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Size distribution of dithiothreitol oxidative potential of atmospheric aerosols at an urban site

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HIGHLIGHTS

- Volume-normalised OP^{DTT} was similar in submicron and coarse PM.
- The PM_1 fraction contain more redox-active species and is more toxic per unit mass.
- Biomass burning and traffic species were the main drivers of PM_1 OP^{DTT} in winter.
- SOA and road dust components were major contributors to PM_1 OP^{DTT} in summer.
- The drivers of OP^{DTT} in coarse PM were less clear.

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ABSTRACT

PM_1 and PM_{10} samples were collected at a downtown site in Elche, Spain, for one year. The oxidative potential (OP) of the samples was determined by the dithiothreitol (DTT) assay, along with the chemical composition, in order to identify the key components affecting OP of fine and coarse PM. The water-soluble organic carbon (WSOC) content, which comprises many constituents identified as redox-active species in previous works, was measured for the first time at the sampling site. More than 70 % of WSOC was associated with submicron particles since it came mainly from biomass burning during winter and was formed by atmospheric photochemical reactions during the summer season. Average volume-normalised OP was very similar in the submicron and coarse fractions (0.21 and 0.17 nmol min^{-1} m^{-3}, respectively), with values twice as high in winter than in summer. However, the intrinsic OP (OP of PM per unit mass) was notably higher in PM_1 than in PM_{10-1} (28 and 14 pmol min^{-1} μg^{-1}), indicating that submicron particles have a higher potential to generate reactive oxygen species and are potentially more hazardous. During winter PM_1 OP was strongly associated with biomass burning species, including WSOC, due to the emissions of redox-active organic components from this source, and also with traffic tracers related to both exhaust and non-exhaust emissions. In contrast, during the warm season, the results of the correlation analysis point to relevant contributions from secondary organic aerosols and road dust resuspension. On the other hand, the DTT activity measured in PM_{10-1} was related to chemical species derived from exhaust and non-exhaust traffic emissions during winter and to marine species during the summer months.

1. Introduction

Exposure to airborne particulate matter (PM) poses a serious concern due to its detrimental impacts on both the environment and human health. PM has been associated with adverse effects including cardiovascular and respiratory diseases, and even cancer (Shahriyari et al., 2022; WHO, 2021). A crucial aspect of PM toxicity is related to its chemical composition, which plays a critical role in its negative health impacts (Lelieveld et al., 2015; Li et al., 2019; Pope et al., 2002). PM comprises primary and secondary species, with a composition strongly dependent on its major emission sources and formation processes, which includes variable proportions of metals, carbonaceous species and inorganic salts (Cheng et al., 2024; Pandolfi et al., 2016; Popovicheva et al., 2024).

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The oxidative potential (OP) of atmospheric aerosols, defined as its capacity to generate harmful reactive oxygen species (ROS) in biological systems that can trigger inflammatory processes, oxidative stress, and cellular damage, contributing to different diseases, has been proposed as an interesting metric to understand the PM toxicological response (Bates et al., 2015; Costabile et al., 2019; Perrone et al., 2019). Among the different OP analytical methods (Pietrogrande et al., 2019), the dithiothreitol (DTT) assay is a commonly used acellular method to evaluate the ability of PM to deplete thiol antioxidants (Guascito et al., 2021) and can be considered as a preliminary metric to assess health risks (Fang et al., 2025). DTT acts as a reducing agent, which can be oxidised by PM; therefore, measuring its consumption provides insights into the potential of PM to induce oxidative stress.

Several studies have employed the DTT assay, highlighting its sensitivity to various PM components such as organic carbon (OC) and elemental carbon (EC), considered tracers of combustion processes, including vehicular emissions and biomass burning (Clemente et al., 2023a; Giannossa et al., 2022; Hu et al., 2008; Samara et al., 2017). These components are often rich in redox-active species that readily react with DTT. In this line, some previous works have found a strong association between OP and the carbonaceous fraction of PM, particularly tracers of biomass combustion such as levoglucosan (Janssen et al., 2014; Li et al., 2024; Pietrogrande et al., 2019; Samara, 2017). Transition metals, such as iron, copper or manganese, can directly generate ROS, contributing also to DTT activity, especially in fine particles (Simonetti et al., 2018; Zhang et al., 2024). Finally, secondary aerosol components, such as quinones and sulfate, can also contribute to DTT loss in PM extracts (Clemente et al., 2023a; Li et al., 2024; Pietrogrande et al., 2019). In the case of sulfate, this can be explained considering that it produces highly acidic particles which facilitates the dissolution of primary transition metals that can contribute to aerosol oxidative activity (Fang et al., 2017a). Other studies have also pointed out the important role of sulfur and metal content on the magnitude of OP^{DTT} and health outcomes (Weichenthal et al., 2021).

