

The impact of biomass burning on the oxidative potential of PM_{2.5} in the metropolitan area of Milan

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HIGHLIGHTS

- Impact of dominant PM sources on associated OP was studied in Milan.
- Alarmingly high total PAH concentrations (72.81 ± 16.59) were observed in winter.
- PM associated dithiothreitol (DTT) activity levels were higher during the wintertime.
- Multiple linear regression (MLR) was used to link PM OP to emission sources.
- Biomass burning activities contributed to 41% of PM OP in Milan metropolitan area.

ARTICLE INFO

Keywords:

Dithiothreitol (DTT)
Biomass burning
Po valley
Milan
Oxidative potential
Polycyclic aromatic hydrocarbons (PAH)

ABSTRACT

In this study, we investigated the impact of biomass burning on the oxidative potential of PM_{2.5} in the metropolitan area of Milan, Italy. PM_{2.5} samples were collected on quartz filters during cold (December 2018–February 2019) and warm (May 2019–July 2019) seasons at the Municipality of Bareggio, a small town located approximately 14 km northwest of the Milan city center. The PM_{2.5} constituents were chemically analyzed, and its corresponding oxidative potential was measured by means of the dithiothreitol (DTT) assay. Total PM_{2.5} mass concentration was significantly higher in winter ($71.82 \pm 4.17 \mu\text{g}/\text{m}^3$) compared to summer ($16.67 \pm 0.27 \mu\text{g}/\text{m}^3$), mainly a result of enhanced biomass burning emissions combined with higher atmospheric stability and lower mixing during the cold season. The enhanced biomass burning activities during the winter period also resulted in very high polycyclic aromatic hydrocarbons (PAHs) concentrations ($72.81 \pm 16.59 \text{ ng}/\text{m}^3$) which were more than 150-fold higher than the warm period values ($0.40 \pm 0.07 \text{ ng}/\text{m}^3$). PAH concentrations were highly correlated with chemical markers of biomass burning (i.e., levoglucosan ($R^2 = 0.79$), and K^+/K ($R^2 = 0.87$)) in the winter period. Spearman correlation analysis between DTT and PM_{2.5} chemical species showed a dominant role of secondary organic aerosols (SOA) and vehicular emissions in summer-time PM_{2.5} oxidative potential (i.e., the capacity of PM_{2.5} species to oxidize target molecules), while in the wintertime, the DTT values were highly correlated with chemical markers of biomass burning, vehicular activities, and re-suspended road dust. Multiple linear regression (MLR) analysis identified biomass burning (41%) as the dominant contributor to DTT, followed by SOA (20%), re-suspended road dust (18%), and vehicular emissions (16%). Our results underscore the importance of biomass burning to the overall oxidative potential of PM_{2.5} in the metropolitan area of Milan, urging the need to promulgate effective mitigation policies targeting these emissions.

1. Introduction

Long-term and short-term exposure to particulate matter (PM) has

been consistently associated with several adverse health effects, including respiratory disorders, cardiovascular diseases, neurological disorders, adverse birth outcomes, and increase in lung cancer risk

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<https://doi.org/10.1016/j.atmosenv.2020.117328>

Received 25 November 2019; Received in revised form 26 January 2020; Accepted 1 February 2020

Available online 3 February 2020

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(WHO, 2016; Campbell et al., 2005; Delfino et al., 2005; Penttinen et al., 2001; Raaschou-Nielsen et al., 2013; Wilhelm and Ritz, 2005). In particular, PM_{2.5} (PM with aerodynamic diameter < 2.5 μm) has been the focus of several studies due to its physico-chemical characteristics, diverse sources, and harmful health effects (Dockery and Stone, 2007; Gauderman et al., 2015; Pope, 2007; Pope III et al., 2002; Valavanidis et al., 2008). A number of studies have attributed many of these adverse health effects to the generation of reactive oxygen species (ROS) in cells, which causes oxidative stress responses involving several pro-inflammatory cascades that ultimately lead to adverse health outcomes (Esposito et al., 2014; Paszti-Gere et al., 2012; Tao et al., 2003). Accordingly, several researchers have attempted to develop biological and chemical assays that measure the oxidative potential of airborne particles (Bates et al., 2019). The dithiothreitol (DTT) assay quantifies the capability of PM to increase the transfer rate of electrons from DTT to oxygen to produce superoxide radicals, which is directly related to the oxidative potential of PM (Borlaza et al., 2018; Cho et al., 2005; De Vizcaya-Ruiz et al., 2006; Steenhof et al., 2011).

