoul (Karlsson et al., 2008; Jung et al., 2012). Karlsson et al. (2008) compared the ability of subway particles (PM_{10}) to form ROS from a platform in Stockholm with particles from other sources. Subway particles were the only sample that caused a significant increase in ROS when compared to that of cell control and blank control. In an earlier study, Karlsson et al. (2005) found that subway particles were about 4 times more likely to cause oxidative stress in lung cells (on an equal mass basis) compared to controls and street particles. Similarly, Bachoual et al. (2007) found that PM_{10} from the Paris subway elicited oxidative effects (HO-1 expression) in vitro and in vivo.

The high oxidative properties of PM at the underground have in other studies been attributed to the high iron levels (Nieuwenhuijsen et al., 2007). Transition metals stimulate the production of hydroxyl radicals via the Fenton reaction, which involves the reduction of H_2O_2 by a transition metal ion (Shi et al., 2006). Of the PM components included in our study, only Fe and Cu concentrations were elevated by the same order of magnitude as OP^{ESR} at the underground compared

Table 2
Spearman correlation between different OP measures in $PM_{2.5}$ and PM_{10}, expressed per m^3.
Values in the upper part are correlation for all sites (n = 30); and values in the lower part (in bold and italics) present correlation for the outdoor sites only (n = 21).

	$OP^{DTT-PM2.5}$	$OP^{DTT-PM10}$	$OP^{ESR-PM2.5}$	$OP^{ESR-PM10}$	$OP^{AA-PM2.5}$	$OP^{AA-PM10}$
$OP^{DTT-PM2.5}$ (nmol DTT/min/m^3)		0.87[**]	0.83[**]	0.77[**]	0.86[**]	0.77[**]
$OP^{DTT-PM10}$ (nmol DTT/min/m^3)	*0.68*[**]		0.85[**]	0.90[**]	0.89[**]	0.89[**]
$OP^{ESR-PM2.5}$ (A.U/1000/m^3)	*0.52*[*]	*0.61*[**]		0.87[**]	0.96[**]	0.87[**]
$OP^{ESR-PM10}$ (A.U/1000/m^3)	*0.37*	*0.75*[**]	*0.66*[**]		0.91[**]	0.97[**]
$OP^{AA-PM2.5}$ (nmol AA/s/m^3)	*0.63*[**]	*0.71*[**]	*0.89*[**]	*0.79*[**]		0.92[**]
$OP^{AA-PM10}$ (nmol AA/s/m^3)	*0.39*	*0.68*[**]	*0.67*[**]	*0.95*[**]	*0.82*[**]	

[*] p < 0.05.
[**] p < 0.01.

Fig. 2. Relation between OP^{DTT}, OP^{ESR} and OP^{AA} (outdoor sites, n = 21).

4.1.2. Outdoor locations

For the outdoor sites, PM from the farm showed significantly higher $OP^{DTT-PM2.5}$ compared to the urban background and significantly lower OP^{ESR} and $OP^{AA-PM10}$. Samples from the continuous traffic site showed significantly higher OP compared to the urban background for all assays. The higher OP^{DTT}/m^3 at the farm was largely due to higher PM mass concentrations, which were about 65% higher at the farm compared to the urban background. When expressed per μg PM, OP^{DTT} at the farm did not significantly differ from the urban background, whereas the difference for OP^{ESR} and OP^{AA} (both lower at the farm) became more significant.

As was the case for the underground, contrasts were smaller for OP^{DTT} compared to OP^{ESR} and OP^{AA}. Few field studies have compared OP from different sites, and most of these studies have focussed on one specific method to measure OP. Our findings of lower OP^{ESR} at the farm and higher OP^{ESR} at the continuous traffic site are in line with previous studies using OP^{ESR} (Boogaard et al., 2012; Shi et al., 2006; Wessels et al., 2010). Boogaard et al. (2012) found that OP^{ESR} of PM_{10} samples from 8 major streets in the Netherlands was overall 3.6 times higher than at urban background locations and 6.5 times higher than at suburban background locations. Wessels et al. (2010) measured OP^{ESR} on size fractioned PM samples (3–7 μm, 1.5–3 μm, 0.95–1.5 μm; 0.5–0.95 μm, <0.5 μm) at 4 contrasting sites in the UK. For the four larger size fractions, OP^{ESR} (expressed per μg) increased according to remote background > urban background > roadside > road tunnel, with a roughly two orders of magnitude increase between the remote background and the road tunnel. For the smallest PM fraction (<0.5 μm) the trend was reversed, but not statistically significant. Shi et al. (2006) found significant higher OP^{ESR} of both fine and coarse PM in 3 urban/industrial areas compared to a rural area in Germany.

