PAPER

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Oxidative potential of atmospheric particulate matter collected in low-income urban settlements in South Africa

Constance K. Segakweng, [ID] a Pieter G. Van Zyl, [ID] *b Cathy Liousse, [ID] c
S. Gnamien, [ID] cd Eric Gardrat,c Johan P. Beukes,b Kerneels Jaars, [ID] b C. Dumat,e
B. Guinot,c Micky Josipovic,b Brigitte Language,a Roelof P. Burger,a Stuart J. Piketha
and T. Xiongf

Health-related impacts *e.g.* respiratory and cardiovascular morbidity and mortality, associated with exposure to atmospheric particulate matter (PM) are globally considered important and are not completely understood. Oxidative potential (OP), defined as a measure of the capacity of PM to oxidise target molecules, has been previously proposed as an alternative relevant biological metric in health studies to better quantify toxicological responses associated with PM exposure than aerosol mass alone. Several methods are currently used to assess the oxidative capacity of PM. In this study, the dithiothreitol (DTT) assay was used, which is the most commonly used technique to estimate OP. This assessment is easy-to-operate, low-cost, effective and reproducible. The first step was to modify the DTT methodology based on previous applications, which entailed choosing an appropriate extraction procedure and -setup. The redox activity of size-resolved PM samples collected in three low-income urban settlements in South Africa, *i.e.* Jouberton, KwaZamokuhle and Zamdela was evaluated and related to their chemical composition through correlation analysis. Furthermore, it was attempted to determine seasonal variations of DTT redox activity through normalisation according to PM mass (DTTm) and sampled volume (DTTv) for outdoor and indoor environments. The results indicated higher redox activity for the finest (<1 μm) particles compared to the coarser particulates (1–10 μm) for both outdoor and indoor environments. DTT redox activity of PM, especially, in the PM_{1-10} particle size fraction, had strong correlations with elemental (EC) and organic carbon (OC), as well as trace elements and water-soluble inorganic species for outdoor and indoor samples. Possible atmospheric aerosol emission sources suggested from these correlations include primary emissions from domestic- and open biomass burning, vehicles and industrial activities, as well as secondary particle formation (*e.g.* sulphate).

Environmental significance

Health-related impacts associated with exposure to atmospheric particulate matter (PM) are globally considered important and not completely understood. Oxidative potential (OP), which is a measure of the capacity of PM to oxidise target molecules, has been previously proposed as an alternative relevant biological metric in health studies to better quantify toxicological responses associated with PM exposure. The redox activity of size-resolved indoor and outdoor PM samples collected in three low-income urban settlements in South Africa was evaluated. Higher redox activity was determined for the finest (<1 μm) particles compared to the coarser particulates (1–10 μm) for both outdoor and indoor environments. DTT redox activity of PM, especially, in the PM_{1-10} particle size fraction, had strong correlations with elemental (EC) and organic carbon (OC), as well as trace elements and water-soluble inorganic species for outdoor and indoor samples. These findings have dramatic implications for the management of air pollution in South Africa, while the modification of the method used to determine OP will simplify the use of this method in other health-related studies.

aUnit for Environmental Sciences and Management, North-West University, Potchefstroom Campus, South Africa

bAtmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University, Potchefstroom Campus, South Africa. E-mail: pieter.vanzyl@nwu.ac.za

cLaboratoire d'Aérologie, Université Paul Sabatier, Toulouse III, France

dLaboratoire des Sciences de la Matière, de l'Environnement, et de l'Energie Solaire, Université Félix Houphouet Boigny, Abidjan, Ivory Coast

eCentre d'Etude et de Recherche Travail Organisation Pouvoir UMR 5044, Université de Toulouse, France

fSchool of Life Sciences, South China Normal University, China

1. Introduction

Recent studies have shown that humans living in cities, especially in developing countries, are most exposed to aerosol or particulate matter (PM) pollution, due to increased industrial activity, energy demand and vehicular emissions.[1–3] The health impacts associated with the emissions of these species are of global interest and concern due to increases in emissions of

these species in the atmosphere.[4–8] Atmospheric pollution related to these species is rapidly becoming one of the leading causes of increased morbidity and mortality in developing countries such as those in Africa, which includes South Africa.[4,9] PM can penetrate the respiratory system, which can result in a wide range of impacts on human health that include respiratory- and cardiovascular diseases, premature mortality,[10–13] dysfunctions of reproductive and central nervous system (or adverse neurodevelopmental impacts), and cancer.[1,10–12] Several epidemiological studies, such as Kampa and Castanas, 2008, and Du *et al.*, 2016, have shown a clear correlation between increased respiratory and cardiovascular morbidity and mortality, and elevated atmospheric PM concentrations.[3,6]

Health effects resulting from exposure to atmospheric PM are still not completely understood. An important mechanism from which the impacts of atmospheric aerosols on health could be quantified relates to oxidative stress associated with reactive oxygen species (ROS) or free radicals.[14–17] Oxidative stress is a biochemical condition where elevated levels of ROS exceed the natural (cellular counteracting) antioxidant capacity, which can cause damages to biological (structural and functional) molecules such as human tissues and cells, lipids, proteins, DNA, carbohydrates and RNA.[8–19] ROS may enter the human body in many ways, but it is primarily introduced through inhalation. Aerosol oxidative potential (OP), which is defined as a measure of the capacity of PM to oxidise target molecules, has been previously proposed as an alternative a-cellular relevant biological metric in health studies to better quantify toxicological responses associated with PM exposure than aerosol mass alone.[20]

Epidemiological studies in which oxidative stress and inflammation are related to cardiovascular morbidity and mortality are limited. Therefore, the OP of particles can be an important biological metric,[21,22] since it is related to the chemical composition and size of particulates. Previous studies showed the impacts of aerosols on human health can be related to concentrations of PM_{10} (particulates with an aerodynamic parameter $\leq$ 10 μm).[23] However, these studies are not ideal from a toxicological and epidemiological perspective, since PM_{10} also comprise chemical species with low toxicity, *e.g.* sea salt and crustal species.[24–27] More significant impacts on health are associated with fine ($PM_{2.5}$ – particulates with an aerodynamic parameter $\leq$ 2.5 μm) and ultrafine (PM_1 – particulates with an aerodynamic parameter $\leq$ 1 μm) aerosols, since these species can diffuse through membranes into human tissue and cells. In addition, these smaller particulates have a larger surface area for exposure to chemical species, which is important in pro-inflammation as indicated through studies on animals and in *in vitro* tests.[9,21] Atmospheric aerosols comprise inorganic and organic compounds, of which a number have studies have indicated the impacts of these chemical species on toxicological responses. Val *et al.*,[9] for instance, conducted an *in vitro* study on the biological reactivity of urban African particulate matter on human bronchial epithelial cells, as well as their relationship with physical and chemical properties of aerosol species. It was found from the correlation of the gene expression signature with the main chemical compounds in PM

that PM-induced responses are mostly associated with organic species (carbonaceous aerosols) and the finest size fraction had the highest toxicity. In addition, the OP is also related to the concentration of PM in the atmosphere and could therefore be considered as a complementary measurement. Although the chemical composition is important, previous studies have showed concentrations to be the primary driver for total OP.

There are several methods used to assess the oxidative capacity of PM, which include cellular assays (*e.g.* antioxidants depletion assays, antioxidants inactivation assays, and Fenton and Fenton-type reactions), as well as a-cellular assays (*e.g.* dithiothreitol, DTT, electron spin resonance, ESR, ascorbate acid depletion, AA and reductive acridinium triggering, CRAT).[17,20,28] Each of these assays has a different sensitivity to compounds generating ROS. In this study, an a-cellular assay, *i.e.* DTT, was applied, which is a simple method that uses DTT as a chemical surrogate of cellular antioxidants that do not involve human cells. The consumption of DTT is typically based on the simulation of electron transfer catalysed by PM to form oxygen and generate superoxide.[22,29]

Previous OP studies utilising DTT used various mediums to extract PM from filters, which include water,[20,30–32] dichloromethane[33] and methanol.[20,28,30,34] However, the recovery rate when using these methods is very low. For example,[20,35] and Rattanavaraha *et al.*[30] reported that trace metals, which are important to PM toxicity, might potentially be lost or contaminated during these extraction processes. Therefore, the method to determine DTT activity was modified in this study to be more efficient and simpler. The novelty in this study was to directly incubate filters and 1,4-naphthoquinone (1,4-NQ – used as a positive control with DTT) without any extractant, which, according to the knowledge of the authors, has not been performed before. Note that uncertainty may also exist with our newly developed method due to offline OP measurements after the collection of samples. Indeed, there are a few recent studies that investigated how atmospheric ageing of aerosols impacts the OP of PM using the DTT assay methodology.[36–40] There would be a loss of short-lived redox active species in the samples stored for days, weeks or months before they are analysed for OP: the samples might be biochemically less active than those collected and analysed immediately. This would result in an undervaluation of the ROS concentration of the ambient particle bound.[41,42] For example, Carlino *et al.*[41] investigated the stability of ROS over samples stored for up to four months and found that the stability of ROS was decreasing with increased storage time. Approximately 60% of ROS in that study were highly reactive and this indicated how quick real-time online ROS analyses need to be considered in the future.

In this study, our newly developed method was applied to different types of filters, namely Teflon™, Quartz and Nucleopore filters, which could also influence the OP measurements. These filter types were used in this study, since it allows measurement of OP of particulates and chemical composition (organic and inorganic species). Finally, this newly DTT method developed at Laboratoire d'Aérologie (Toulouse, France) was applied to outdoor and indoor aerosol samples collected on Nucleopore filters in low-income urban settlements in South Africa.

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2. Materials and methods

2.1. Sampling sites and methods

Detailed descriptions of the sampling sites and methods are presented in Segakweng et al.[43] PM samples collected at three of the four low-income urban settlements located in the north-eastern interior of South Africa described in Segakweng et al.[43] were subjected to OP (DTT) analysis, i.e. ambient aerosols collected at Zamdela (S −26.837, E 27.843) and KwaZamokuhle (S −26.138, E 29.739), and indoor PM samples collected at Jouberton (S −26.906, E 26.584). This is the largest industrialised area in South Africa, holding several pyrometallurgical industries, mines, coal dumps, two large petrochemical plants and a cluster of coal-fired power stations.[44] Furthermore, this region is influenced by seasonal regional open biomass burning during the dry season,[45] while household combustion is also an important source of atmospheric pollutants in this densely populated region.[44,46] The South African Highveld is characterised by a distinct dry and wet season with the dry season usually occurring from mid-May to mid-October, which coincides with the South African winter from June to August. Higher concentrations of atmospheric pollutants during winter are associated with more pronounced inversion layers trapping pollutants near the surface. Ambient measurements performed at KwaZamokuhle and Zamdela were conducted within the framework of the air quality offset programme in South Africa,[47] while sampling at Jouberton was conducted as part of the Prospective Household cohort study of Influenza, Respiratory Syncytial virus and other respiratory pathogens community burden and Transmission dynamics in South Africa (PHIRST).[48]

Winter and summer sampling campaigns were conducted at Zamdela (15 to 30 July 2016 and 09 to 23 March 2017, respectively) and Jouberton (01 August to 16 August 2016 and 18 April to 19 May 2016, respectively), while only a summer campaign was conducted at KwaZamokuhle (23 February until 07 March 2016) due to logistical limitations. Indoor PM samples collected during winter and summer sampling campaigns at Jouberton were used for DTT analysis. However, due to the required sample load for DTT analysis, only ambient aerosol samples collected during winter at Zamdela and only one ambient PM sample collected during summer at KwaZamokuhle could be utilised for DTT analysis.