Although total PM mass concentration has been widely used as the key parameter to investigate PM health effects (Boldo et al., 2011; Lu et al., 2015; Riediker et al., 2004; Schwartz et al., 1996), specific PM components, including carbonaceous species (i.e., elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC), and polycyclic aromatic hydrocarbons (PAHs)) as well as transition metals such as V, Mn, Ni, and Cu have been consistently associated with the oxidative potential of PM (Akhtar et al., 2010; Bae et al., 2017; Charrier and Anastasio, 2012; Cho et al., 2005; Decesari et al., 2017; Janssen et al., 2014; Kim et al., 2013; Lin et al., 2015; Pirhadi et al., 2019; Samara, 2017; Strak et al., 2012; Yang et al., 2019). Since most of the toxic PM components are originated from a multitude of primary and secondary sources, direct assessment of the oxidative potential of PM from each of these sources and formation mechanisms becomes vital for the development of effective mitigation strategies. This approach is of particular importance when investigating the toxic burden induced by PM on all residents of an urban metropolitan area who are exposed to a mixture of PM emissions.

The Po Valley, located in the heart of the Lombardy region of northern Italy, has experienced several air pollution episodes in the past decades (Lonati et al., 2008; Putaud et al., 2002). Unique topography, high population density in the surrounding region, and wintertime high stability conditions favoring fog formation exacerbate particulate air pollution in the area (Decesari et al., 2017; Tositti et al., 2014). Previous studies in Po Valley indicated that summer-time ambient PM_{2.5} is impacted by traffic emissions and secondary organic aerosol (SOA) formation (Daher et al., 2012; Lonati et al., 2005; Perrone et al., 2012), while in the wintertime, biomass burning emissions combined with local meteorological conditions (i.e., haze and fog processing) elevate PM_{2.5} concentrations (Vecchi et al., 2004; Belis et al., 2011; Decesari et al., 2017; Giannoni et al., 2012). Gualtieri et al. (2011) have found that wintertime ambient PM in the area of Milan induced premature mitosis and DNA strand break, and attributed the intracellular production of reactive oxygen species (ROS) to increased PAH and transition metal concentrations during that period. Sancini et al. (2014) showed that daily exposure to PM_{2.5} in Milan poses an acute threat principally to susceptible people, such as the elderly and those with unrecognized coronary artery or structural heart disease.

Considering the alarming air quality conditions in the urban/suburban regions of Po Valley, particularly at the metropolitan area of Milan in wintertime, there is a need to link the PM toxicity to its sources and formation mechanisms in that area. Daher et al. (2012) have previously reported high concentrations of PM_{2.5} and its associated oxidative potential (measured by a different assay to the one used in the current study) in an urban site at the city center of Milan, heavily impacted by vehicular emissions, and confirmed the predictable influence of traffic emissions on PM_{2.5} toxicity. Complementary to the work of Daher et al. (2012), the main goal of this study was to obtain a

“baseline estimate” of the urban background PM_{2.5} toxicity affecting the general population of the metropolitan area of Milan by investigating the relationship between the oxidative potential of PM_{2.5} (measured by the DTT assay) to its sources in a suburban background far from the city center, not directly impacted by vehicular emissions.

2. Methodology

2.1. Study area and sample collection

PM_{2.5} sampling was conducted at the Municipality of Bareggio, a small town within the Milan metropolitan area located 14 km to the north-west of central Milan (map shown in Fig. S1(a)), during a cold (from December 2018 to February 2019) and a warm (from May 2019 to July 2019) period. Due to its location and predominant wind direction shown in Fig. S1, the site is mostly upwind of the abundant vehicular emissions of the city center. The seasonal averages of temperature, relative humidity, and wind speed are also presented in Table S1, based on 10-hr average metrological measurements obtained from the closest meteorological station, Roveda di Sedriano (MI) (station ID: IMILA-NOR2) (located within 2 km north-west of Bareggio sampling site). According to Table S1, the mean temperature decreased significantly from 21.6 ± 0.3 °C in summer to 3.6 ± 0.3 °C during winter season, whereas wind speed and relative humidity increased from summer (2.7 ± 0.1 m/s and 68.5 ± 1.0%, respectively) to winter (3.3 ± 0.2 m/s and 72.8 ± 1.7%, respectively).