Although it is well-known that particle size is a critical variable in PM toxicity (Kelly and Fussell, 2012; Mirowsky et al., 2013), there are still relatively few studies on the size distribution of OP. Previous research indicates a size-dependence of OP responses (expressed both per unit mass and per m^3), with fine particles (<2.5 μm in diameter) exhibiting higher OP values than coarse particles (>2.5 μm) due to their larger surface area and higher content of redox-active species (Giannossa et al., 2022; Li et al., 2024; Samara, 2017). The size distribution of the OP may vary depending on the type of sampling site and the period of the year (Fang et al., 2017b; Li et al., 2024), since DTT activity is strongly influenced by the changing composition of redox-active species resulting from primary emissions and secondary aerosol formation. In addition, the oxidative potential may be influenced by the interactions (additive, synergistic, or antagonistic) between PM chemical components (Pietrogrande et al., 2022; Yu et al., 2018), which vary between locations.

The present study aims to analyse the size distribution of aerosol DTT-measured OP at an urban station located in southern Europe, close to the Mediterranean coast. Organic matter and secondary inorganic ions (NO_3^-, SO_4^{2-} and NH_4^+) are the main chemical components of PM_1 at the study site (~80 %), with a relevant contribution from local and long-range transported dust particles (~12 %). For PM_{10}, the relative contribution of the organic fraction is roughly half that of PM_1, especially during summer when the proportion of secondary inorganic aerosols, mineral dust and marine aerosols increases (Galindo et al., 2020). Local sources have been identified as the major contributors to PM_{10} concentrations, primarily road traffic (Clemente et al., 2023b). However, biomass burning (including both wood combustion for house heating and agricultural waste burning) is also expected to play a role on the variability of PM concentrations, particularly during late autumn and winter, as suggested by other works performed in this area (Clemente et al., 2024; López-Caravaca et al., 2023).

In order to achieve the goal of this study, PM_1 and PM_{10} samples were collected in parallel and analysed to determine OP^{DTT} values and chemical composition, including OC and EC, water-soluble organic carbon (WSOC), ions, levoglucosan, and major and trace metals. The components with the highest influence on DTT activities in the submicron and coarse PM fractions were evaluated, thereby deepening our understanding of the complex correlations between PM composition and its ability to induce the formation of ROS in the Mediterranean basin.

2. Materials and methods

2.1. Sampling site and PM measurements

The sampling site was situated in Elche, a city located in south-eastern Spain, about 12 km from the coast. With a current population of approximately 191,000 inhabitants, the urban area is characterised by a lack of heavy industry, making traffic the primary anthropogenic source of air pollutants within the city.

Samplers were placed on the first floor of a municipal office building, inside a canyon road of approximately 7 m width with two traffic lanes in a single direction. One of the lanes is a bus lane, while the other lane is left for general traffic. Street canyons tend to exhibit high PM levels due to insufficient ventilation, including roads with low traffic flows (Parsons and Salter, 2003). Wind direction plays a key role in pollutant dispersion in canyon-like streets; thus, dispersion is more difficult if the wind is perpendicular to the urban canyon (Girotti et al., 2025). The coarse fraction is generally more sensitive to traffic volumes than the fine fraction due to non-exhaust vehicle emissions (Namdeo et al., 1999; Nicolás et al., 2020). Further details of the sampling location can be consulted in Nicolás et al. (2020).

PM_1 and PM_{10} samples were collected during 24-h periods three times per week onto quartz fibre filters (47 mm diameter, AHLSTROM MK360) from March 2022 to February 2023. Two Derenda 3.1 low-volume samplers operating at a flow rate of 2.3 m^3 h^{-1} were employed for sample collection.

All filters were weighted in quadruplicate before and after sampling, after conditioning for at least 24 h in a room with controlled temperature and humidity set at 20 ± 1 °C and 50 ± 5 %. An Ohaus AP250D balance with 10 μg sensitivity was used. After the measurement of PM mass concentrations, filters were kept at 4 °C until chemical analyses. A total of 148 PM_1 and 155 PM_{10} valid samples were collected during the sampling campaign.

2.2. Analytical procedures

Elemental analyses were conducted by Energy Dispersive X-Ray Fluorescence (ED-XRF) as described in Chiari et al. (2018).

After the elemental analysis, a 1.5 cm^2 punch was cut from each filter for the quantification of elemental carbon (EC) and organic carbon (OC) concentrations using the thermal-optical transmittance method with the Sunset Laboratory OC/EC analyser (Sunset Laboratories Inc.), following the EUSAAR-2 protocol (Cavalli et al., 2010).