The ambient and indoor aerosol samples from low-income urban settlements in South Africa were collected on Nucleo-pore, Teflon and Quartz filters using a set of three cascade Sioutas impactors with 5-stages connected to pumps running in parallel at a flow rate of 9 L min^{-1}. These impactors collected PM in the 2.5–10 μm, 1.0–2.5 μm, 0.50–1.0 μm, 0.25–0.50 μm and <0.25 μm aerodynamic diameter size ranges. One impactor was equipped with Nucleopore filters for the health tests for the DTT redox activity assay. 72 hours ambient aerosol samples were collected at KwaZamokuhle and Zamdela during two-week periods, while at Jouberton, 24 hours indoor PM samples were collected for a duration of seven days in three houses (sampling was only conducted at two of the three houses during the winter campaign due to logistical restraints). The samples were stored in the fridge for two to three years prior to DTT analysis. As previously mentioned, storing sampled filters for long periods can result in the loss of redox active species, which is acknowledged and should be considered when interpreting results presented in this study. However, in view of logistical restraints e.g. effort associated with sampling in these low-income settlements, samples could not be analysed earlier. Results presented can be considered indicative of OP of aerosols collected in these low-income settlements.

2.2. DTT modified method

2.2.1. Introduction of the method. As previously mentioned, the DTT assay is a chemically redox-active method, which is based on the ability of a PM sample to catalyse electron transfers between DTT and oxygen.[30] This assay is a measure of the oxidation of DTT to its disulphide bonded 6-membered ring with the remaining non-oxidised DTT then being reacted with 5,5′-dithio-bis-(2-nitrobenzoic acid) (DTNB). The latter process generate a mixture of the disulphide ring compound and 5-mercapto-2-nitrobenzoic acid (TNB), which is determined through ultraviolet absorption at 412 nm.[22] The consumption of DTT by the PM sample is monitored under a set of conditions, which allows the rate to be proportional to the concentration of the catalytically redox-active species contained in the PM sample.[22,31] In this study, the DTT method was modified from the more general procedures previously followed e.g. Kumagai et al.[29] and Cho et al.[22] As mentioned above, in previous studies PM were first extracted with water, dichloromethane or methanol.[14,20,30,49,50] In the novel method presented in this study PM particles directly reacted with DTT without any extraction medium (detailed description in subsequent Section 2.2.4). A filter of known mass or a positive control (PC) with 1,4-NQ was immediately incubated with 3 mL of 60 μM DTT solution at 37 °C. The solution was then placed in an ultrasonic bath for 20 minutes, and the intrinsic absorbance (Abs$_i$) of the solution was determined with the Infinite F200 PRO TECAN. Similar to the

Table 1 Reagents used for modified DTT assay

Reagent	Symbol	Supplier	Purity
Potassium phosphate dibasic	K$_2$HPO$_4$	Sigma-Aldrich	≥98%
Dithiothreitol (DTT)	C$_4$H$_{10}$O$_2$S$_2$	Amresco	
5,5′-Dithio-bis-(2-nitrobenzoic acid) (DTNB)	C$_{14}$H$_8$N$_2$O$_8$S$_2$	PanReac AppliChem	≥98%
1,4-Naphthoquinone (1,4-NQ)	C$_{10}$H$_6$O$_2$	Sigma-Aldrich	97%
Potassium dihydrogen phosphate	KH$_2$PO$_4$	Alfa Aesar	99.0%
Ethylenediaminetetraacetic acid (EDTA)	C$_{10}$H$_{16}$N$_2$O$_8$	Alfa Aesar	99.4+%

Table 2 Absorbance of the reaction products of DTT (3 mL) and DTNB (10 mM)

DTT	DTNB	Abs
20 μM	10 μL	0.12989
50 μM	50 μL	0.24640
50 μM	60 μL	0.24689
60 μM	50 μL	0.45284
100 μM	50 μL	0.51361
200 μM	100 μL	1.12030

original method, 10 mM DTNB solution was then added to the solution prior to analysis with the Infinite F200 PRO TECAN, which measured the final absorbance of all the elements (Abs), *i.e.* the absorbance of the 2-nitro-5-thiobenzoic acid (TNB) that is formed during the reaction, at 412 nm. Linear regression of DTT consumption against time can be established and the calculation of absorbance can be expressed as $Abs' = Abs - Abs_i$. The ideal time of the entire experiment/analysis should not exceed 30 min.[14]

2.2.2. Preparation of reactants for DTT analysis. All reagents used for the modified DTT assay conducted in this study are presented in Table 1. A 0.1 M phosphate buffer was prepared from K_2HPO_4, KH_2PO_4, EDTA and ultrapure water (18 MΩ). A phosphate buffer was used in this study because Pietrogrande *et al.*[28] reported the solution as the solvent of choice with the highest extraction efficiency compared to methanol and Gamble's solution. The solution was dissolved in an ultrasonic bath and the pH of the solution was determined to be 7.3 ± 0.1. This buffer was then used for the preparation of a 5 mM DTT stock solution and a 10 mM DTNB solution. All prepared solutions were stored in a fridge. A 60 μM DTT solution was prepared from the DTT stock solution every day prior to analysis and kept in the fridge in between analyses. A PC solution or instrument control was prepared from 1,4-NQ and ultrapure water (18 MΩ), which was used as the external standard. Details on the concentrations of reagents are described in more detail in (Section 2.2.4).

2.2.3. Data calculation and analysis. In order to assess and compare the OP determined with modified DDT assay in this study to previous studies, the residual DTT (nmol), the mass- and volume-normalised DTT activity (nmol min^{-1} μg^{-1} and nmol min^{-1} m^{-3}), as well as the normalised index of oxidant generation and toxicity (NIOG) were calculated. Residual DTT (nmol) was an indicator of the remaining DTT after the catalytic redox reaction with a decrease in residual DTT corresponding to increased DTT consumption.

$$\text{Residual DTT} = \text{Total DTT amount} \times \frac{Abs'}{Abs_0},$$

where Abs_0 is the absorbance associated with DTT added in a blank sample and Abs' is the absorbance of the formed TNB as mentioned previously.

DTT activity is expressed as the rate of DTT consumption per mass of sample (nmol min^{-1} μg^{-1}) or per volume of sampled air (nmol min^{-1} m^{-3}).[30] The DTT consumption rate normalised by PM mass (DTTm) represents intrinsic DTT activity of the aerosol

OP, while the DTT consumption rate normalised the by total volume of air passing through the filter (DTTv) represents the relevant atmospheric OP.[51]

$$\text{DTT activity} = \frac{\text{DTT consumption}}{t \times m} \text{ or } \frac{\text{DTT consumption}}{t \times v}$$

where $\text{DTT consumption} = \text{Total DTT amount} \times \frac{Abs - Abs'}{Abs_0}$, t is the reaction time (min), m is the PM mass (μg) and v is the volume of sampled air.

The NIOG is used to standardise the data obtained from the DTT assay. NIOG is expressed as the ratio of the index of oxidation generation (IOG) of the sample and the IOG of 1,4-NQ ($IOG_{1,4\text{-NQ}}$) that is used as an external standard:

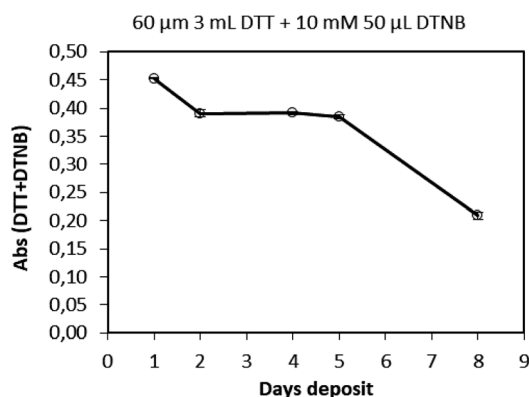$$\text{NIOG}_{\text{sample}} = \frac{\text{IOG}_{\text{sample}}}{\text{IOG}_{1,4\text{-NQ}}},$$

where $\text{IOG} = \frac{Abs_0 - Abs'}{Abs_0} \times \frac{100}{t \times m}$, t = reaction time (min), m = sample mass (μg), Abs_0 = absorption when no DTT was reacted, Abs' = absorption from the remaining DTT after the catalytic redox reaction.

2.2.4. Optimisation of modified DTT method. Total particulate matter (TPM) samples were collected from a diesel car exhaust on 47 mm Teflon™ and Quartz filters for 24 hours, which were used for validating and/or quantifying the modified DTT methodology. Quartz filters were pre-treated in an oven at 450 °C for 48 hours to remove any impurities. All filters were weighed before and after sampling with the mass of samples collected on Teflon filters ranging between 409 to 904 μg, while the mass of PM collected on Quartz filters ranged from 175 to 758 μg.

The modified DTT assay conducted in this study was optimised by investigating the influence of the following parameters on the calculated OP:
- Concentration and volume of DTT and DTNB;
- Influence of sonication and filtration;
- Use of positive control (1,4-NQ); and
- Influence of reaction time.

2.2.4.1 Concentration and volume of DTT and DTNB. A sufficient DTT concentration and volume is required to react

Fig. 1 Absorbance (Abs) of the reaction product of DTT and DTNB over a period of eight days.