Ambient PM_{2.5} samples were collected on prebaked quartz filters (37 mm, Pall Life Sciences, 2-μm pore size, Ann Arbor, MI) weekly (i.e., each sample corresponding to a 5-day period), using 3 collocated Sioutas™ Personal Cascade Impactor Samplers (PCISs, SKC Inc., Eighty-Four, PA, USA) (Misra et al., 2002; Singh et al., 2003), each operating at flow rate of 9 L/min. Although the PCIS design consists of 4 impaction stages followed by an after-filter, in this study we used only the first impaction stage “A” to remove coarse PM (particles with aerodynamic diameter > 2.5 μm) followed by the “after-filter” to collect PM_{2.5}. Particle bounce from the impaction plate was prevented by applying a thin layer of grease (Super Lude, NY, USA) on the surface of the impaction plate. The weekly average PM_{2.5} mass concentration was determined gravimetrically as the difference between weights of the unloaded and loaded quartz filters after equilibration under controlled laboratory conditions (i.e., temperature of 22–24 °C and relative humidity of 40–50%), using a microbalance (MT5, Mettler Toledo Inc., Columbus, OH), with a precision of ±0.001 mg.

2.2. Chemical analysis

The PM_{2.5} collected samples were analyzed for their chemical components, including elemental and organic carbon (EC, OC), water-soluble organic carbon (WSOC), levoglucosan (a tracer of biomass combustion (Hennigan et al., 2010; Simoneit and Elias, 2001)), polycyclic aromatic hydrocarbons (PAHs), water-soluble ions, total metals, and trace elements by the Wisconsin State Lab of Hygiene (WSLH). EC and OC mass concentrations were quantified by means of a model-4-semi-continuous OC/EC field analyzer (Sunset Laboratory Inc, USA) following thermo-optical transmittance (TOT) analysis. WSOC concentration was measured through extraction (via ultrapure water) and filtration (0.22 μm pore size) of the collected filters by a Sievers 900 total organic carbon analyzer (Stone et al., 2008). Water-soluble inorganic ions as well as total metals and trace elements were determined by ion chromatography (IC) and inductively coupled plasma mass spectroscopy (ICP-MS), respectively (Lough et al., 2005). The concentrations of levoglucosan and other organic species were measured using gas chromatography/mass spectrometry (GC/MS) analysis (Schauer et al., 1999).

2.3. Oxidative potential of PM_{2.5}

The DTT assay has been widely employed to investigate the PM oxidative potential (Cho et al., 2005; Kumagai and Shimojo, 2002; Shima et al., 2006; Verma et al., 2011). This assay examines the depletion of cellular antioxidants during DTT conversion to its disulfide form, in which the rate of DTT consumption is proportional to the oxidative potential of PM. Previous studies have documented a wide range of PM components including PAHs, quinones, redox-active metals such as Fe, Cu, Ni, Mn and Zn, and WSOC as the driving factors in DTT consumption rate (Charrier and Anastasio, 2012; Chung et al., 2006; Li et al., 2003; Verma et al., 2009). In our study, PM_{2.5} slurries (i.e., methanol-extracted quartz filters) were filtered in a cell-free system, and the linear rate of DTT depletion (per units of time) was determined. More details about the performance of the DTT assay can be found in Shafer et al. (2016). The DTT consumption rate was normalized to both PM mass as well as sampled air volume to obtain the intrinsic (in units of nmol/min. µg of PM) and extrinsic (in units of nmol/min. m³ of air) oxidative potentials, respectively. The intrinsic DTT value relates to the oxidative properties of PM per unit mass, whereas the extrinsic DTT value takes also into account the PM emission rates and atmospheric dilution, and can be directly related to population exposure (Fang et al., 2015; Pietrogrande et al., 2018; Tuet et al., 2016). Our statistical analysis was therefore based on the extrinsic DTT values, being more relevant for human exposure to ambient PM and its associated toxicity (Visentin et al., 2016; Yu et al., 2019).