The lower contrast between sites found for OP^{DTT} is in line with findings from the Los Angeles area (Hu et al., 2008), who measured OP^{DTT} in size-segregated PM samples concurrently at 4 sampling sites in the Los Angeles-Long Beach port area, at a background location near the harbor of the Los Angeles port and at an urban site further north, serving as a representative site of the urban Los Angeles air quality. The rather low variability in OP^{DTT} (expressed per μg) in that study was attributed to the fairly homogenous distribution of organic species on a per mass basis among the three size ranges in the area (Hu et al., 2008). When expressed per m^3, $OP^{DTT-PM2.5}$ and $OP^{DTT-PM10}$ (calculated as the sum of the different fractions) were 1.3 to 2.0 times lower at the harbor background site compared to the other locations. Differences with the urban background location were less pronounced. The Los Angeles-Long Beach harbor constitutes a complex environment where, in addition to harbor activities, other local PM sources include heavily traveled freeways, local street traffic and multiple petroleum refineries and commercial businesses (Arhami et al., 2009). Therefore none of the 4 sampling sites in the harbor area was dominated by traffic, as was the case for the continuous traffic site in our study (where OP^{DTT} was significantly higher compared to the urban background).

Other studies that have measured OP^{DTT} in PM collected at contrasting sites have mostly used the VACES to collect PM (Cho et al., 2005; Ntziachristos et al., 2007). These studies were generally not aimed to study differences in OP between sites, but rather to collect size-fractionated PM with varying composition for further characterization. Cho et al. (2005) found little variation in DTT activity per μg in the Fine + UF and coarse fraction of PM collected at two traffic sites, an urban background site and a so-called receptor site (45 km downwind of Los Angeles). Ntziachristos et al. (2007) observed the highest OP^{DTT} in samples from a road tunnel, but relatively low OP^{DTT} at the edge of a highway, whereas Steenhof et al. (2011) found marked higher OP^{DTT} at two traffic sites compared to 5 other outdoor sites. However, results of these studies have to be interpreted with caution, as samples were not collected simultaneously at the different sites and temporal variation was not taken into account.

to the outdoor sites. Conversely, the lowest contrast in OP between the underground and the outdoor sites was found for OP^{DTT}, which was, on an equal mass basis, not significantly higher at the underground compared to the continuous traffic sites (i.e. the outdoor site with the highest OP). These findings are in line with the general notion that the OP^{ESR} method is highly sensitive and the OP^{DTT} method less sensitive to transition metals (Shi et al., 2003a,b; Cho et al., 2005).

Table 3
Spearman correlation between different OP measures and physicochemical characteristics (underground excluded; n = 21).