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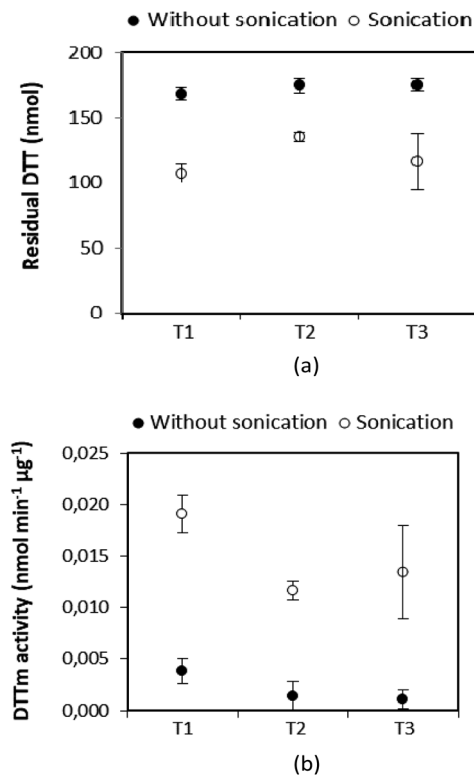*Environ. Sci.: Atmos.*, 2025, **5**, 48–66 | 51

Fig. 2 Comparison of (a) residual DTT and (b) DTTm activity of three Teflon filters (T1, T2 and T3) with or without sonication. The error bars indicate the standard deviations.
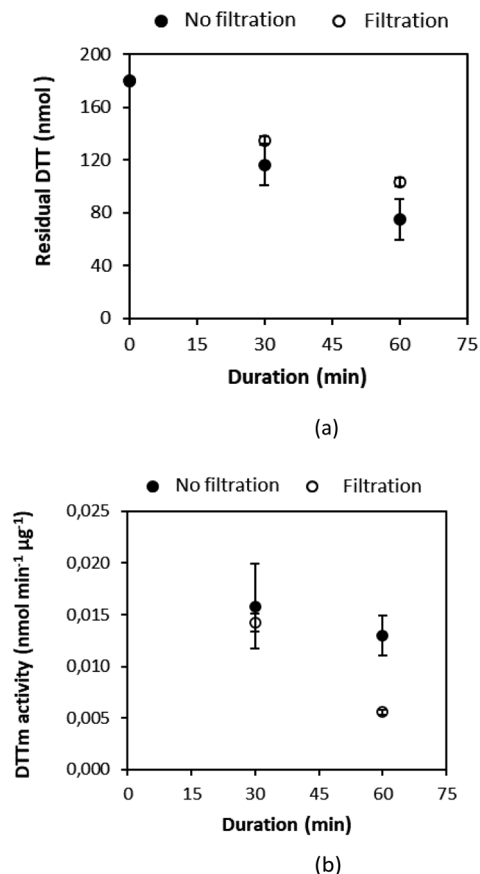

Fig. 3 Comparison of (a) residual DTT and (b) DTTm activity against time (0, 30 and 60 min) on diesel exhaust (Teflon filters) with or without filtration. The error bars indicate the standard deviation.

with the total amount of PM, while the concentration and volume of the DTNB solution should be adequate to consume the residual DTT. An absorbance value of 0.45 is considered a stable absorbance in the pH range between 5.5 and 8.0.[31] Therefore, different concentrations of DTT and different volumes of DTNB were evaluated of which the results are listed in Table 2. Similar to previous studies, a fixed DTT volume of 3 mL was chosen, which allows complete immersion of a quarter of the filter for extraction, while a fixed concentration of 10 mM DTNB was used.[22] The concentration of DTT was varied from 20–200 μM, while the volume of DTNB ranged from 10–100 μL. It is evident from Table 2 that the absorbance increased with increasing concentration of DTT and for larger volumes of DTNB. According to these tests, the DTT concentration and volume were then fixed at 60 μM and 3 mL, respectively, while a volume and concentration of 10 mM and 50 μL, respectively was used for DTNB (i.e. absorbance of 0.45).[31] During these tests, it was also observed that, due to oxidation, the 60 μM DTT solution (prepared from the 5 mM DTT stock solution) is not stable for more than one day. In Fig. 1 the absorbance of a 60 μM DTT solution was monitored for eight days, indicating a daily decline in the measured absorbance. Therefore, in this modified methodology, 5 mM DTT stock solution was prepared once a week, while 60 μM DTT diluted solutions were prepared daily.

2.2.4.2 Influence of sonication and filtration. Three sampled Teflon™ filters (test samples collected from the diesel car exhaust as described above) were cut into four equal parts and separated into two groups to determine the influence of sonication on the reaction with DTT. One-quarter of the sampled filter was immersed in the 3 mL DTT buffer solution, and immediately incubated at 37 °C and shaken for 30 minutes (without sonication). Another quarter of the filter was immersed in the same 3 mL DTT buffer solution in a bottle, and then placed in an ultrasonic bath for 30 minutes, after which it was incubated at 37 °C. The DTNB solution was then added to both reaction solutions and absorbance was measured at 412 nm (each sample was analysed four times). In Fig. 2(a) the residual DTT and (b) DTT activity per mass unit (DTTm) determined for each of the three Teflon™ filters that were sonicated and without sonication are presented. It is evident from Fig. 2 that the DTT response improved when sonicated with significantly more DTT (~34%) being consumed after sonication compared to ~4% DTT consumption without sonication. Therefore, all samples were sonicated in the modified DDT assay presented in this study.

The residual DTT (a) and DTTm activity (b) determined for sonicated test sampled (diesel car exhaust) Teflon™ filters with and without filtration of the solution are presented in Fig. 3. Equal amounts of the incubated mixtures were filtered through a 0.2 μm syringe filter in order to remove insoluble components
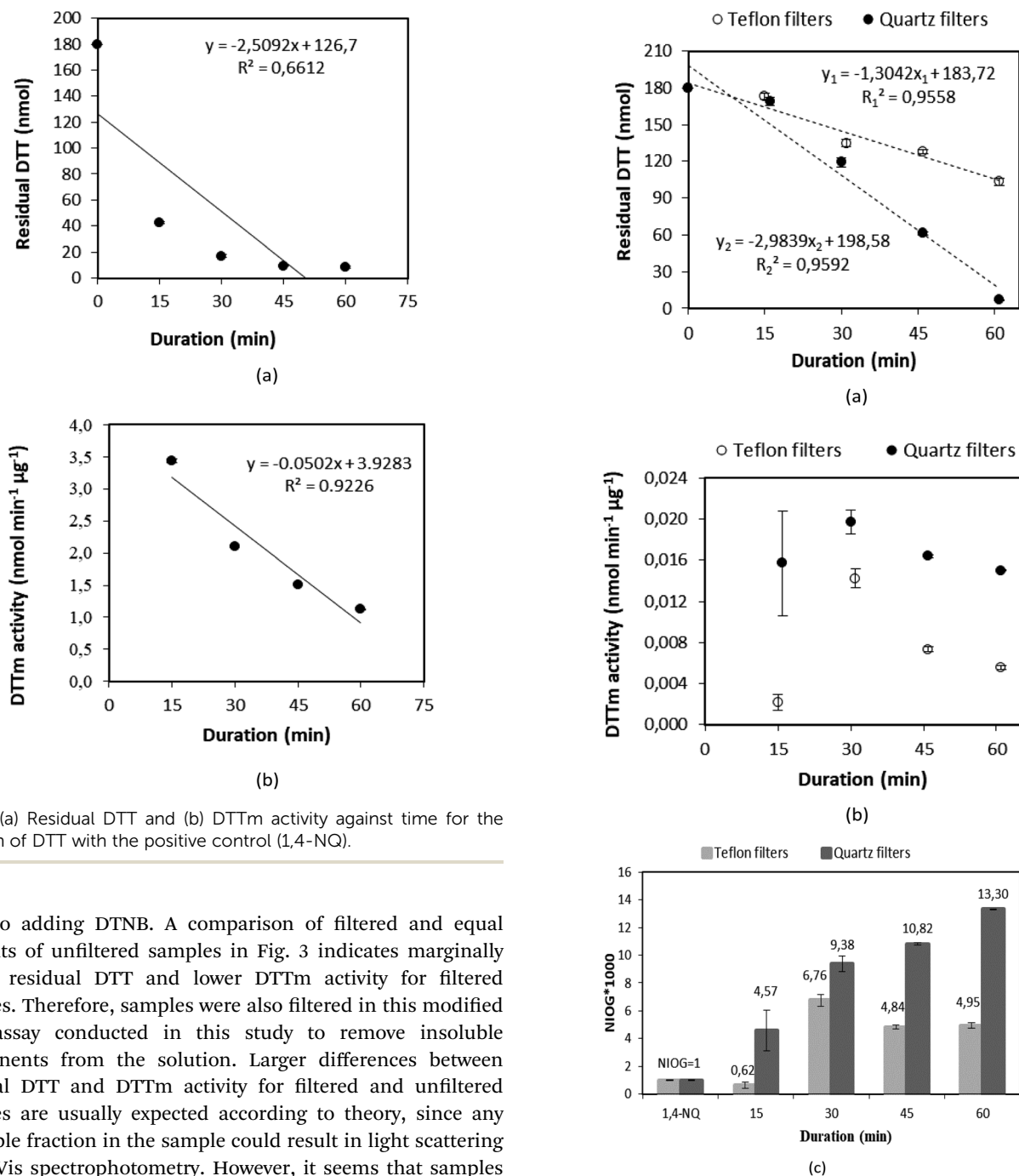
Fig. 4 (a) Residual DTT and (b) DTTm activity against time for the reaction of DTT with the positive control (1,4-NQ).

Fig. 5 (a) Residual DTT, (b) DTTm activity and (c) NIOG*1000 against time. The error bars show the standard deviation.

prior to adding DTNB. A comparison of filtered and equal amounts of unfiltered samples in Fig. 3 indicates marginally higher residual DTT and lower DTTm activity for filtered samples. Therefore, samples were also filtered in this modified DDT assay conducted in this study to remove insoluble components from the solution. Larger differences between residual DTT and DTTm activity for filtered and unfiltered samples are usually expected according to theory, since any insoluble fraction in the sample could result in light scattering in UV-Vis spectrophotometry. However, it seems that samples extracted in this study either had very low levels of insoluble species or insoluble species did not influence the analytical method. Also indicated in Fig. 3 is the difference between the addition of DTNB after 30- and 60 min reaction time of PM with DTT. Lower DTTm activity was determined for the reaction mixture subjected to DTNB after 60 min. Therefore, the optimum reaction time of 30 min prior to the addition of DTNB was chosen in the modified DTT assay.