2.4. Source apportionment of the oxidative potential of PM_{2.5}

We employed bivariate regression and multiple linear regression (MLR) analysis to examine the relationship between the oxidative potential of PM_{2.5} with its chemical composition and source contributions. Bivariate correlation analysis was done between the extrinsic DTT values (in units of nmol/min. m³) and the mass concentrations of EC, OC, WSOC, levoglucosan, inorganic ions, metals, and trace elements. We used the calculated Spearman's rho coefficient (R) as a preliminary indicator to identify species that are highly correlated with DTT. Then, we employed MLR between DTT and the target species identified in the previous step as source-specific tracers. DTT was treated as the dependent variable while different combinations of chemical source markers were selected as independent variables to derive an optimum solution resulting in the maximum coefficient of determination (R²) value for statistically significant species (P_{value}<0.05). The relative source contribution to the oxidative potential of PM_{2.5} was estimated according to the derived R² value and the standardized regression coefficients (Beta) based on the approach that we have already employed in earlier studies (Saffari et al., 2014; Shirmohammadi et al., 2016; Taghvaei

et al., 2019).

3. Results and discussion

3.1. PM_{2.5} mass concentrations and chemical speciation

Fig. 1 illustrates the mass concentration of ambient PM_{2.5} as well as the bulk chemical composition of collected samples during the warm and cold periods. PM_{2.5} chemical constituents were categorized as organic matter (OM), elemental carbon (EC), nitrate, sulfate, ammonium, and other water-soluble ions (i.e., PO₄³⁻, Cl⁻, Na⁺, and K⁺), as well as crustal metals and trace elements. We used conversion factors of 2.0 and 1.8 to convert OC to OM concentrations in the cold and warm seasons, respectively (Saarikoski et al., 2012; Turpin and Lim, 2001). Moreover, crustal materials (CM) were calculated based on the oxidized form of metal elements utilizing the following equation (Chow et al., 1994; Hueglin et al., 2005; Marczan et al., 2001):

$$CM = 1.89 Al + 1.21 K + 1.43 Fe + 1.40 Ca + 1.66 Mg + 1.7 Ti + 2.14 Si(1)$$

In the above equation, Si concentration was estimated as $3.41 \times Al$ (Hueglin et al., 2005), since this species is not quantified by the ICP-MS analysis.

As presented in Fig. 1, PM_{2.5} mass concentrations were significantly higher (P_{value} = 0.02) in the cold season ($71.82 \pm 4.17 \mu\text{g}/\text{m}^3$) compared to that of warm season ($16.67 \pm 0.27 \mu\text{g}/\text{m}^3$). The higher PM_{2.5} levels are attributed to the more stable meteorological conditions and lower mixing height in the colder periods of the year (Marczcan et al., 2001; Vecchi et al., 2004), and, as it will be discussed in following sections, to the increased PM_{2.5} emissions from biomass burning. The average PM_{2.5} mass concentration was $44.22 \pm 12.81 \mu\text{g}/\text{m}^3$ throughout the year, exceeding the European Union (EU) annual mean PM_{2.5} limit of $25 \mu\text{g}/\text{m}^3$ (Council Directive, 2008). Moreover, the total PM_{2.5} mass concentration determined gravimetrically was in very good agreement ($86.2 \pm 4.0\%$ confidence) with the reconstructed PM_{2.5} mass by adding up the measured chemical species. We also observed higher mass concentrations of OM in the colder period, again as a result of more stable meteorological conditions combined with increased PM emissions from biomass burning. Higher concentrations of ammonium nitrate were also observed during the cold season, because the lower temperature and higher relative humidity during the cold period favor the particle phase formation of NH₄NO₃ (Mozurkewich, 1993; Stelson and Seinfeld, 1982). Finally, the concentrations of sulfate were low and comparable (P_{value} = 0.28) in both seasons.