	$PM_{2.5}$			PM_{10}			$PM_{10}–PM_{2.5}$		
	OP^{DTT}	OP^{ESR}	OP^{AA}	OP^{DTT}	OP^{ESR}	OP^{AA}	OP^{DTT}	OP^{ESR}	OP^{AA}
PM mass	0.86[**]	0.34	0.55[*]	0.75[**]	0.46[*]	0.47[*]	0.20	0.31	0.12
PM absorbance	0.32	0.64[**]	0.68[**]	0.71[**]	0.78[**]	0.70[**]			
Monitor data									
PNC	0.21	0.40	0.48[*]	0.49[*]	0.56[**]	0.51[*]	0.48[*]	0.57[**]	0.47[*]
NO_2	0.45[*]	0.47[*]	0.53[*]	0.80[**]	0.65[**]	0.59[**]	0.62[**]	0.70[**]	0.52[**]
O_3	−0.05	−0.22	−0.24	−0,54[*]	−0.42	−0.34	−0.69[**]	−0.50[*]	−0.26
HVS data[a]									
SO_4^{2-}	0.41	0.18	0.30	0.59[*]	0.27	0.23	0.46	0.23	0.02
NO_3^-	0.51[*]	0.13	0.29	0.47[*]	0.25	0.33	0.16	0.06	0.03
OC	0.69[**]	0.13	0.27	0.45[*]	0.15	0.15	−0.13	−0.06	−0.12
EC	0.24	0.55[**]	0.62[**]	0.64[**]	0.76[**]	0.67[**]	0.40	0.69[**]	0.59[**]
Cu	0.25	0.59[**]	0.74[**]	0.54[*]	0.81[**]	0.79[**]	0.47[*]	0.71[**]	0.69[**]
Fe	0.31	0.47[*]	0.60[**]	0.47[*]	0.68[**]	0.67[**]	0.44[*]	0.64[**]	0.63[**]
Ni	0.01	−0.02	0.03	0.25	0.13	0.02	0.34	0.35	0.33
V	−0.11	−0.03	0.08	0.27	0.25	0.20	0.51[*]	0.53[*]	0.49[*]
Pyrene	0.07	0.44[*]	0.46[*]	0.52[*]	0.59[*]	0.52[*]	−0.10	0.22	0.21
Benzo(a)anthracene	0.30	0.64[**]	0.65[**]	0.61[**]	0.74[**]	0.69[**]	0.22	0.27	0.34
Benzo(e)pyrene	0.32	0.67[**]	0.64[**]	0.62[**]	0.74[**]	0.66[**]	−0.11	0.16	0.14
Benzo(a)pyrene	0.47[*]	0.68[**]	0.59[**]	0.47[*]	0.51[*]	0.52[*]	−0.07	0.05	0.07
Benzo(ghi)perylene	0.23	0.46[*]	0.54[*]	0.52[*]	0.60[**]	0.58[**]	−0.30	0.02	0.07

[a] OP from PM_{10} filters correlated with composition data from HVS calculated as ($PM_{2.5}$ + $PM_{2.5-10}$).
[*] p < 0.05.
[**] p < 0.01.

Less comparative information is available for OP^{AA}. In our previous publications, $OP^{AA–PM10}$ (calculated as the sum of $OP^{AA–RTLF}$ from size-fractioned MOI filters, see underground discussion section and supplement S2) showed smaller differences between sites, with PM_{10} samples from both traffic sites having about 50% higher OP^{AA} compared to the urban background site and no difference between the traffic sites and the farm (Strak et al., 2012). Using the same method to measure OP, Godri et al. (2011) found no robust differences in OP sampled at seven school sampling sites reflecting roadside (3 schools) and urban background in London. This lack of differences was attributed to high temporal variability in concentrations of PM components of the one-week sampling campaigns, as schools were monitored one at a time. This explanation was illustrated with data from the London Air Quality Network (LAQN), which for the specific sampling periods at each school also did not indicate any significant increments in PNC or NOx at the roadside sites compared to the urban background sites whereas significant differences were observed for equivalent extended periods (Godri et al., 2011).

4.2. OP of different PM size fractions (PM_{10}, $PM_{2.5}$)

In addition to differences in contrasts for OP^{DTT} and OP^{ESR}, these two OP metrics also differed in respect to differences between size fractions: OP^{DTT}/μg was significantly higher for $PM_{2.5}$ compared to PM_{10}, whereas the reverse was the case for OP^{ESR}/μg. This suggests that, on a per mass basis, for OP^{DTT} the fine fraction contributes most to $OP^{DTT–PM10}$, whereas for OP^{ESR} the coarse fraction has the higher contribution. These findings are in line with previous publications, that have demonstrated higher OP^{DTT} in the fine compared to coarse fraction (Cho et al., 2005; Ntziachristos et al., 2007; De Vizcaya-Ruiz et al., 2006) and higher OP^{ESR} in coarse compared to fine PM (Shi et al., 2003b, 2006). For example, De Vizcaya-Ruiz et al. (2006), found about twofold higher OP^{DTT}/μg of the fine fraction compared to the coarse fraction in PM samples from different regions in Mexico City, whereas Shi et al. (2003b) found about two times higher OP^{ESR}/μg in coarse compared to fine PM in Dusseldorf, Germany. Conversely, Shi et al. (2003a) found no substantial difference in OP^{ESR}/μg between the fine and coarse fraction in PM samples from both a rural and an industrial town in Germany. As we have compared $PM_{2.5}$ and PM_{10}, the difference between fine and coarse PM would be