2.2.4.3 Use of positive control (1,4-NQ). 1,4-NQ present in diesel car exhaust particles[33,52] has a relatively high content of quinones[33] and are commonly used as a reference quinone,[31,53–54] while it exhibits high OP and cytotoxicity. The reaction of 1,4-NQ with DTT was also explored to ascertain the

efficiency of the DTTm and DTNB concentrations, as well as to normalise the OP and toxicity of samples. In Fig. 4, the residual DTT and DTTm activity for the reaction of DTT with 1,4-NQ is plotted against time. It is evident that the DTTm activity decreased significantly with increased reaction time, which can be attributed to the catalytic redox reaction rates being higher with an increased reaction time. Therefore, these experiments confirmed the 30 minutes reaction time as determined in the previous section.
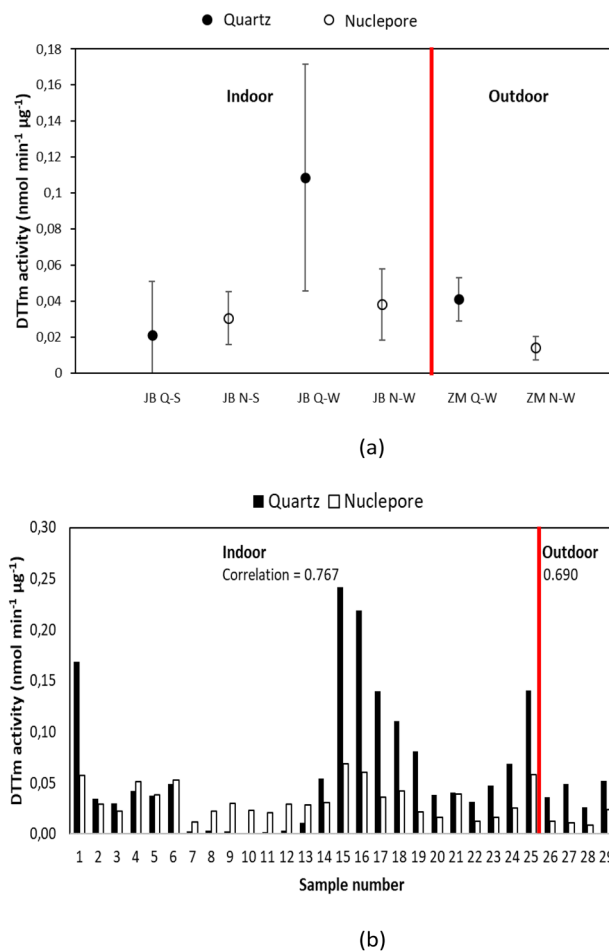
(a)

(b)

Fig. 6 Comparison of DTTm activity determined for PM₂.₅ collected on quartz and nucleopore filters at Jouberton (indoor) and Zamdela (ambient) for (a) the entire sampling campaign and (b) individual samples. JB-S = Jouberton summer, JB-W = Jouberton winter and ZM-W = Zamdela winter.
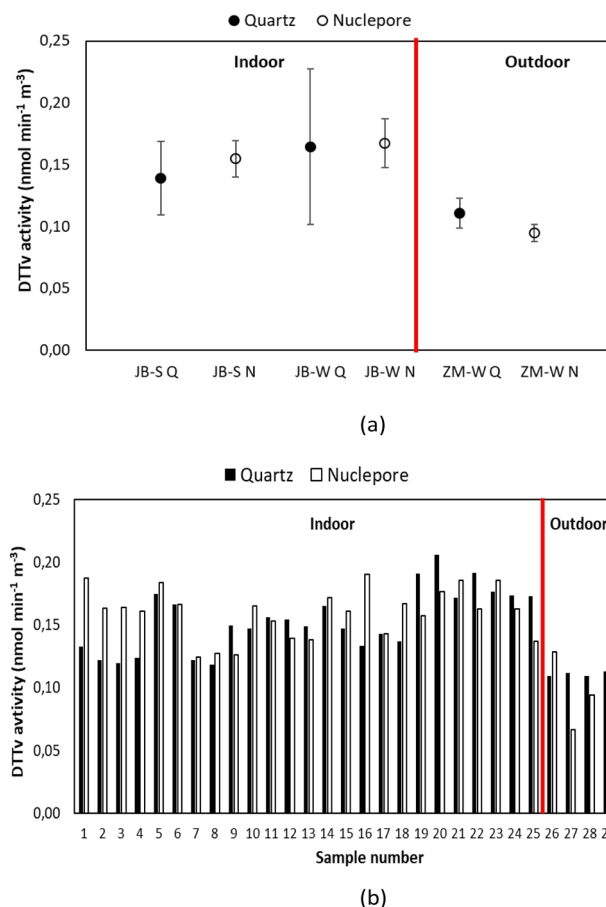

(a)

(b)

Fig. 7 Impacts of DTT redox activity determined for (a) total volume (mean values) on quartz and nucleopore filter types for PM₂.₅ collected at all the sites and for (b) individual samples. JB-S = Jouberton summer, JB-W = Jouberton winter and ZM-W = Zamdela winter.

2.2.4.4 Influence reaction time. Residual DTT and DTTm activity were determined on Quartz and Teflon™ filters at the optimised conditions determined in the previous tests at different reaction times. In addition, the NIOG for each of these experiments was also determined. These results are presented in Fig. 5. It is evident that higher DTTm activity was determined for Quartz filters (Fig. 5b and c) for all the reaction times, which can be attributed to Quartz filters absorbing more DTT during sonication to react with PM. It is also evident that the highest DTTm activity was determined for a reaction time of 30 min, which supports the optimised reaction time determined in the previous tests. DTTm activities determined were in the same order than DTTm activities determined in previous studies using extractants (*e.g.* Rattanavaraha *et al.*[30] and Geller *et al.*[32]).

2.2.5. Filter type. In addition to the above comparison of TPM collected from a diesel car exhaust on Quartz and Teflon filters, the OP determined with Nucleopore filters were also compared to the OP measured with Quartz filters for indoor and ambient PM₂.₅ collected at Jouberton (25 samples) and Zamdela (4 samples), respectively, which are presented in Fig. 6.

According to the knowledge of the authors, this comparison between OP determined with Quartz and Nucleopore filters has not been done before. With the exception of indoor particulates collected during summer, higher DTTm activity was determined for PM collected on Quartz filters. This suggests that organic species (which are reactive components) were readily extracted from the quartz filter samples during incubation with DTT. Lower DTTm activity values were associated with indoor samples collected on Quartz filters during summer at Jouberton (Fig. 6(a) and sample 4 to 13 in (b)) can possibly be ascribed to the removal of insoluble species during the filtration process. Despite the observed differences between the DTTm activity determined with Quartz and Nucleopore filters, a moderate to relatively strong correlation is determined between DTTm activity of PM collected on these two filter types, *i.e.* 0.767 and 0.690 for indoor and ambient samples, respectively. This implies that although the type of filter on which PM is collected for the DTT assay has an influence on the absolute DTT value, the relative contribution of PM collected on different filters will be meaningful. As mentioned previously, in this study PM was collected on nucleopore filters specifically for health tests, which were subsequently subjected to DTT redox activity assay.
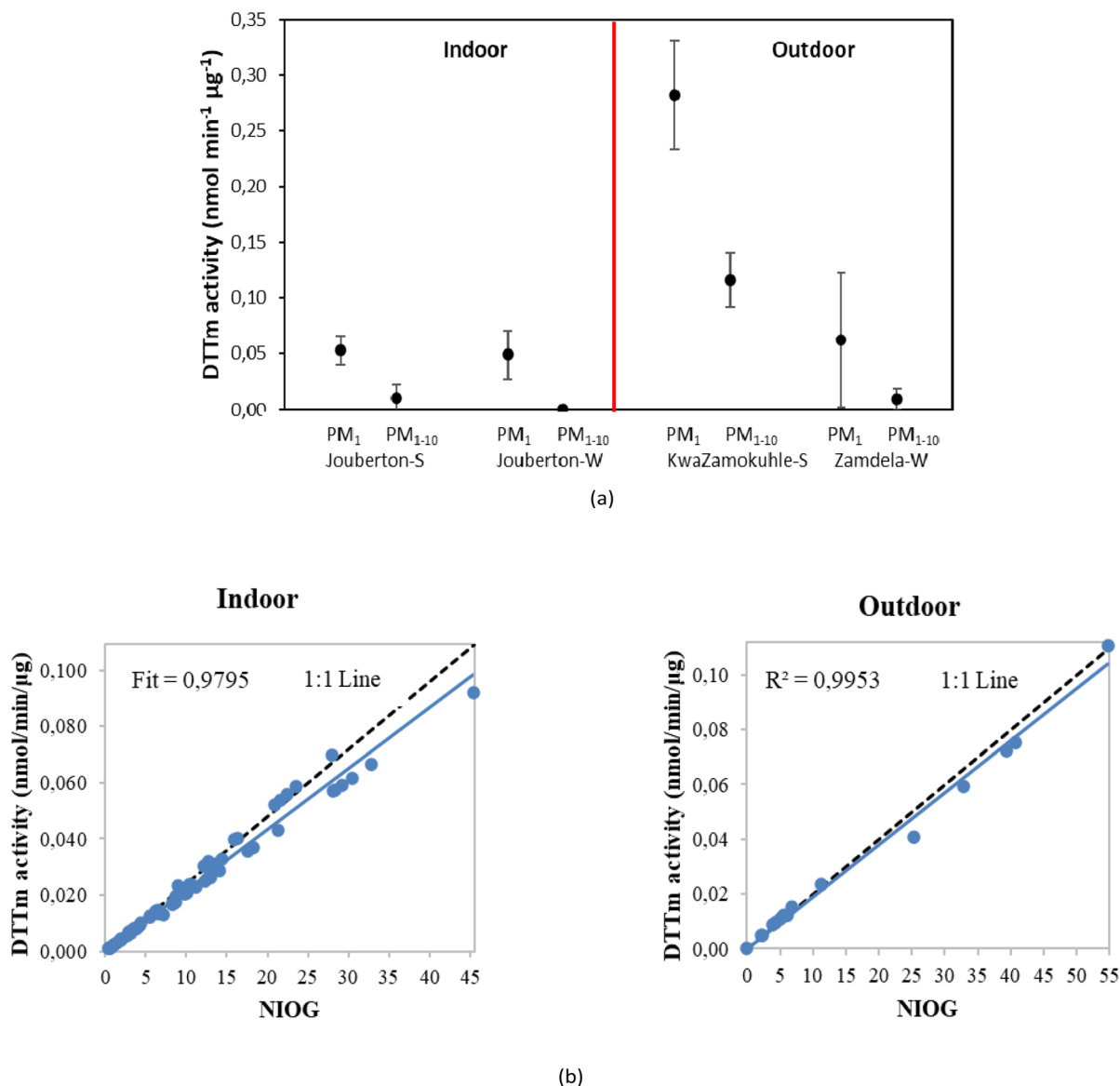
Fig. 8 (a) DTTm activity (nmol min^{-1} µg^{-1}) for PM nucleopore samples collected from Jouberton (summer and winter), KwaZamokuhle (summer) and Zamdela (winter) for PM$_1$ and PM$_{1-10}$ size fractions, and (b) correlation between DTTm activity and NIOG for outdoor and indoor samples.