Fig. 2 presents the seasonal average concentrations of selected crustal metals and trace elements in our sampling location. Previous studies have indicated that metals and trace elements can originate from

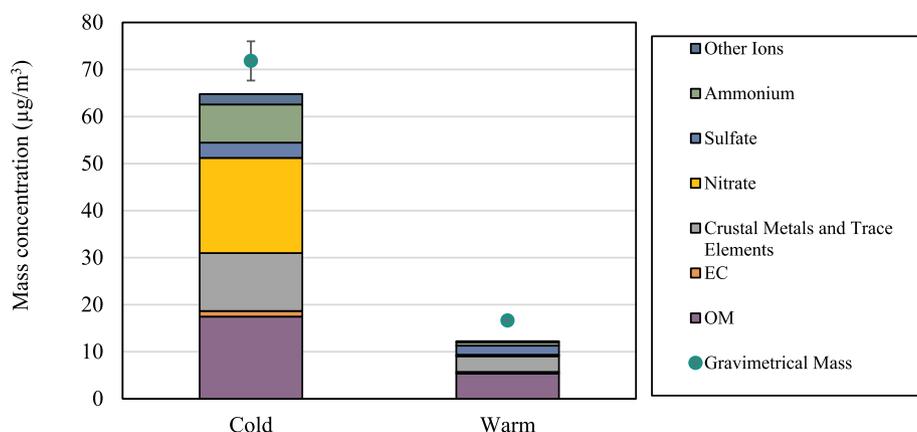


Fig. 1. Bulk chemical composition and gravimetric mass concentrations of ambient PM_{2.5} samples collected during warm and cold periods. Error bars correspond to one standard error (SE).

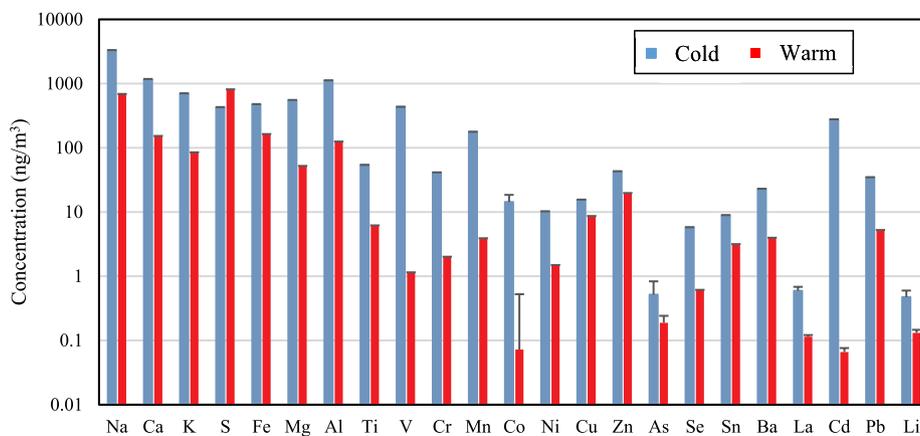


Fig. 2. Average concentrations of trace elements and transition metals in warm and cold periods of the study. Error bars indicate one standard error (SE).

both anthropogenic and natural sources, including re-suspended road dust, and industrial emissions (Almeida et al., 2006, 2005; Harrison et al., 2012; Mousavi et al., 2018b; Tian et al., 2016) as well as resuspension of crustal soil dust (Almeida et al., 2005; Tian et al., 2016). Chemical markers of mineral and road dust (i.e., Ca, Al, Fe, Li, Ti, Cr, Mn, Ni, Cu, Zn, and Ba (Harrison et al., 2012; Taghvaei et al., 2018; Tian et al., 2016; Yu et al., 2013)) and industrial activities (i.e., Se, As, Cd, Pb, and V (Chung et al., 2014; Grezzi et al., 2011; Hagelstein, 2003; Thomaidis et al., 2003)) showed higher levels in the colder period of the year, due to the higher atmospheric stability and lower mixing height in that period. To further investigate the contribution of mineral and road dust to $PM_{2.5}$ mass concentrations, we performed Spearman correlation analysis between crustal elements (i.e. surrogates of mineral dust and road dust) and tracers of vehicular activities (e.g., EC). Al, Ca, Mn, and Fe were highly correlated (with R values in the range of 0.62–0.98), leading us to the conclusion that these species are emitted by resuspension of mineral (soil) dust. Fe, Cu, and Ni (surrogates of non-tailpipe emissions (Godri et al., 2011; Wu et al., 2014) were also highly correlated (with R values in the range of 0.73–0.96) with EC (a tracer of tailpipe emissions), corroborating traffic emissions and road dust as the main sources of these $PM_{2.5}$ redox-active trace metals in the area.