larger than the factor 0.8 (OP^{DTT}/μg) and 1.3 (OP^{ESR}/μg) presented here. Boogaard et al. (2012) found much larger differences in OP^{ESR} between $PM_{2.5}$ and PM_{10} filters (factor 3.1 on a per mass basis). In that study, transition metals were especially present in the coarse fraction of PM_{10}, which, as the ESR assays is especially sensitive to transition metals, could explain the larger difference in OP^{ESR}. Likewise, in the study by Shi et al. (2003a), the Cu content was similar in fine and coarse PM, which could explain the lack of difference in OP^{ESR} between fine and coarse PM in that study. Notably, several studies have shown the highest OP^{DTT} on a per PM mass basis in the ultrafine fraction of $PM_{2.5}$ (Cho et al., 2005; Ntziachristos et al., 2007; Hu et al., 2008), which was not measured in our study.

4.3. Correlation among OP^{DTT}, OP^{ESR} and OP^{AA}

The high OP observed at the underground for all OP methods, as well as highly elevated concentrations of PM mass and most of the measured PM characteristics resulted in high correlations among the different OP methods and other PM characteristics. For the outdoor sites, OP^{ESR} and OP^{AA} were highly correlated, whereas lower correlations were observed with OP^{DTT}, especially for the $PM_{2.5}$ fraction. Few inter-assay comparisons have been published so far. Yang et al. (2014) also found a high correlation between OP^{ESR} and OP^{AA} (Spearman R > 0.9 for methanol extracted Teflon filters) and a lower correlation with OP^{DTT} (Spearman R 0.4–0.6) in 15 $PM_{2.5}$ samples from an urban background site and traffic site in the Netherlands. Mudway et al. (2011) compared the DTT and AA assay, using both the RTLF method and the method used in our study. They observed a low correlation between DTT and the two AA assays, and a significant correlation (Pearson R 0.74 for $PM_{2.5}$ and 0.51 for PM_{10}) between the two AA assays. Kuenzli et al. (2006) found a Pearson's R of 0.65 between annual mean OP^{ESR} and OP^{AA} (RTLF method) measured in $PM_{2.5}$ samples from 20 European cities.