From the remaining filter, one quarter was extracted with 6.5 mL of ultrapure water. The solution was sonicated for 45 min and analysed for water-soluble ions by ionic chromatography. Another quarter of the filter was used for WSOC determination after water extraction. Finally, the remaining filter was extracted ultrasonically using 6.5 mL of MQ-grade water and analysed to determine the DTT-oxidative potential and the concentration of levoglucosan. The DTT analysis was carried out following a procedure similar to that proposed by Massimi et al. (2020), while levoglucosan concentrations were measured by high-performance anion exchange chromatography with pulsed amperometric detection. A detailed description of the analytical procedures and operation conditions can be consulted in Gómez-Sánchez et al. (2024) and the Supplementary material.

2.3. Statistical analysis

Student's t-tests were used to assess if the differences between seasonal average values were statistically significant at a confidence level of 95 % ($p < 0.05$). Pearson's correlation analysis was conducted to assess the degree of linear correlation between OP values and PM chemical components. Correlations were considered statistically significant at $p < 0.05$. Resulting correlation coefficients were interpreted as follows: 0.45–0.70 moderate, ≥0.7 strong (Calas et al., 2018; Janssen et al., 2014).

3. Results and discussion

3.1. PM chemical composition

Annual mean concentrations of PM_1, PM_{10} and chemical components during the sampling period are shown in Table S1 (Supplementary material). As the composition of atmospheric aerosols at the sampling site has been discussed in previous papers (e.g. Clemente et al., 2023b; Galindo et al., 2020; Yubero et al., 2015), only a short description is included here, except for WSOC, which was measured for the first time in the present study. WSOC is an important contributor to the total organic carbon and, in the absence of biomass burning, can be considered a proxy for secondary organic aerosols formed from photochemical oxidation reactions (Duong et al., 2011). Additionally, the water-soluble fraction of OC is known by its negative implications on the environment and human health (Almeida et al., 2024; Andreae and Gelencsér, 2006), significantly influencing the OP measured by the DTT assay (Farahani et al., 2022; Vimukthi et al., 2025).

PM levels were a little lower than the values found in recent studies performed at the same site (9–12 μg m^{-3} for PM_1 and ~28 for μg m^{-3} for PM_{10}; Galindo et al., 2019; Clemente et al., 2024), which was most likely due to natural year-to-year variations driven by changes in meteorological conditions, emissions from sources and the frequency and intensity of pollution episodes. As expected, carbonaceous compounds (OC + EC) accounted for the major fraction of PM_1 and PM_{10} mass concentrations (46 % and 24 %, respectively, similarly to previous results at the same sampling site; Galindo et al., 2019), followed by secondary inorganic ions (~16 %). Sulfate, formed from the photochemical oxidation of SO_2, is primarily of regional origin. In contrast, nitrate is associated with local sources since it is generated from the oxidation of the NO_x emitted by road traffic (Clemente et al., 2023b). It is interesting to mention that the average contribution of nitrate to the submicron fraction (<4 %) was notably lower than the average value found at urban background sites across Europe (18 %, Bressi et al., 2021). This is due to lower ammonia levels at our study area that are insufficient to neutralise both sulfate and nitrate (Fig. 1), as previously suggested (Clemente et al., 2022). In fact, low submicron nitrate concentrations have been registered at the sampling site since 2017 (Clemente et al., 2022).

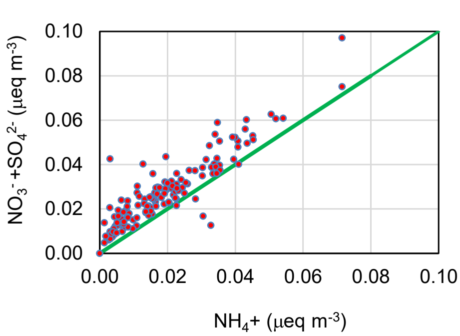

Fig. 1. Correlation between the sum of sulfate and nitrate vs ammonium in PM_1. The green line represents the 1:1 line. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1 shows annual and seasonal averages of EC, OC and WSOC. Mean levels of carbonaceous species in PM_1 were around twice those found at an urban background station situated in an open area on the outskirts of the city of Elche (López-Caravaca et al., 2023), where the impact of direct traffic emissions is lower and pollutants are easily dispersed. The mean concentration of WSOC in the submicron fraction (1.92 μg m^{-3}) was also higher than those measured in $PM_{2.5}$ at other urban sites in Europe such as Dunkerque (0.7 μg m^{-3}; Allouche et al., 2024) or Brindisi (1.5 μg m^{-3}; Genga et al., 2017). In contrast, WSOC concentrations in PM_1 and PM_{10} were lower than those found in Gdynia (Poland), where most of the energy is produced from coal plants (2.6 μg m^{-3} in PM_1 and 4.4 μg m^{-3} in PM_{10}; Witkowska and Lewandowska, 2016). The average concentration of WSOC in PM_{10} during winter was also lower than that reported for Thessaloniki (Greece), one of the most crowded European cities (4.2 μg m^{-3}; Kitanovski et al., 2020).