Furthermore, DTT redox activity was normalised by total volume (DTTv) and assessed for PM$_{2.5}$ collected on Quartz and Nucleopore filters (Fig. 7). A significantly higher correlations are observed for DTTv, *i.e.* correlations of 0.97 and 0.94 for ambient and indoor samples, respectively, which implies that any filter type is suitable for DTTv analysis.

2.3. Chemical analysis

Detailed descriptions of the chemical analyses of PM collected at the three low-income urban settlements are presented in Segakweng *et al.*[43] In brief, concentrations of inorganic ions and water-soluble organic acids, organic- and elemental carbon (OC and EC, respectively), and trace elements were determined. Inorganic ionic species measured included sodium (Na$^+$),

ammonium (NH$_4^+$), potassium (K$^+$), magnesium (Mg^{2+}), and calcium (Ca^{2+}), fluoride (F$^-$), chloride (Cl$^-$), nitrate (NO$_3^-$) and sulphate (SO$_4^{2-}$), while-soluble organic acids included oxalic-(C$_2$O$_4^{2-}$), acetic-(CH$_3$COO$^-$), propionic-(C$_2$H$_5$COO$^-$) and formic acid (COO$^-$). These species were extracted in an ultrasonic bath with ultrapure water (resistivity ≈ 18.2 MΩ) and analysed with a Dionex ICS 3000 ion chromatograph (IC).[55,56]

Particulate OC and EC were quantified with a G4 ICARUS carbon analyser equipped with a non-dispersive infrared detector-NDIR, following a two-step thermal procedure developed by Cachier *et al.*[57] In this method, one part of the filter is firstly treated with a pre-combustion technique to remove OC to determine EC content and the other part is directly analysed with the carbon analyser to determine total carbon (TC). OC

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concentration can then be determined as the difference between TC and EC.

Trace elements were extracted from sampled filters with hot acid leaching,[58] with the extractant comprising aqueous HNO_3 and HCl solutions. The cooled-down extracts were then diluted with deionised water in volumetric flasks and subjected to analysis with an Agilent 7500c inductively coupled plasma mass spectrometer (ICP-MS). A total of 35 trace elements could be detected with ICP-MS analysis, which include Be, B, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Co, Ni, Zn, As, Se, Rb, Sr, Mo, Pd, Ag, Cd, Sb, Ba, Pt, Au, Hg, Tl, Pb, Bi, Th and U. Trace element concentrations below the detection limit of the ICP-MS were considered to have concentrations half the detection limit of the species considered, which is a precautionary assumption that is frequently used in health-related environmental studies (*e.g.* Van Zyl *et al.*[59]).

3. Results and discussions

3.1. DTTm redox activity of PM collected at low-income urban settlements

As indicated above, five PM size fractions were collected in this study (>2.5, 1.0–2.5, 0.50–1.0, 0.25–0.50, and <0.25 μm). However, due to the sample load on the nucleopore filters, it was decided to combine the three smaller size fractions, *i.e.* PM_1 and the two larger size fractions, *i.e.* PM_{1-10} for the modified DTT assay. The DTTm activity determined for the ambient and indoor particulates are presented in Fig. 8(a), while the 1 : 1 plot of DTTm activity *versus* NIOG is presented in Fig. 8(b). The mean DTTm activity values for indoor PM_{1-10} samples ranged between 0.001 and 0.056 nmol min^{-1} $μg^{-1}$, while DTTm activity for indoor PM_1 ranged between 0.017 and 0.149 nmol min^{-1} $μg^{-1}$. Ambient PM_{1-10} had DTTm activities that ranged from 0.004–0.116 nmol min^{-1} $μg^{-1}$, while DTTm activities of ambient PM_1 ranged from 0.019–0.282 nmol min^{-1} $μg^{-1}$. In Table 3, the DTTm activities determined in this study are compared with DTTm activities determined in previous studies conducted in other parts of the world. It is evident from Table 3 that the DTTm activities determined in this study for PM collected at low-income urban settlements are in the same range as DTTm activities reported in literature. However, some studies reported DTTm redox activities as high as 0.49 nmol min^{-1} $μg^{-1}$ for $PM_{2.5}$ collected at a peri-urban site in Beijing,[60] while DTTm activity values of 0.666, 0.617 and 0.484 nmol min^{-1} $μg^{-1}$ were reported for $PM_{0.18}$, $PM_{2.5}$ and $PM_{2.5-10}$ samples collected at an underground train station site in the Netherlands.[61]

It is evident from Fig. 8(a) that PM_1 had the highest DTTm activity at all three sampling sites, which also corresponds with literature (*e.g.* Janssen *et al.*[67] and Steenhof *et al.*[61]). In addition,

Table 3 Contextualisation of DTTm redox activity determined in this study[a]

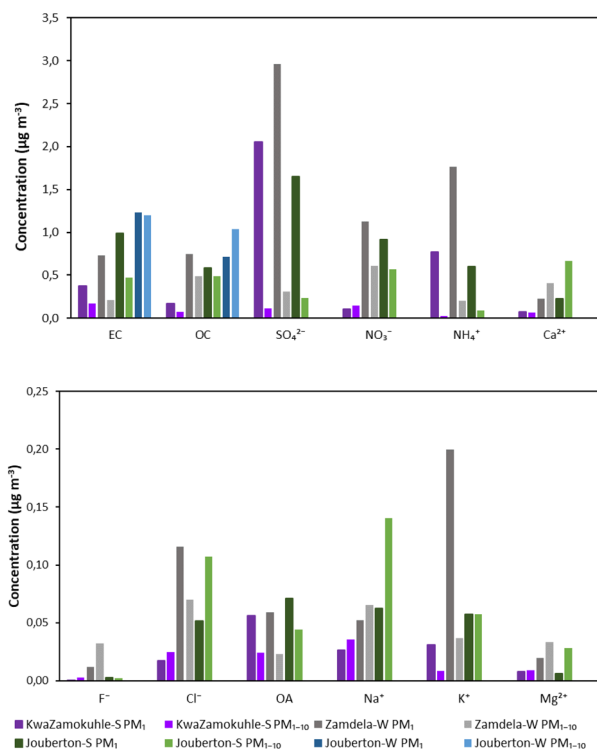| Source	Place	Particle size	DTTm activity (nmol min^{-1} $μg^{-1}$)
This study	South Africa (indoor)	PM_1	0.017–0.149 (mean = 0.061)
		PM_{1-10}	0.001–0.056 (mean = 0.011)
		Various	0.001–0.091 (mean = 0.025)
	South Africa (outdoor)	PM_1	0.019–0.282 (mean = 0.117)
		PM_{1-10}	0.004–0.116 (mean = 0.036)
		Various	0.004–0.150 (mean = 0.038)
Other countries			
Pietrogrande *et al.*[28]	Northern Italy	$PM_{2.5}$	0.006–0.014
Yu *et al.*[62]	Beijing	$PM_{2.5}$	0.13 ± 0.1
Samara[49]	Thessaloniki. Greece (UT)	Various	0.016–0.306 & 0.036–0.271
	Thessaloniki. Greece (UB)	Various	0.052–0.459 & 0.012–0.340
Chirizzi *et al.*[63]	Lecce. Southern Italy	$PM_{2.5}$	0.015 ± 0.008
		PM_{10}	0.011 ± 0.007
Vreeland *et al.*[51]	Atlanta (side street commute)	$PM_{2.5}$	0.05 ± 0.03
	Atlanta (highway commute)	$PM_{2.5}$	0.07 ± 0.07
Perrone *et al.*[64]	Milan. North Italy	TSP	0.33–3.43
Velali *et al.*[65]	Thessaloniki. Greece (UB)	Various	0.12–0.46 & 0.03–0.34
	Thessaloniki. Greece (UT)	Various	0.02–0.31 & 0.05–0.27
Shirmohammadi *et al.*[66]	Los Angeles	$PM_{2.5}$	0.020–0.045
		$PM_{0.18}$	0.020–0.060
Samara *et al.*[50]	Thessaloniki. Greece (UT)	PM_{10}	0.018–0.060
Janssen *et al.*[67]	Netherlands	$PM_{2.5}$	0.03–0.18
Liu *et al.*[60]	Beijing (peri – urban)	$PM_{2.5}$	0.11–0.49 (mean = 0.19)
	Beijing (central site)	$PM_{2.5}$	0.09–0.32 (mean = 0.24)
Saffari *et al.*[68]	Los Angeles. Basin	$PM_{2.5}$	0.03–0.11
Verma *et al.*[69]	South-eastern United States	$PM_{2.5}$	0.005–0.1
Charrier and Anastasio[70]		$PM_{2.5}$	0.02–0.06
Steenhof *et al.*[61]	Netherlands	$PM_{0.18}$	0.010–0.666
		$PM_{2.5}$	0.030–0.617
		$PM_{2.5-10}$	0.022–0.484

[a] UT=urban traffic, TSP=total suspended particles.

Fig. 9 Mean concentration of EC, OC, inorganic ions, and water-soluble organic acids (OA) at KwaZamokuhle, Zamdela and Jouberton in PM_1 and PM_{1-10} size fractions.
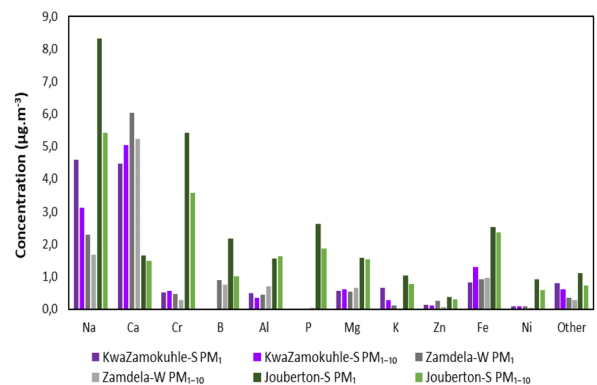

Fig. 10 Mean concentration of trace elements at KwaZamokuhle, Zamdela and Jouberton in PM_1 and PM_{1-10} size fractions.

the DTTm activities determined for outdoor samples were higher than the DTT values established for indoor PM, except for DTT measured in the PM_{1-10} size fraction at Zamdela. The highest DTTm activity were determined for ambient PM at KwaZamokuhle in both size fractions. Most studies have shown that ultrafine particles (UPFs) (particles of aerodynamic diameter < ~0.25 μm) had higher DTTm activity.[61,66,71,72] UPFs are strongly associated with impacts of cardiovascular diseases, oxidative stress and systemic inflammation, as well as activation of platelets.[73] Josipovic et al.[74] (Vaal Triangle, South African study) reported a higher percentage of DTT depletion in UPFs during the wet season and for larger particles during the dry season. Seasonal patterns could not be discerned due to the limitations in the collection of samples (no winter campaign was conducted for KwaZamokuhle), while the sample load of PM collected at Zamdela during summer was too low for DTT assay. No significant differences were observed in DTTm activity determined for indoor samples collected during winter and summer at Jouberton. A strong correlation is observed between DTTm redox activity and NIOG for indoor and ambient PM (R^2 = 0.9795 and 0.9953, respectively), which confirms the quality of the DTT assay conducted in this study.