4.4. Correlation between OP and PM composition

For the outdoor sites, OP^{DTT} showed the highest correlation with PM mass, OC (with $OP^{DTT–PM2.5}$) and PM-absorbance and NO_2 (with $OP^{DTT–PM10}$). Delfino et al. (2013) also observed a high correlation between $OP^{DTT–PM2.5}$ (expressed per m^3) and PM mass and OC (Spearman
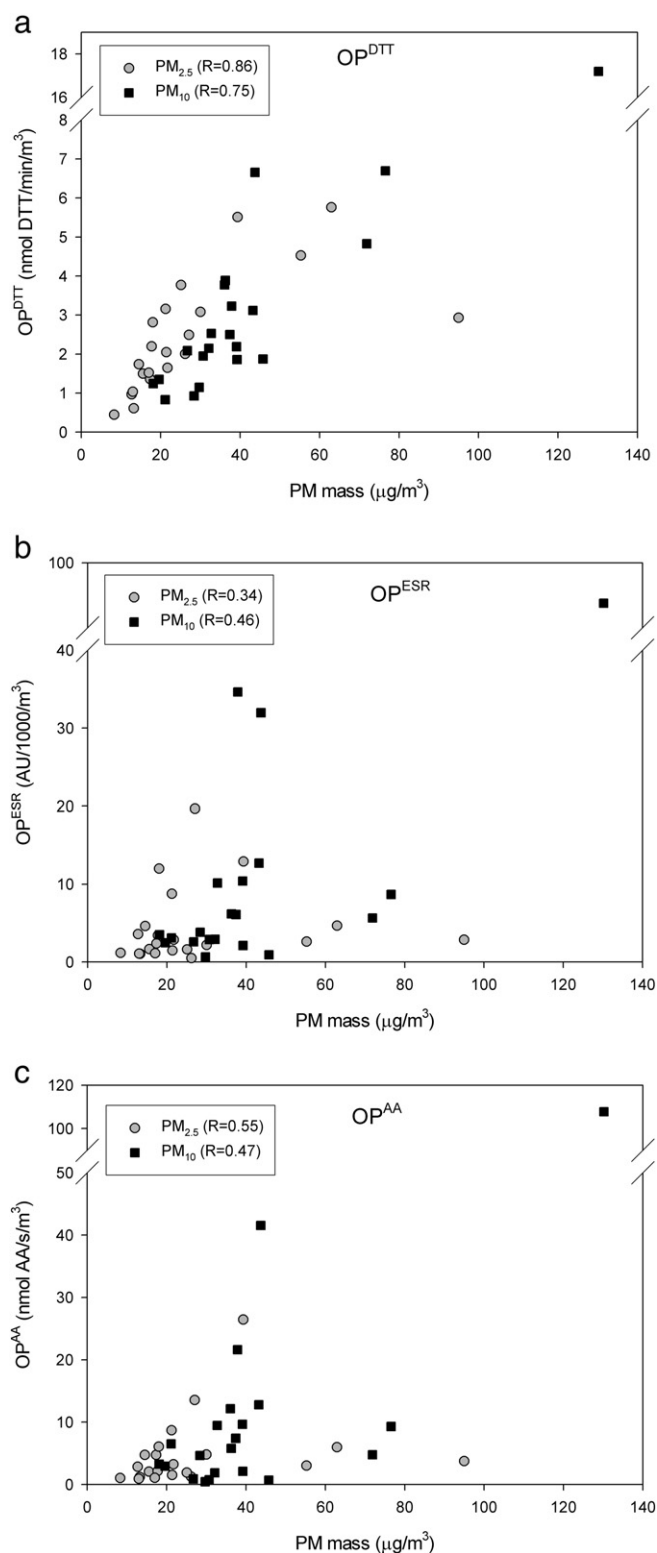
Fig. 3. Relation between OP^{DTT}, OP^{ESR}, OP^{AA} and PM mass concentrations (outdoor sites, n = 21).

R > 0.8). Several studies that have assessed the correlation between OC and OP^{DTT} on a per mass basis found a high correlation (R 0.73–0.91) (Cho et al., 2005; Hu et al., 2008; Ntziachristos et al., 2007; Verma et al., 2012). In most of these studies, OP^{DTT} was also highly correlated with EC. We did not calculate correlations for OP/μg as no PM mass concentrations for the HVS samples were available.

The high correlations for OP^{ESR} and OP^{AA} with transition metals are in line with previous observations, especially for PM_{10} (Boogaard et al., 2012; Godri et al., 2011; Kuenzli et al., 2006): For PM_{10}, high correlations with Cu and Fe were found for OP^{ESR} by Boogaard et al. (2012) (R 0.84–0.89), and with OP^{AA} by Godri et al. (2011) (R 0.76–0.78). For $PM_{2.5}$ Kuenzli et al. (2006) reported moderate correlations for both OP^{ESR} (R 0.39–0.45) and OP^{AA} (R 0.59–0.60). These studies also showed a poor correlation between OP^{ESR} and/or OP^{AA} and PM mass concentrations, with the exception of Godri et al. (2011).

For $PM_{2.5}$ and PM_{10}, OP^{ESR} and OP^{AA} were also moderately to highly correlated with PAHs, with generally the highest correlations for benzo(a)anthracene (Spearman R 0.64–0.76; p < 0.01). For $PM_{2.5–10}$, no significant correlation between OP and PAHs was observed, possibly due to the relatively low levels of PAHs in the coarse fraction. None of the other studies that measured OP^{ESR} or OP^{AA} evaluated its correlation with PAHs. OP^{DTT} was moderately correlated with all of the included PAHs for PM_{10} (Spearman R 0.47–0.62; p < 0.05) and with benzo(a) pyrene for $PM_{2.5}$ (Spearman R 0.47; p < 0.05). Several studies in the Los Angeles area have found a higher correlation between OP^{DTT} and PAHs (Cho et al., 2005; Hu et al., 2008; Ntziachristos et al., 2007). However, according to Ntziachristos et al. (2007), although these species are not expected to contribute to OP^{DTT} by means of a direct chemical mechanism, their presence in the statistical associations demonstrate that they act as surrogates of a particularly redox active PM source.