WSOC was mainly distributed in the submicron fraction (74 %), which was not unexpected considering that soluble organic compounds are mainly of secondary origin or emitted from biomass burning (Ni et al., 2021; Park et al., 2013). In fact, during winter, WSOC was strongly correlated with levoglucosan ($r = 0.77$ for PM_1 and 0.80 for PM_{10}) and soluble potassium ($r = 0.92$ for PM_1 and 0.89 for PM_{10}), both considered as reliable tracers of biomass combustion. In contrast, during the summer season strong correlations were found with oxalate in PM_1 ($r = 0.73$), suggesting that a significant fraction of submicron WSOC is secondary (Petit et al., 2019; Zhang et al., 2012). These results are consistent with those previously found at an urban background station situated near the sampling site (López-Caravaca et al., 2023, 2024). In fact, biomass burning emissions accounted for more than 50 % of the WSOC measured in PM_1 at the urban background station during winter, while during the summer season WSOC was mainly associated with the ammonium sulfate source (López-Caravaca et al., 2023), suggesting mainly a regional origin (Clemente et al., 2023b). Moderate to strong correlations were also found between WSOC and EC during winter ($r = 0.69$ for PM_1 and 0.56 for PM_{10}), most likely because a fraction of EC is co-emitted with water-soluble organics during biomass combustion. Interestingly, water-insoluble organic carbon (WIOC), determined by subtracting WSOC from OC concentrations, showed moderate to strong correlations with EC during both summer ($r = 0.65$ for PM_1 and PM_{10}) and winter ($r = 0.71$ for PM_1 and $r = 0.79$ PM_{10}), which points to traffic as a major source of WIOC at the sampling site independently of the season of the year.

Although, as described in previous works (Galindo et al., 2019), OC showed a clear seasonal pattern, with higher levels in winter than in summer, the increase in WSOC concentrations during winter was much lower (Fig. 2). Indeed, in PM_{10} differences between winter and summer WSOC levels were not statistically significant. These outcomes reveal that the water-insoluble organic fraction had a higher influence on the seasonal variation of OC levels. The absence of significant differences between summer and winter WSOC concentrations has been stated in previous research (Custódio et al., 2016). High WSOC levels during the cold season are the result of unfavourable dispersions conditions, lower temperatures that promote the condensation of semi-volatile species and higher emissions from residential wood combustion and agricultural waste burning (Chalbot et al., 2014; López-Caravaca et al., 2023; Qiao et al., 2015). In addition, significant amounts of secondary organic aerosols (SOA) can be formed in the study area during winter, as previously reported (Galindo et al., 2019; Yubero et al., 2015). On the other hand, the increase in WSOC during summer could be attributed to the formation of secondary species from both anthropogenic and biogenic origin (Lemou et al., 2020; Qiao et al., 2015). In fact, an increase in biogenic SOA formation during the summer season has been documented in previous works (Yu et al., 2021; Zhang et al., 2012). This is due to larger emissions of biogenic precursors under high ambient temperatures combined with intense solar radiation, which favours their

Table 1
Average concentrations of carbonaceous components (± standard deviation) for the entire period, summer (from June to August), and winter (from December to February). Concentrations are given in μg m^{-3}.

	Annual		Summer		Winter	
	PM_1	PM_{10}	PM_1	PM_{10}	PM_1	PM_{10}
EC	0.77 ± 0.36	1.18 ± 0.44	0.62 ± 0.21	1.07 ± 0.27	0.92 ± 0.38	1.30 ± 0.56
OC	3.79 ± 1.17	5.31 ± 1.72	3.60 ± 0.96	4.99 ± 1.41	4.94 ± 1.35	6.67 ± 2.20
WSOC	1.92 ± 0.49	2.61 ± 0.77	1.93 ± 0.45	2.76 ± 0.61	2.29 ± 0.54	2.96 ± 0.92

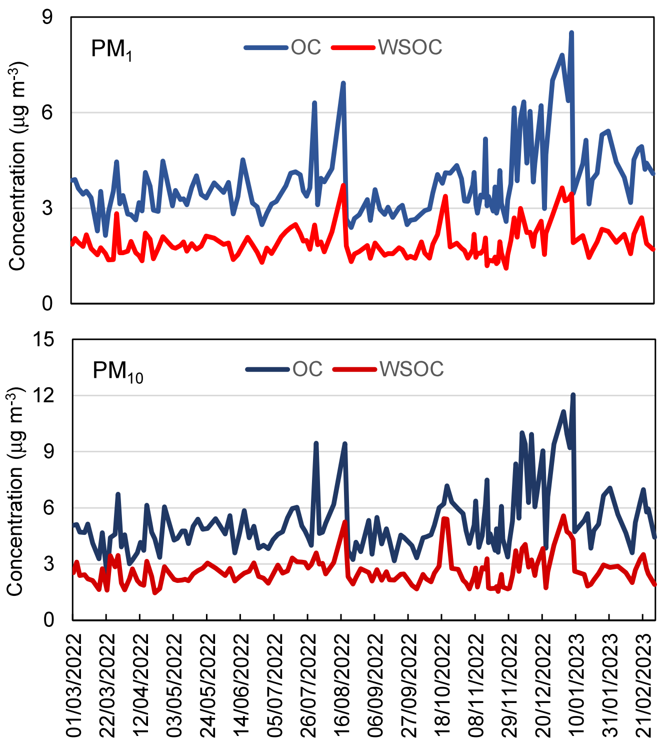

Fig. 2. Temporal variability of OC and WSOC in PM_1 (top panel) and PM_{10} (bottom panel) from March 2022 to February 2023.