3.2. $PM_{2.5}$ carbonaceous components

The average seasonal concentrations of WSOC, water-insoluble organic carbon (WIOC), and EC are illustrated in Fig. 3(a). All of these species had significantly higher mass concentrations in the cold period compared with the warm period (P_{value} ranging from 0.002 to 0.08), due to the higher biomass burning activities as well as lower mixing height in the cold season, as discussed earlier. It should be noted that the biomass burning fraction of WSOC ($WSOC_{bb}$) was calculated following the method suggested by Fine et al. (2004). Briefly, the biomass burning fraction of total OC (OC_{bb}) was estimated by multiplying the levoglucosan concentration by 0.135 (Fine et al., 2004), followed by multiplication of OC_{bb} by a factor of 0.71, as suggested by Sannigrahi et al. (2006) and Stone et al. (2008) to derive the $WSOC_{bb}$. The OC concentrations in the sampling site of Bareggio were within the range of previously conducted studies in Northern Italy (Perrino et al., 2014; Ricciardelli et al., 2017), reporting a range of 2–3.5 $\mu\text{g}/\text{m}^3$ and 5–10.5 $\mu\text{g}/\text{m}^3$ in warm and cold periods, respectively. Similarly, Perrino et al. (2014), and Ricciardelli et al. (2017) reported EC concentrations of 0.2–1.0 $\mu\text{g}/\text{m}^3$ (warm season), and 0.5–2.0 $\mu\text{g}/\text{m}^3$ (cold season) which are in line with the EC levels (0.3–1.7 $\mu\text{g}/\text{m}^3$) measured in the current study.

Previous studies have utilized Radon (Rn) concentration to differentiate the effects of atmospheric dilution from temporal variations in emission sources (Marcazzan et al., 2001; Vecchi et al., 2007). Since Rn

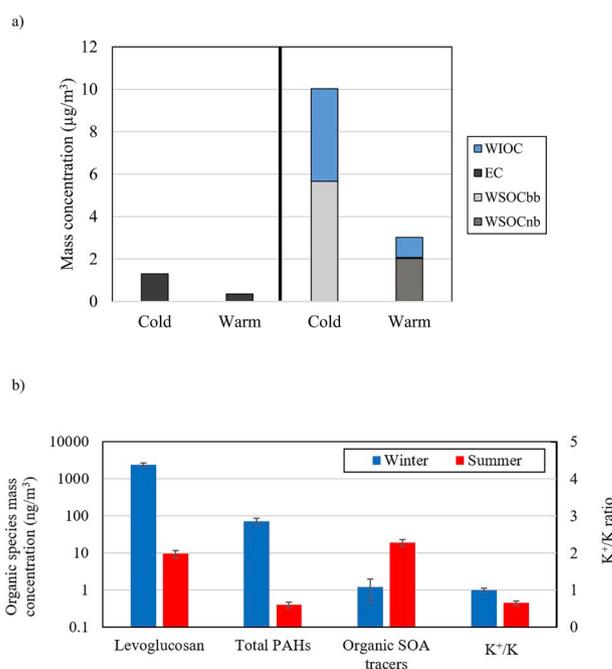


Fig. 3. Mass concentration of: a) carbonaceous components (i.e., elemental carbon (EC), organic carbon (OC), water soluble organic carbon (WSOC), and water insoluble organic carbon (WIOC)); and b) organic chemical tracer species (i.e., levoglucosan, organic SOA tracers, total PAHs) and K^+/K ratio in both sampling periods. Error bars correspond to standard error (SE).

concentration was not measured during our sampling campaign, we investigated the variations in mass concentration of several PM components to evaluate the effect of mixing height. Most of the $PM_{2.5}$ -bound metals and trace elements in Lombardy are emitted from anthropogenic sources with rather low seasonal variability (e.g., vehicular emissions, industrial activities, and power plants (Braga Marcazzan, 1998; Vecchi et al., 2004)). Therefore, their temporal variation can be mostly attributed to the different seasonal meteorological conditions (e.g., atmospheric mixing height). We investigated the winter-to-summer ratio of average mass concentration for selected metals and crustal elements, and the average of the calculated ratios for the metals and trace elements was 4.2 (± 2.0), demonstrating the significant effect of lower mixing height during the winter season on $PM_{2.5}$ components. In addition to the winter versus summer mass concentration trends of the selected metals and trace elements, as shown in Fig. 3 (a), the mass concentration of EC and WIOC increased by a factor of 3.7 and 4.6, respectively. This trend is in agreement with the observed temporal variation in metals and trace

elements levels, which can also be mainly attributed to the effect of atmospheric stability prevailing during the cold-period, rather than significant variations in the emission sources.