4.5. Limitations

Measurements were not conducted simultaneously at all sites for logistical reasons, thus some of the differences between the sites could be due to temporal variation in general background air pollution concentrations. This could particularly be an issue since sampling days were not randomly selected but had to meet certain meteorological criteria (Strak et al., 2011). As no information on background OP concentrations was available, we used PM_{10} and black carbon data from the Dutch National Air Quality Monitoring Network (NAQMN) to characterize the temporal variation. Although OP/m^3 measured on the site was significantly associated with PM_{10} and BC from the NAQMN, the adjustment only affected results for the farm, caused by one day with high background PM_{10} concentrations (86 μg/m^3). For the traffic locations, specific components such as EC, Fe, Cu were 2–3 times higher at the stop&go location compared to the urban background, which is in line with previous observations along busy inner-city roads in the Netherlands (factor 2–4) (Boogaard et al, 2011; Janssen et al., 1997). For the continuous traffic site, the contrast for these components was larger (factor 4–5 for EC; 5–7 for Fe and Cu), and in line with findings for black smoke along a highway in Amsterdam (factor 5) (Roemer and van Wijnen, 2001) and for Fe and Cu measured along a heavily trafficked 6 lane road in central London (factor 5–6) (Gietl et al., 2010). We therefore think that the contrasts between sites in our study are not substantially biased by the differences in the sampling periods.

In the present study, OP was measured on $PM_{2.5}$ and PM_{10} low volume samples (HI), whereas PM composition was derived from $PM_{2.5}$ and $PM_{2.5–10}$ HVS samples. Correlation between OP and other PM characteristics may therefore be lower than would be obtained if both were measured on the same (type of) samples. In addition, we used ICP-MS to determine to role of transition metals, which does not provide information on the oxidation state. Shi et al. (2003a) showed a high ability for Cu(II), V(II), V(V) and Fe(II) and less ability for Fe(III) and Ni(II) to generate OP^{ESR}. Furthermore, relations between PM composition and OP were only evaluated using univariate correlation analyses, because of the high correlation between PM characteristics (e.g. metals and PAHs) and the small samples size (21 sampling days for the outdoor sites). However, we did not aim to perform a detailed assessment of which specific PM characteristics drive the OP of PM. Rather, we aimed to assess whether the differences in the relations between OP and composition for different assays, found among studies that have

focused on one specific measurement method for OP, would also be apparent in a dataset that included results for different OP methods, derived from the same samples. Our study shows that different PM components contribute to OP^{DTT} compared to OP^{ESR} and OP^{AA}. The often moderate correlations document that OP is not easily predicted by single chemical components.

5. Conclusions

Our study has shown highly elevated OP of PM$_{2.5}$ and PM$_{10}$ at an underground train station compared to outdoor locations. For the outdoor locations, OP^{ESR} and OP^{AA} were significantly lower at a farm compared to urban background, whereas PM along a highway with continuous traffic showed the highest OP for all OP methods. Contrast between sites for OP exceeded contrasts in PM mass, and were lower for OP^{DTT} compared to OP^{ESR} and OP^{AA}. Furthermore, on a per mass basis, OP^{DTT} was significantly higher in PM$_{2.5}$ compared to PM$_{10}$, whereas the reverse was the case for OP^{ESR}. The OP methods studied also differed in respect to their correlation with other PM characteristics: OP^{ESR} and OP^{AA} were highly correlated with the traffic-related PM components (i.e. EC, Fe, Cu, PAHs), whereas OP^{DTT} showed the highest correlation with PM mass and OC. Our study indicates that OP has several dimensions and that different measures for OP provide different results. Consequently, a combination of two or more OP measure may be needed to create an accurate predictor for health effects. Of the assays used in our study, either OP^{ESR} or OP^{AA} and OP^{DTT} can complement each other in providing information regarding the oxidative properties of PM, which can subsequently be used to study health effects.

Conflict of interest

The authors declare that they have no competing interest regarding the submitted article.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.11.099.

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