photochemical oxidation to less volatile products (Mahilang et al., 2021).

The average WSOC/OC ratio was around 0.5 in both PM_1 and PM_{10}, with a slightly statistically significant increase ($p < 0.05$) from winter (~0.45) to summer (~0.55). The WSOC/OC ratio has been used to evaluate the extent of secondary organic aerosol formation. Thus, the increase in the WSOC/OC ratio from winter to summer points to a larger contribution of photochemically formed secondary organic aerosols to total OC during summer, in agreement with previous studies (Du et al., 2014; Miyazaki et al., 2006). WSOC/OC ratios at our sampling site are in the lower range of those recently reported for other urban sites in Europe (between approximately 0.4 and 0.7; Allouche et al., 2024; Custódio et al., 2016; Genga et al., 2017; Paraskevopoulou et al., 2023).

3.2. OP values

Table 2 shows average PM concentrations and OP values normalised by volume of sampled air (OP_V) and by mass of PM (OP_m). OP_V is considered as a suitable metric to assess inhalation exposure, while OP_m represents the intrinsic PM toxicity, which depends on its sources (Besis et al., 2023; Fang et al., 2025; Shirmohammadi et al., 2016).

The mean OP values of PM_{10} (Table 2) were very similar to those previously measured at the same site (Clemente et al., 2023a). With respect to PM_1, relatively few studies have reported OP values of this fraction so far. The mean OP_V measured in the submicron fraction was in general much lower than the values observed in other European and Spanish cities (Camman et al., 2024; Melzi et al., 2024; in't in 't Veld et al., 2023), although in the absence of a standardised method comparisons are not straightforward.

The seasonal cycle of OP_V of both the submicron (PM_1) and coarse fractions ($PM_{10\text{-}1}$) (Fig. 3) was the same as those commonly found in other urban areas worldwide, with higher values during winter (Fang

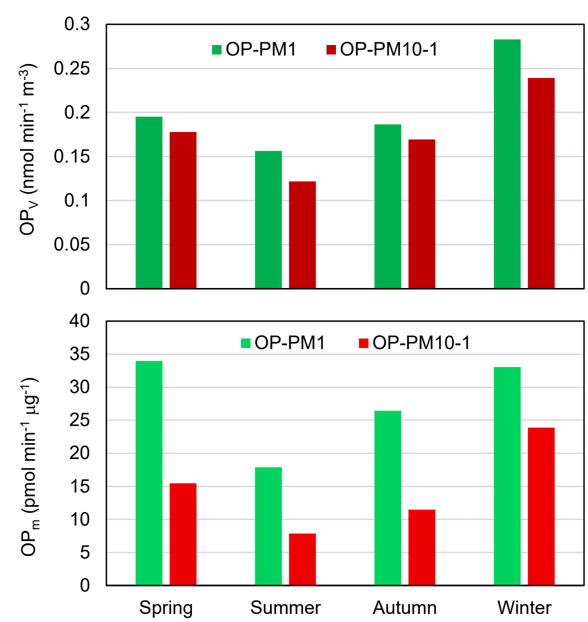

Fig. 3. Seasonal variability of volume-normalised OP^{DTT} (top panel) and mass-normalised OP^{DTT} (bottom panel).

Table 2
OP and PM average values (± standard deviation) for the entire period, summer (from June to August), and winter (from December to February). PM concentrations are expressed in μg m^{-3}, OP_V in nmol min^{-1} m^{-3}, and OP_m in pmol min^{-1} μg^{-1}. $PM_{10\text{-}1}$ concentrations were calculated as the difference between PM_{10} and PM_1 concentrations. Equivalently, OP^{DTT} values for the coarse fraction were calculated as the difference between values measured for PM_{10} and PM_1.