Differences between the OP of outdoor and indoor aerosols have been reported in previous studies. Yang et al.[75] indicated the OP of outdoor $PM_{2.5}$ being twice as high as indoor $PM_{2.5}$ at Nanjing, China. This was attributed to a decrease in the oxidative reduction of PM during outdoor-to-indoor transport. However, Khurshid et al.[76] reported indoor OP (using electron paramagnetic resonance spectrometry assay) being ~3.5 times higher than that of outdoor OP of aerosols, which were influenced by several factors, such as ventilation rate, temperature, and relative humidity.

3.2. DTTm activity and aerosol chemistry

In Segakweng et al.[43] a detailed assessment of the chemical composition of PM_1, $PM_{1-2.5}$ and $PM_{2.5-10}$ collected in these low-income urban settlements is presented. However, in order to relate the chemical characteristics of PM to the DTTm activities determined in this study, the average concentrations measured for inorganic ions, water-soluble organic compounds, OC, EC and trace elements in PM_1 and PM_{1-10} collected at KwaZamokuhle, Zamdela and Jouberton are presented in Fig. 9 (inorganic ions, water-soluble organic acids, OC and EC) and in Fig. 10 (trace elements). As mentioned above, no PM was collected on

Table 4 OC/EC, SO_4^{2-}/EC, EC/TPM, aSO_4^{2-}/TPM and TE/TPM ratios in PM_1 and PM_{1-10} size fractions for outdoor (KwaZamokuhle summer and Zamdela winter) and indoor (Jouberton summer and winter) sites

Ratio	KwaZamokuhle-S		Zamdela-W		Jouberton-S		Jouberton-W	
	PM_1	PM_{1-10}	PM_1	PM_{1-10}	PM_1	PM_{1-10}	PM_1	PM_{1-10}
OC/EC	0.46	0.44	1.02	2.33	0.59	1.03	0.58	0.87
SO_4^{2-}/EC	5.50	0.66	4.07	1.50	1.67	0.51	—	—
EC/TPM	0.05	0.03	0.03	0.01	0.03	0.01	0.04	0.02
SO_4^{2-}/TPM	0.26	0.02	0.11	0.01	0.04	0.01	—	—
TE/TPM	1.67	1.85	0.45	0.39	0.79	0.48	—	—

Teflon™ filters during the winter campaign at Jouberton due to issues with sampling instruments. As indicated and discussed in detail by Segakweng et al.,[43] the highest concentrations of most species (e.g. SO_4^{2-}, NH_4^+, water-soluble OAs, EC and OC) were in the PM_1 size fraction, while higher levels of these species were generally determined for indoor particulates with the exception of certain important species e.g. SO_4^{2-}, NO_3^-, NH_4^+ and Ca. The highest DTTm activities presented above correspond to the highest concentrations of chemical species being in the PM_1 size fraction. Other deductions from the comparison of aerosol chemistry to DTTm activity are not that obvious, which can be attributed to the logistical constraints in this study and complex atmospheric chemistry. In addition, seasonal variability could also no be distinctly established for DTTm activity and for aerosol chemistry.

OC/EC, SO_4^{2-}/EC, EC/TPM (total particulate matter), SO_4^{2-}/ TPM and TE (total trace elements)/TPM ratios are presented in Table 4 for PM_1 and PM_{1-10}. Higher SO_4^{2-}/EC, EC/TPM and SO_4^{2-}/TPM ratios are observed for PM_1 at all sites. In addition, TE/TPM was also higher for the PM_1 size fraction apart from of this ratio calculated for KwaZamokuhle. OC/EC ratios were higher in the PM_{1-10} size fraction except for the OC/EC ratio determined at KwaZamokuhle, which was marginally higher in PM_1. As explained in Segakweng et al.,[43] higher SO_4^{2-}/EC and SO_4^{2-}/TPM ratios observed in outdoor sites indicate the influence of industrial combustion emissions, while higher EC/TPM ratios indicate the impact of domestic and open biomass burning.

3.3. Statistical correlations between DTTm activity and concentrations of chemical species

DTTm activity for ambient and indoor PM_1 and PM_{1-10} statistically correlates with the chemical species. In these correlations, both the mass normalised DTT activity (nmol min^{-1} μg^{-1}) and the mass normalised concentrations of chemical species (through calculation of the ratio between the concentrations of chemical species and the total PM concentrations) were used. These correlations are presented in Table 5. Good correlation between DTTm redox activity and chemical species is obtained on the PM_{1-10} size fraction for both outdoor and indoor measurements. For indoor samples, a good correlation was observed between DTTm activity and EC/PM, TC/PM, F$^-$/ PM, NO_3^-/PM, NH_4^+/PM and WSI (sum of ionic species)/PM. Indoor (Jouberton summer and winter) also displayed higher OC/EC ratios in the PM_{1-10} size fraction. Most of the ratios (EC/ PM, TC/PM, SO_4^{2-}/PM, NO_3^-/PM, K$^+$/PM, OA/PM and overall WSI/PM) for outdoor samples displayed a good correlation with DTTm activity of PM on the PM_{1-10} size fraction. Note that a strong correlation was obtained between OA/PM for outdoor samples in both size particle fractions as well as EC/PM and TC/ PM. This agrees with the OC/EC values observed in both size particle fractions in KwaZamokuhle. Strong correlation between DTTm activity and trace elements was also observed in the PM_{1-10} size fraction for both outdoor and indoor measurements, with outdoor displaying an important correlation (even redox-active elements such as Cu, Fe and Mn). This is in agreement

with the total TE/TPM ratio, which is higher in the PM_{1-10} for outdoor samples.

To conclude, Table 5 shows that lower correlations are obtained for the PM_1 size fraction than for the PM_{1-10} size fraction, which may be unexpected. However, it is important to mention that fine particles are included in our PM_{1-10} size fraction with noticeable effects on oxidative potential. Moreover, as it may be

Table 5 Correlation between mass normalised DTTm activity, and the ratio between the concentrations of chemical species and the total PM concentrations

Ratios	>0.70	0.50 − 0.70	0.00 − 0.50	<0.00
	Indoor		Outdoor	
	PM_{1-10}	PM_1	PM_{1-10}	PM_1
EC/PM	0.94	0.47	0.99	0.85
OC/PM	0.39	0.10	−0.32	0.69
TC/PM	0.85	0.42	0.98	0.82
F$^-$/PM	0.83	−0.19	−0.07	−0.78
Cl$^-$/PM	0.33	0.25	−0.53	−0.95
SO_4^{2-}/PM	0.41	−0.37	0.88	−0.67
NO_3^-/PM	0.80	−0.07	0.87	−0.73
Na$^+$/PM	0.37	0.05	0.20	−0.33
NH_4^+/PM	0.83	−0.20	0.42	−0.93
K$^+$/PM	0.49	0.08	0.70	−0.94
Mg^{2+}/PM	0.41	0.09	−0.09	−0.60
Ca^{2+}/PM	0.44	−0.20	0.22	−0.49
OA/PM	0.37	0.10	0.98	0.93
WSI/PM	0.67	−0.27	0.73	−0.85
Be/PM	0.80	0.02	0.70	−0.11
B/PM	0.58	0.09	−0.72	−0.66
Na/PM	0.58	0.75	1.00	0.00
Mg/PM	0.40	0.37	0.97	0.89
Al/PM	0.75	0.08	0.99	−0.27
P/PM	−0.18	0.67	−0.99	−0.69
K/PM	0.86	−0.13	1.00	−0.50
Ca/PM	0.58	−0.19	0.99	0.86
Ti /PM	0.74	0.30	0.98	−0.30
V/PM	0.62	0.35	−0.97	−0.69
Cr/PM	0.48	0.59	−0.87	−0.61
Mn/PM	0.57	0.47	0.99	−0.67
Fe/PM	0.59	0.39	0.97	−0.47
Co/PM	0.16	0.22	−0.19	−0.59
Ni/PM	0.40	0.24	−0.28	−0.63
Cu/PM	0.39	0.14	0.99	−0.45
Zn/PM	0.52	0.46	0.89	−0.01
As/PM	0.70	0.08	−0.66	−0.70
Se/PM	0.84	0.03	0.21	0.17
Rb/PM	0.89	0.17	0.99	−0.38
Sr/PM	0.69	−0.20	0.99	0.51
Mo/PM	0.68	0.51	−0.99	−0.65
Pd/PM	0.70	−0.14	0.95	−0.35
Ag/PM	−0.04	0.20	0.29	−0.18
Cd/PM	0.48	−0.29	−0.12	0.15
Sb/PM	0.70	0.12	−0.78	−0.49
Ba/PM	0.72	−0.15	0.98	0.92
Pt/PM	0.42	−0.21	0.99	0.59
Au/PM	0.13	−0.15	−0.54	0.06
Tl/PM	0.25	0.19	0.21	−0.05
Pb/PM	−0.07	0.24	1.00	0.86
Bi/PM	0.85	−0.32	0.95	0.95
Th/PM	−0.14	−0.07	0.90	0.26
U/PM	0.67	0.36	0.95	0.64
TE/PM	0.65	0.34	0.99	0.83

Table 6 Comparison between DTT activity correlations with chemical species determined in this study with correlations determined in other studies