Conversely, mass concentration of WSOC_{bb} (a tracer of biomass burning emissions) increased by a factor of ~ 110 , from $0.05 \pm 0.03 \mu\text{g}/\text{m}^3$ during summer to $5.66 \pm 2.58 \mu\text{g}/\text{m}^3$ in winter. This substantial increase in WSOC_{bb} mass concentration cannot solely be justified by the lower wintertime mixing height, and it underscores the role of biomass burning activities during winter. Finally, the increase in the WSOC_{nb} from almost zero in winter to $2.02 \pm 0.64 \mu\text{g}/\text{m}^3$ during summer is related to enhanced photochemical activity during the summer, as will be discussed in section 3.3 of the manuscript.

The above-mentioned discussion regarding the role of atmospheric stability in the concentrations of PM_{2.5} mass concentration and its constituents during different seasons is in line with previous studies in the area (Marcazzan et al., 2001; Vecchi et al., 2004).

3.3. Levoglucosan mass concentration

Fig. 3(b) indicates the average mass concentration of levoglucosan, which is a tracer of biomass burning (Hennigan et al., 2010; Simoneit and Elias, 2001), during both periods of the sampling period. According to the figure, very high mass concentrations (~ 2000 – $2500 \text{ ng}/\text{m}^3$) were observed for this chemical marker of biomass burning emissions in the cold season. The levoglucosan mass concentrations measured in this study were drastically higher than previously reported values of $\sim 70 \text{ ng}/\text{m}^3$ at an urban site in the city center of Milan (Daher et al., 2012). This observation is in agreement with the results of Mousavi et al. (2019), who reported a much higher biomass burning fraction of black carbon (BC_{bb}) in the Milan suburbs compared to the city center.

Moreover, the results of linear regression analysis revealed a significantly high correlation ($R^2 = 0.71$) between WSOC and levoglucosan during the cold period, further indicating that the majority of WSOC in winter is emitted by biomass burning. On the other hand, we observed no correlation ($R^2 = 0.06$) between WSOC and levoglucosan during the warm season, confirming the minimal contribution of biomass burning to PM_{2.5} in this period. While previous studies have documented WSOC as a tracer of SOA formation (Snyder et al., 2009; Sun et al., 2011), this carbonaceous compound could also be emitted by biomass burning activities. The extremely high levoglucosan mass concentrations during the cold season yielded WSOC_{bb} values virtually identical to the measured WSOC, implying that all WSOC in the cold season comes from biomass combustion. To investigate the origin of WSOC in the warm period, measured concentrations of organic SOA species (shown in parentheses) produced from the oxidation of known precursors such as isoprene (i.e., 2-methylthreitol), α -pinene (i.e., 3-hydroxyglutaric acid, 3-acetyl hexanedioic acid, pinic acid, 2-hydroxy-4-isopropyladipic acid), and toluene (i.e., 2,3-dihydroxy-4-oxopentanoic acid) were summed and considered as organic SOA tracers in our analysis (Carlton et al., 2009; Claeys et al., 2007; Harrison et al., 2016; Hu et al., 2008). Based on the linear regression analysis, WSOC was strongly correlated ($R^2 = 0.73$) with organic tracers of SOA in the warm season. As shown in Fig. 3(b), the concentrations of organic SOA tracers increased substantially from the cold ($1.21 \pm 0.73 \text{ ng}/\text{m}^3$) to warm ($18.96 \pm 3.98 \text{ ng}/\text{m}^3$) period as a result of higher photochemical activities during the warm season. Therefore, WSOC during the warm period can be mostly attributed to the photochemical oxidation of primary aerosols.

The WSOC concentrations and the K⁺/K ratio (a tracer of biomass burning (Jung et al., 2014; Mousavi et al., 2018a; Soleimani et al., 2019)) were also highly correlated ($R^2 = 0.76$) during the colder period of our sampling campaign, once again corroborating the major impact of biomass burning emissions on WSOC concentration in the cold season. In contrast, no meaningful associations were observed between K⁺/K and WSOC during the warm period.