	Mean			Winter			Summer		
	PM_1	$PM_{10\text{-}1}$	PM_{10}	PM_1	$PM_{10\text{-}1}$	PM_{10}	PM_1	$PM_{10\text{-}1}$	PM_{10}
PM	8.7 ± 3.7	15.7 ± 10.7	23.9 ± 12.4	9.5 ± 4.8	12.5 ± 8.0	20.9 ± 10.4	9.5 ± 3.3	16.5 ± 5.2	26.1 ± 7.3
OP_V^{DTT}	0.21 ± 0.10	0.17 ± 0.11	0.38 ± 0.17	0.29 ± 0.10	0.26 ± 0.12	0.54 ± 0.18	0.16 ± 0.07	0.12 ± 0.06	0.27 ± 0.09
OP_m^{DTT}	26 ± 13	14 ± 11	19 ± 9	33 ± 9	26 ± 13	27 ± 7	18 ± 10	8 ± 4	11 ± 4

et al., 2016; Massimi et al., 2024; Melzi et al., 2024; Shirmohammadi et al., 2016; Weber et al., 2021). This indicates that the capacity of PM to generate ROS, and hence its potential toxicity, increases during the cold months. The most likely reason is that OP sources vary with the season of the year, as also pointed out by the significant increase in OP_m values from summer to winter. Shirmohammadi et al. (2016) suggested that the increase of volume-normalised DTT activity during winter can be explained by the lower dispersion of atmospheric pollutants and by a shift in the gas-aerosol partitioning of redox active semi-volatile organic compounds towards the particle phase.

Although average OP_V values of PM_1 and $PM_{10\text{-}1}$ were very similar, the mass-normalised DTT activity was significantly higher for the submicron than for the coarse fraction (Table 2), in line with the outcomes of many previous works, which found a higher intrinsic DTT activity for the fine ($PM_{2.5}$) and submicron fractions than for the coarse fraction (Giannossa et al., 2022; Janssen et al., 2014; Massimi et al., 2020; Ntziachristos et al., 2007; Samara, 2017). These results indicate that fine particles are enriched with redox-active components capable of generating ROS and therefore are potentially more harmful to health than coarse particles. However, OP_m provides only a partial indication of the intrinsic toxicity of ambient PM, which should be complemented with cellular assays and epidemiological studies (Bates et al., 2015; Fang et al., 2025). It is worth mentioning that, although volume-normalised OP values of fine and coarse particles were comparable, the potential risks of the coarse fraction are lower since they do not penetrate deep into the lungs (Bui et al., 2020).

3.3. Influence of the chemical composition on OP values

While particle size is a critical factor in determining OP values and health hazards, many previous works have underlined that OP is highly source- and composition-dependent (Daellenbach et al., 2020; Fang et al., 2025; Salana et al., 2024). The linear correlation coefficients between volume-normalised OP values and PM mass concentrations are presented in Table 3. The scatter plots are shown in the Supplementary material (Fig. S1). Stronger correlations were found when the data were seasonally divided, which can be explained considering that OP sources vary as a function of the season, as already mentioned. The correlation coefficients were higher for the submicron than for the coarse fraction, especially during winter. These outcomes suggest, on the one hand, that PM_1 mass concentrations play a significant part in the overall aerosol toxicity (Salana et al., 2024), although PM masses alone may not always be suitable to evaluate aerosol health effects. On the other hand, during the cold months the components that contribute to total PM_1 mass concentrations were almost the same as those contributing to the ROS-generating potential, as pointed out by the high correlation coefficient obtained between PM_1 and OP^{DTT} for this season (Bates et al., 2015). Different degrees of correlation between OP^{DTT} values and $PM_{2.5}$ concentrations have been reported in previous works. For instance, no correlation was observed in São Paulo (Brazil; Serafeim et al., 2023), while moderate to strong correlations were found in Atlanta (USA; Bates et al., 2015), Lecce (Italy; Perrone et al., 2019) and the Netherlands (Janssen et al., 2014). In a recent study (Salana et al., 2024), significant correlations between $PM_{2.5}$ and OP^{DTT} were observed at many stations worldwide, although the slopes of the linear regressions changed from site to site. Since it has been suggested that OP is largely an intrinsic property more related to PM composition than to PM mass (Serafeim et al., 2023), the differences observed among sites are related to variations in aerosol sources and chemical composition (Salana et al., 2024).

Table 3
Pearson's correlation coefficients between OP_V^{DTT} and PM mass concentrations for the whole period, summer (from June to August) and winter (from December to February). All correlations were significant at the 95 % confidence level.

	Whole period	Summer	Winter
PM_1	0.50	0.69	0.86
PM_{10-1}	0.28	0.50	0.51

Pearson's correlation coefficients between OP_V values and the concentrations of the components measured in both the submicron and coarse fractions were calculated in order to identify the key components/sources affecting the oxidative potential (Table 4). The data were seasonally divided, since the chemical species and/or sources influencing the DTT activity are expected to be different during summer and winter, as already reported in previous studies (Clemente et al., 2023a; Fang et al., 2016; Hakimzadeh et al., 2020; Perrone et al., 2019).