	This study Indoor PM_1	Indoor PM_{1-10}	Outdoor PM_1	Outdoor PM_{1-10}	(Pietrogrande et al. 2021)[28] P Buffer $PM_{2,5}$	Gamble $PM_{2,5}$	MeOH $PM_{2,5}$	(Yang et al. 2019)[79] Gasoline direct injection vehicles	(Pietrogrande et al. 2018)[14] Northern Italy (industrial) PM_{10}	Background PM_{10}	(Karavalakis et al. 2017)[77] Heavy-duty vehicles	(Perrone et al. 2016)[64] Milan, Northern Italy	(Janssen et al. 2014)[20] $PM_{2,5}$	$PM_{2,5-10}$	PM_{10} ($PM_{2,5+}$ $_{2,5-10}$)	(Yang et al. 2014)[14] Met Q	Met T	H_2O T	All	(Ntziachristos et al. 2007)[78] $PM_{0,15}$	$PM_{2,5}$
EC	0.47	0.94	0.85	0.99	0.51	0.78	0.63	—	—	—	—	0.27	0.24	0.64	0.40	0.38	0.35	0.32	0.26	0.14	−0.18
OC	0.10	0.39	0.69	−0.32	0.42	0.67	0.55	—	—	—	—	−0.30	0.69	0.45	−0.13	0.88	0.95	0.96	0.12	0.92	0.79
Al	0.08	0.75	−0.27	0.99	—	—	—	0.18	0.25	0.35	—	−0.21	—	—	—	0.80	0.74	0.72	—	−0.10	−0.67
Cr	0.59	0.48	−0.61	−0.87	—	—	—	0.40	−0.06	−0.13	—	—	—	—	—	0.57	0.41	0.46	0.65	0.53	0.86
Cu	0.14	0.39	−0.45	0.99	0.34	0.54	0.42	0.20	0.58	0.69	1.00	−0.24	0.25	0.54	0.47	0.62	0.66	0.63	—	0.95	0.94
Fe	0.39	0.59	−0.47	0.97	0.36	0.61	0.47	0.21	0.38	0.60	0.99	−0.43	0.31	0.47	0.44	0.63	0.68	0.64	—	0.95	0.96
K	−0.13	0.86	−0.50	1.00	—	—	—	0.09	0.75	0.79	—	—	—	—	—	0.82	0.87	0.90	—	−0.06	−0.69
Mn	0.47	0.57	−0.67	0.99	0.27	0.87	0.76	0.24	0.61	0.68	—	−0.35	—	—	—	0.67	0.65	0.61	—	0.90	0.78
Ni	0.24	0.40	−0.63	−0.28	—	—	—	0.32	0.36	0.41	—	0.18	0.01	0.25	0.34	0.15	0.13	0.20	—	0.55	−0.46
Pb	0.24	−0.07	0.86	1.00	0.43	0.47	0.68	0.08	0.3	0.68	—	−0.52	—	—	—	0.33	0.56	0.54	—	0.95	0.88
Ti	0.30	0.74	−0.30	0.98	—	—	—	0.55	—	—	—	—	—	—	—	0.34	0.09	0.20	—	0.66	0.67
V	0.35	0.62	−0.69	−0.97	0.08	0.44	0.23	0.29	0.09	0.23	—	−0.46	−0.11	0.27	0.51	−0.05	−0.10	−0.05	—	0.32	0.19
Zn	0.46	0.52	−0.01	0.89	—	—	—	0.41	0.51	0.68	—	−0.40	—	—	—	0.63	0.68	0.67	—	0.93	0.52
Ca	−0.19	0.58	0.86	0.99	—	—	—	0.18	0.50	0.55	—	−0.19	—	—	—	—	—	—	—	0.55	−0.62
P	0.67	−0.18	−0.69	−0.99	—	—	—	0.61	—	—	—	—	—	—	—	—	—	—	—	—	—
Na	0.75	0.58	0.00	1.00	—	—	—	0.04	0.56	0.61	—	—	—	—	—	—	—	—	—	−0.66	0.03
Mg	0.37	0.40	0.89	0.97	—	—	—	0.46	—	—	—	−0.55	—	—	—	—	—	—	—	—	−0.52
Mo	0.51	0.68	−0.65	−0.99	—	—	—	0.43	—	—	—	—	—	—	—	—	—	—	—	—	—
Pd	−0.14	0.70	−0.35	0.95	—	—	—	0.16	—	—	—	—	—	—	—	—	—	—	—	—	—
Sr	−0.20	0.69	0.51	0.99	—	—	—	0.32	0.41	0.45	—	−0.22	—	—	—	—	—	—	—	0.74	0.70
Co	0.22	0.16	−0.59	−0.19	—	—	—	0.04	—	—	—	−0.13	—	—	—	—	—	—	—	—	—
As	0.08	0.70	−0.70	−0.66	—	—	—	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—
Ag	0.20	−0.04	−0.18	0.29	—	—	—	0.26	—	—	—	—	—	—	—	—	—	—	—	—	—
Sb	0.12	0.70	−0.49	−0.78	—	—	—	0.68	—	—	—	—	—	—	—	—	—	—	—	—	—
Rb	0.17	0.89	−0.38	0.99	—	—	—	0.01	0.83	0.85	—	−0.46	—	—	—	—	—	—	—	—	—
Cd	−0.29	0.48	0.15	−0.12	—	—	—	—	—	—	—	−0.21	—	—	—	—	—	—	—	—	—
Ba	−0.15	0.72	0.92	0.98	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.89	0.92
Total	0.34	0.65	0.83	0.99	0.24	0.64	0.40	0.92	—	—	—	—	—	—	—	—	—	—	—	0.44	−0.12
TE	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NO_3^-/NO_3	−0.07	0.80	−0.73	0.87	0.24	0.36	0.31	—	0.40	0.45	—	−0.11	0.51	0.47	0.16	—	—	—	—	−0.63	−0.81
SO_4^{2-}/SO_4	−0.37	0.41	−0.67	0.88	0.45	0.38	0.50	—	0.47	0.7	—	0.16	0.41	0.59	0.46	—	—	—	—	−0.75	−0.80
F^-	−0.19	0.83	−0.78	−0.07	—	—	—	—	—	—	—	−0.47	—	—	—	—	—	—	—	—	—
Cl^-	0.25	0.33	−0.95	−0.53	0.47	0.40	0.47	—	0.09	0.17	—	−0.35	—	—	—	—	—	—	—	—	—
Na^+	0.05	0.37	−0.33	0.20	—	—	—	—	0.32	0.24	—	—	—	—	—	—	—	—	—	—	—
NH_4^+	−0.20	0.83	−0.93	0.42	—	—	—	—	0.46	0.67	—	0.06	—	—	—	—	—	—	—	—	—

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Table 6 (Contd.)

	This study				(Pietrogrande et al. 2021)[28]			(Yang et al. 2019)[79]	(Pietrogrande et al. 2018)[14]		(Karavalakis et al. 2017)[77]	(Perrone et al. 2016)[64]	(Janssen et al. 2014)[20]			(Yang et al. 2014)[14]				(Ntziachristos et al. 2007)[78]	
	Indoor		Outdoor		P Buffer	Gamble	MeOH	Gasoline direct injection vehicles	Northern Italy (industrial)	Background	Heavy-duty vehicles	Milan, Northern Italy				Met Q	Met T	H₂O T	All		
	PM₁	PM₁₋₁₀	PM₁	PM₁₋₁₀	PM₂,₅	PM₂,₅	PM₂,₅		PM₁₀	PM₁₀		PM₁₀	PM₂,₅	PM₂,₅₋₁₀	PM₁₀ (PM₂,₅₋₁₀)					PM₀,₁₅	PM₂,₅
K⁺	0.08	0.49	−0.94	0.70	—	—	—	—	0.77	0.84	—	−0.39	—	—	—	—	—	—	—	—	—
Mg²⁺	0.09	0.41	−0.60	−0.09	—	—	—	—	0.57	0.62	—	—	—	—	—	—	—	—	—	—	—
Ca²⁺	−0.20	0.44	−0.49	0.22	—	—	—	—	0.52	0.57	—	−0.27	—	—	—	—	—	—	—	—	—
OA	0.10	0.37	0.93	0.98	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
WSI	−0.27	0.67	−0.85	0.73	—	—	—	—	0.57	0.73	—	—	—	—	—	—	—	—	—	—	—

seen, better correlations between EC/PM, OC/PM, TC/PM, and OA/PM and DTTm activities for the PM₁ size fraction may be observed for outdoor than for indoor samples. This could be due to the different relative contributions of EC and organic aerosol in the samples.

Furthermore, the correlations between DTTm activity and individual chemical species in this study are compared to those of previous studies, which are presented in Table 6 for different size fractions. Cu, Fe and Mn strongly correlate with DTTm activity on the PM₁₋₁₀ size fraction for outdoor compared to indoor samples, whereas the other redox-active transition elements show negative to moderate positive correlation for both size fractions. Previous studies also reported a good correlation between DTTm activity and redox-active transition elements.[77,78] Crustal elements such as Al, K, Mg, Ti and Ca also show good correlation for PM₁₋₁₀ size particles with outdoor displaying the strongest correlation. The correlation is higher than that reported in previous studies.[79] Pietrogrande et al.[14] reported moderate to good correlation for crustal elements (Cu, Fe, K, Mn and Ca) ranging from 0.55–0.79 on the PM₁₀ size fraction. A strong correlation between crustal elements and DTTm activity (0.61–0.90, except for Ti) was also reported previously for different extraction methods with no information on particular size fraction.[20] Overall, trace elements in this study conducted at low-income informal settlements in South Africa display a good correlation with DTTm activity. Yang et al.[79] reported strong correlations (0.92 for total PM with particle size not specified), while Pietrogrande et al.[28] indicated good or moderate correlations (0.64) for PM₂,₅ between the total sum of trace elements and DTTm activity. In contrast, Ntziachristos et al.[78] reported weak correlation between metals/elements and DTTm activity (−0.19 to 0.44). Outdoor samples, in this study, displayed the strongest correlation between trace elements and DTTm activity for both size fractions.

Outdoor and indoor samples show good correlation between EC/PM and DTTm activity compared to OC/PM. This agrees with the study of Janssen et al.[67] for PM₂,₅₋₁₀ and PM₁₀, Pietrogrande et al.[28] for PM₂,₅ and Ntziachristos et al.[78] for various sizes and is the opposite from findings from other studies.[20] Good correlation between EC/PM and DTTm activity is stronger on the PM₁₋₁₀ size fraction with outdoor displaying a strong correlation in both size fractions. A good correlation between DTTm activity and OC/PM is observed in the PM₁ size fraction (0.69) for outdoor measurements, which is interesting as it is similar to that of previous studies of 0.67 for PM₂,₅ (ref. 28) and 0.69 for PM₂,₅.[20] Puthussery et al.[42] found a good correlation between DTTm activity (intrinsic OP, mass normalised DTT activity) and oxygenated organic aerosol species (aged aerosols) (r = 0.79), a family of CHO>1 (r = 0.80), K (r = 0.70) and SO₄²⁻ (r = 0.68).

Finally, as stated above, good correlation between WSI and DTTm activity is mainly observed in the PM₁₋₁₀ size fraction. This agrees with literature where SO₄²⁻, HN₄⁺, K⁺, Mg²⁺, Ca²⁺ and overall WSI showed moderate to good correlation (0.52–0.84) for PM₁₀,[14] while correlations in previous studies were negative to moderate.[64,67,78] The good correlation between DTTm activity and OA/PM for both size fractions observed in this study is not reported in previous studies.
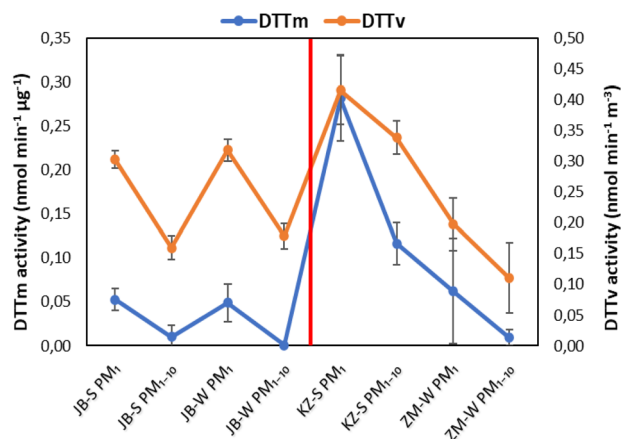
Fig. 11 Comparison of DTTm and DTTv in low-income urban settlements for outdoor and indoor samples. JB-S = Jouberton summer, JB-W = Jouberton winter, KZ-S = KwaZamokuhle summer and ZM-W = Zamdela winter.