During winter, PM_1 OP was best correlated with soluble potassium and WSOC, which points to an important contribution from biomass burning emissions to the DTT activity of the submicron fraction, as confirmed by the significant correlation between OP^{DTT} and levoglucosan concentrations. The association between OP^{DTT} and biomass burning tracers in PM has been proven in many previous works (Fang et al., 2016, 2025; Hakimzadeh et al., 2020; Li et al., 2024; Perrone et al., 2019). The positive correlations do not necessarily mean causation, since PM chemical components tend to highly covariate and some species strongly correlated with OP^{DTT} are not redox-active (Charrier and Anastasio, 2012). For example, strong correlations have been often found between OP^{DTT} and the concentration of polycyclic aromatic hydrocarbons (PAHs), although these species are not redox-active. Therefore, the correlation between OP^{DTT} and PAHs concentrations is most like due to the relationship between PAHs and quinones, some of which can oxidise DTT. Quinones are co-emitted with PAHs during incomplete combustion processes or can be formed from the atmospheric oxidation of PAHs (Cho et al., 2005). In summary, the relationship between OP^{DTT} and biomass burning tracers during winter is due to the emissions of redox-active water-soluble organic compounds, such as quinones or humic-like substances, from this source (Verma et al., 2015; Yu et al., 2022).

Strong correlations were also obtained between OP^{DTT} measured in PM_1 during winter and EC, WIOC, nitrate and Zn concentrations, suggesting that the traffic source is a main driver of the volume-normalised DTT activity in the submicron fraction. The dominant contribution of traffic-related metals (coming from the wear of vehicle components or the resuspension of road dust) and exhaust emission components to OP^{DTT} values has been previously observed in other studies (Calas et al., 2018; Fang et al., 2016; Perrone et al., 2019; Shirmohammadi et al., 2016; Yao et al., 2024). However, these findings differ from those

Table 4
Pearson's correlation coefficients between OP_V^{DTT} and PM components during summer (from June to August) and winter (from December to February).

	Winter (N = 36)		Summer (N = 31)	
	PM_1	PM_{10-1}	PM_1	PM_{10-1}
OC	0.89[a]	0.69[a]	0.66[a]	0.22
EC	0.73[a]	0.50[a]	0.33	0.31
WSOC	0.89[a]	0.39[a]	0.55[a]	0.27
IC	0.05	0.14	0.68[a]	0.33
WIOC	0.74[a]	0.66[a]	0.45[a]	0.09
Cl^-	0.14	0.24	0.46[a]	0.66[a]
NO_3^-	0.75[a]	0.27	0.40[a]	0.53[a]
SO_4^{2-}	0.48[a]	0.31	0.34	0.25
$C_2O_4^{2-}$	0.44[a]	0.23	0.65[a]	0.12
Na^+	0.02	0.05	0.52[a]	0.60[a]
NH_4^+	0.42[a]	0.24	0.09	0.19
K^+	0.92[a]	0.30	0.33	0.69[a]
Mg^{2+}	0.06	0.28	0.39[a]	0.63[a]
Ca^{2+}	0.19	0.41[a]	0.38[a]	0.04
Levoglucosan	0.74[a]	0.38[a]	0.41[a]	0.21
Fe	0.39[a]	0.55[a]	0.62[a]	0.20
Cu	–	0.62[a]	–	−0.50
Zn	0.72[a]	0.45[a]	0.05	−0.28

Correlations between PM_1 OP and Cu were not calculated since this element was not detected in most of the PM_1 samples.
[a] Correlations statistically significant ($p < 0.05$).

reported for the city of Barcelona, located on the northeastern Mediterranean coast of Spain, where the significant presence of industrial sources (such as smelters and cement kilns) results in PM_1 OP^{DTT} being dominated by industry emissions (in 't Veld et al., 2023).

Correlations between OP values and the chemical species analysed in PM_1 were generally weaker during summer. Correlation coefficients higher than 0.6 were observed for OC, IC, oxalate and Fe. IC and Fe can be considered as tracers of road dust resuspension and/or break wear (Clemente et al., 2023b, and references cited therein), while oxalate is an indicator of the production of secondary organic aerosols (Petit et al., 2019). A significant contribution of road dust to PM_{10} OP has also been reported in previous works (Calas et al., 2018), which is not surprising as road dust particles are mainly distributed in the coarse size range. However, this source has also been identified as an important driver of $PM_{2.5}$ OP (Hakimzadeh et al., 2020; Wang et al., 2019). The relationship of PM_1 OP with oxalate and organic carbon points to a relevant contribution from secondary organic aerosols since, as already discussed (section 3.1), oxalate can be considered a tracer of secondary organic particles (Petit et al., 2019; Zhang et al., 2012). This finding is consistent with the outcomes of previous research (Hakimzadeh et al., 2020). The statistically significant correlation coefficient obtained with WSOC seems to support this conclusion, as the soluble organic fraction is mainly of secondary origin during summer (López-Caravaca et al., 2023). It should be noted that this interpretation is based on the available tracers (oxalate, OC, and WSOC). The inclusion of additional organic tracers in future studies could provide a more comprehensive understanding of the sources contributing to PM_1 oxidative potential.

As regards the coarse fraction, the correlation coefficients of the DTT activity with most of the analysed species were generally lower than those calculated for PM_1. The largest correlation coefficients during winter were found with OC, the insoluble fraction of OC, followed by Cu, Fe and Zn, indicating that OP^{DTT} in coarse PM is most likely associated with exhaust and non-exhaust traffic emissions. These results are aligned with prior research in the Mediterranean basin linking PM_{10} OP^{DTT} to combustion and dust sources (in 't Veld). Several previous studies have shown the important role of traffic emissions, especially non-exhaust emissions, on coarse particle concentrations, with contributions higher than 60 % (Grivas et al., 2018; Matthaios et al., 2022). These emissions are characterised by a high content of transition metals such as Cu and Ba (generated by brake wear), Zn, Fe and Mn (tyre wear), and Fe and Ti (road wear and road dust resuspension) (Fussell et al., 2022), most of which are known by its close relationship with OP values and adverse health effects (Weichenthal et al., 2021). Surprisingly, during the warmer months, moderate correlations with sea-salt components were observed. However, ions are not active in the DTT assay (Ntziachristos et al., 2007), which suggests that other species co-emitted or transported along with marine ions could contribute to the measured OP. Previous research has revealed that water-soluble nitrogenous organics, which can be released into the atmosphere from the sea (Cape et al., 2011), are highly DTT-active (Patel and Rastogi, 2020). This could explain the observed relationship between OP^{DTT} and marine species.

Although bivariate correlation analysis is useful to investigate the associations between OP and PM components and has been previously applied in a number of studies (Besis et al., 2023; Fang et al., 2016; Hakimzadeh et al., 2020; Perrone et al., 2019; Serafeim et al., 2023), this approach has some limitations such as the covariation of some species present in PM samples. This implies that the relationship between OP and PM constituents may be caused by similar variations in the concentrations of PM components rather than a causal association between OP and a specific component (Serafeim et al., 2023). Alternatively, other approaches such as receptor models (e.g. positive matrix factorisation and chemical mass balance) have to be used in order to quantify source contributions to OP levels.

4. Conclusions

This study provides a comprehensive characterization of the oxidative potential associated with particulate matter of different size fractions (PM_1 and PM_{10}) in a Mediterranean urban environment, offering new insights into the size-dependent toxicity of atmospheric aerosols. Seasonal variations in volume- and mass-normalised OP^{DTT} values were observed in both the submicron (PM_1) and coarse fractions (PM_{10-1}). DTT activities were generally higher during winter, suggesting that particles were more enriched in redox-active compounds and therefore exhibited a higher OP. These seasonal differences reflect changes in the contribution of components capable of generating ROS, which are closely linked to the dominant aerosol sources and atmospheric processes during each season.

Species emitted from biomass combustion and traffic-related sources were strongly associated with PM_1 OP^{DTT} during winter, whereas secondary organic aerosols and road dust appeared to be the major contributors during the summer season. In the coarse fraction, associations between OP^{DTT} and PM components were generally weaker, although moderate correlations with exhaust and non-exhaust traffic-related species were observed during winter. During summer, the DTT activity was best correlated with sea spray components (Cl^-, Na^+, Mg^{2+}, and K^+), despite their redox-inactive nature, suggesting that other compounds transported along with marine ions may contribute to the measured oxidative activity. These results point to complex source–component interactions affecting OP that are not fully captured by traditional markers.

The temporal variability of OP_V and PM concentrations differed in most cases (with the exception of PM_1 during winter), indicating that the dominant sources controlling OP and PM do not generally overlap. The results of the present work reinforce the conclusion from previous studies that PM masses alone may be inadequate to assess the health hazards of PM exposure, depending on particle size, seasonality and site-specific characteristics.

All these findings have important implications for air quality monitoring and health impact assessment, suggesting that regulatory strategies based exclusively on PM mass may underestimate potential health risks associated with specific size fractions. Future studies should extend this framework by integrating long-term datasets, detailed source apportionment and additional toxicity assays, as well as by exploring the incorporation of OP-based metrics into routine monitoring networks and exposure assessments.

CRediT authorship contribution statement

M. Alfosea-Simón: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **N. Galindo:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. **N. Gómez-Sánchez:** Writing – review & editing, Investigation. **J. Gil-Moltó:** Writing – review & editing, Writing – original draft. **Á. Clemente:** Writing – review & editing, Formal analysis. **J.F. Nicolás:** Writing – review & editing, Visualization, Project administration, Funding acquisition. **J. Crespo:** Writing – review & editing, Supervision. **E. Yubero:** Writing – review & editing, Supervision, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2025.121756.

Data availability

Data will be made available on request.

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