3.4. Comparison between DTTv and DTTm

The highest DTT_v (representing the atmospheric aerosol OP) activity is also displayed in the PM_1 size fraction at all three sites (Fig. 11). For indoor aerosols, DTTv is marginally higher in winter compared to summer in both size fractions. This could be due to increased grass and waste burning practices in Jouberton that occur during either season. As previously mentioned, not much can be said about seasonality in the outdoor environments due to sampling logistics and less sample loading on some of the filters. Comparisons between DTTm (DTT consumption rate normalised by PM mass) and DTTv at three low-income urban settlements indicate that both DTTm and DTTv are higher in the PM_1 size fraction for all the sites. In addition, DTTv are higher than DTTm in all samples collected at the three sites in both size fractions. Pietrogrande et al.[28] also reported higher DTTv values (ranging from 0.02–0.41 nmol min^{-1} m^3) compared to DTTm (ranging from 0.001–0.021 nmol min^{-1} µg^{-1}) for ambient $PM_{2.5}$ samples extracted with a different solvent mixture.

DTTv for outdoor and indoor PM_1 and PM_{1-10} is statistically correlated with the chemical species. These correlations are presented in Table 7. Good correlations between DTTv and some chemical species are obtained on the PM_1 size fraction for both outdoor and indoor measurements. For indoor samples, a good correlation is observed between DTTv and Cl^- (0.60) and Mg^{2+} (0.65) on the PM_1 size fraction and SO_4^{2-} (0.64) and Ca^{2+} (0.63) on the PM_{1-10} size fraction. No correlation is observed between DTTv and carbonaceous aerosols for indoors. Most of the ions (SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, OA and overall WSI) for outdoor samples display good to strong correlation with DTTv on the PM_1 size fraction ranging from 0.60 to 1.0. Calas et al.[80] reported good correlation between few ionic species (Cl^-, NO_3^- and K^+) and DTTv of ambient aerosols in the PM_{10} size fraction ranging from 0.60 to 0.83. It is noted that strong correlation of 0.79 is obtained between OC and DTTv for outdoor samples on the PM_{1-10} size particle fraction, whereas the correlation is a bit

Table 7 Correlation between volume normalised DTT activity and the concentrations of chemical species

	>0.70	0.50 – 0.70	0.00 – 0.50	<0.00
	Indoor		**Outdoor**	
	PM_{1-10}	PM_1	PM_{1-10}	PM_1
EC	−0.09	−0.25	−0.22	0.30
OC	0.28	−0.02	0.79	0.59
TC	0.14	−0.13	0.52	0.48
F$^-$	0.45	−0.46	0.49	−0.55
Cl$^-$	0.59	0.60	0.57	−0.01
SO$_4^{2-}$	0.64	−0.57	0.45	0.88
NO$_3^-$	−0.17	0.02	0.06	1.00
Na$^+$	0.56	0.19	0.97	0.91
NH$_4^+$	−0.28	−0.30	−0.16	0.77
K$^+$	0.57	0.10	0.05	0.74
Mg^{2+}	0.59	0.65	0.35	−1.00
Ca^{2+}	0.63	−0.39	0.23	−0.93
OA	0.53	0.12	0.69	0.96
WSI	0.43	−0.42	0.19	0.89
Be	−0.20	0.01	−1.00	0.99
B	−0.32	−0.43	1.00	0.58
Na	0.53	0.53	0.90	0.91
Mg	0.01	−0.48	0.97	0.71
Al	−0.32	−0.13	0.70	0.72
P	0.76	0.73	0.79	0.46
K	−0.47	−0.41	−1.00	0.69
Ca	0.13	−0.20	0.86	0.96
Ti	−0.12	−0.15	0.44	0.88
V	0.48	0.58	0.72	0.96
Cr	0.62	0.64	1.00	0.62
Mn	0.53	0.66	0.15	0.70
Fe	0.45	0.65	0.43	0.60
Co	0.22	0.55	−1.00	−0.99
Ni	0.20	0.63	0.80	1.00
Cu	−0.42	0.18	−0.27	0.79
Zn	0.27	0.24	0.78	0.75
As	0.16	0.36	0.53	0.48
Se	0.01	0.23	0.66	0.49
Rb	−0.20	0.25	0.13	0.70
Sr	−0.32	−0.40	0.80	0.80
Mo	0.47	0.53	0.69	−0.94
Pd	0.59	−0.54	0.74	−0.95
Ag	0.13	0.66	0.36	0.27
Cd	−0.20	−0.37	−1.00	0.60
Sb	0.24	0.36	0.09	0.69
Ba	−0.03	−0.15	0.71	−0.04
Pt	−0.56	−0.51	0.36	−1.00
Au	−0.23	−0.03	0.84	−0.99
Hg	−0.68	−0.45	0.98	0.59
Tl	0.43	0.60	−1.00	−0.99
Pb	−0.31	0.45	0.91	−0.77
Bi	0.16	−0.28	0.96	0.05
Th	0.30	−0.09	0.72	0.40
U	−0.17	−0.32	0.97	0.70
TE	0.34	0.48	0.97	0.65

lower in the PM_1 size fraction, as shown for DTTm in Section 3.3. A strong correlation was also previously observed between DTTv and OC (ranging from 0.75–0.86) and EC (0.64–0.93) for PM_{10} size particles.[80] Good correlations between DTTv and trace elements are observed in both size particle fractions (PM_1 and PM_{1-10}) for outdoor measurements, while for indoor measurements, good correlation is observed on the PM_1 size fraction.

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Outdoor displaying important correlation for redox-active elements such as Cu (0.79), Fe (0.60) and Mn (0.70). Calas *et al.*[80] also obtained good correlation for redox-active elements such as Cu (0.77), Fe (0.76) and Mn (0.68) in one of the urban French sampling sites (Grenoble).

4. Conclusions

The DTT redox activity methodology was successfully modified from previous studies, while the influence of concentration, volume, time, filter type, sonication and filtration were investigated. The optimum DTT concentration and volume determined were 60 μM and 3 mL, respectively, while the DTNB concentration and volume were fixed at 10 mM and 50 μL, respectively. The reaction was performed with sonication and filtration at a reaction time of 30 minutes. Quartz filters displayed higher DTT activity, which therefore indicated that this type of filter is satisfactory for determining DTTm, whereas any filter is adequate to establish DTTv. DTTm activities determined were in the same order than DTTm activities determined in previous studies using extractants.

The DTT activity could be determined for size-segregated PM samples collected at three low-income urban settlements in South Africa, *i.e.* indoor samples at Jouberton during winter and summer, and outdoor samples collected during summer and winter at KwaZamokuhle and Zamdela, respectively. DTTm activity was higher in the PM_1 size fraction for all three sites, which suggested that particles of the coarser mode are less enriched with DTT-active compounds compared to that of the finest (ultrafine) particles. DTTm activity correlated with most of the chemical species on the PM_{1-10} particle fraction, especially for outdoor samples. DTTm activity was strongly correlated with EC (more than OC), indicating the impact of vehicular emissions and other combustion sources on the OP of PM. There was also a strong correlation between DTTm activity and trace elements in general (except for PM_1 indoors), while inorganic ions only revealed strong correlation in the PM_{1-10} size fraction of outdoor and indoor particulates. Results determined for outdoor particles suggest that the OP of PM is influenced by a combination of different contribution sources, including primary emissions such as traffic or vehicular emissions (Fe, Ca, Pb, Mg, EC), biomass burning (EC, K, Rb), industrial or factory (Cu, Zn, NO_3^-, SO_4^{2-}, Ca^{2+}, NH_4^+, Cl^-), as well as secondary particle formation (*e.g.* SO_4^{2-}). The oxidative potential of PM is also affected by domestic and biomass burning (*e.g.* OC, EC and OA) from outdoor atmospheric aerosols. OP of PM in an indoor environment (*e.g.* in Jouberton) may be impacted by different source emissions such as domestic and biomass burning (carbonaceous aerosols), industrial emissions (*e.g.* Cu, Zn, NO_3^-, SO_4^{2-}, Ca^{2+}, NH_4^+, Cl^-), vehicle emissions and unpaved roads (*e.g.* Fe, Ca, Mn, Mg, Al, Ti, K).

DTTv showed good correlations with most of the chemical species on the PM_1 particle fraction, especially for outdoor samples. DTTv activity was strongly correlated with OC (higher than EC), indicating the impact of combustion emissions. There was also a strong correlation between DTTv and trace elements in general (except for indoors), while inorganic ions revealed strong correlation in the PM_1 size fraction of outdoor particulates. In conclusion, variation of DTTm and DTTv values is coherent with that of aerosol chemical composition.

The technique used in this study to relate the potential impact of particulates on human health proved to be effective in establishing the link between atmospheric pollutants and sources and human health. The long-term monitoring of DTT redox activity could be a strong and easy – to – set up indicator to measure the health impact of emission mitigations, especially for decision-makers. However, further research is essential, especially in South Africa, which include assessment of seasonal patterns on DTT redox activity. It would be also interesting to investigate the DTTv on personal exposure samples because it outlines the real exposure of atmospheric aerosols to the population. Other proxy methods to relate the impacts of aerosol on human health could also be considered. Finally, future human health studies, including both *in vitro* and *in vivo* measurements involving humans, would also be needed in South Africa, to improve the assessment of the impacts of atmospheric pollution on human health in terms of diseases, mortality, *etc.*, and the link with oxidative potential and inflammatory impacts.

Data availability

As soon as the manuscript is approved for publication and a permanent DOI number is obtained for the dataset, it will be indicated in the manuscript.

Author contributions

CKS, CL and PGvZ were the main investigators in this study and wrote the manuscript. CKS conducted this study as part of her PhD degree, as well as performed most of the experimental work and data processing. The project was led by PGvZ, CL and JPB, which were also study leaders of the PhD. SG, EG, CD and BG assisted with analysis of aerosols samples, while MJ and BL assisted with particulate sample collection. RPB and SJP provided infrastructure for sampling campaigns. Conceptual contributions were made by KJ and TX.

Conflicts of interest

There are no conflicts to declare.

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