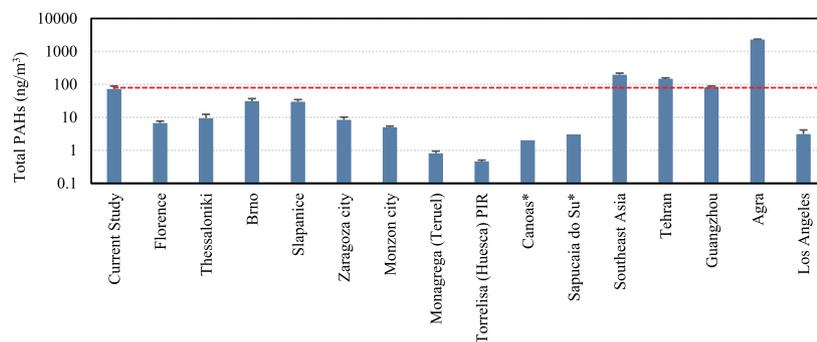
3.4. Total PAHs concentrations

PAHs are organic compounds with multiple aromatic rings, formed during the incomplete combustion of fossil fuels as well as biomass burning (Alves et al., 2015; Galarneau, 2008; Mandalakis et al., 2005; Simoneit, 2002). Fig. 3(b) presents the seasonal average concentrations of total PAHs during the sampling period. The total PAHs mass concentrations were significantly ($P_{\text{value}} = 0.01$) higher in the cold ($72.81 \pm 16.59 \text{ ng}/\text{m}^3$) season, compared to the warm period ($0.40 \pm 0.07 \text{ ng}/\text{m}^3$), as a result of the higher rate of primary emissions, particularly biomass combustion, in the cold season. A comparison of our reported total PAHs levels with prior literature (Agudelo-Castañeda and Teixeira, 2014; Callén et al., 2011; Duan et al., 2007; Hong et al., 2016; Hoseini et al., 2016; Krūmal et al., 2013; Manoli et al., 2016; Martellini et al., 2012; Shirmohammadi et al., 2017) is presented in Fig. 4. The measured PAHs concentrations during the cold season were significantly higher than most of the European urban background/suburban cities, including Thessaloniki ($9.40 \pm 2.94 \text{ ng}/\text{m}^3$), Brno ($31.00 \pm 6.08 \text{ ng}/\text{m}^3$), Florence ($6.7 \pm 1.00 \text{ ng}/\text{m}^3$), and even in Los Angeles freeways ($3.11 \pm 1.04 \text{ ng}/\text{m}^3$) in the US. In fact, the measured PAHs levels were within the range of the highly polluted urban areas of Guangzhou ($80.00 \pm 9.06 \text{ ng}/\text{m}^3$), and Tehran ($148.43 \pm 9.80 \text{ ng}/\text{m}^3$) in Asia. The very high PAHs concentrations recorded in the cold season of our campaign is one of the most significant findings of this study, particularly because they pertain to a suburban site not directly impacted by vehicular PM emissions. The major contribution of biomass burning to the PAHs concentrations is further supported by the high linear correlations between total PAHs and levoglucosan ($R^2 = 0.79$, Fig. S2(a)), and K⁺/K ($R^2 = 0.87$, Fig. S2(b)) during the cold period.

3.5. Oxidative potential of PM_{2.5}

Fig. 5 shows the seasonal variation in the extrinsic PM_{2.5} oxidative potential measured by the DTT assay in the current study in comparison to reported values for urban/suburban sites around the world using the same assay. Our measurements indicated a significant increase in the DTT levels ($P_{\text{value}} = 0.003$) from the warm ($0.85 \pm 0.10 \text{ nmol}/\text{min}\cdot\text{m}^3$) to cold period ($3.38 \pm 0.46 \text{ nmol}/\text{min}\cdot\text{m}^3$). While the measured summer-time DTT consumption rate is almost within the range of previously reported values in Po Valley region ($\sim 0.40 \text{ nmol}/\text{min}\cdot\text{m}^3$) (Pietrogrande et al., 2019), the winter-time rate had significantly higher values in comparison to values reported by previous studies in the area (0.06 – $1.15 \text{ nmol}/\text{min}\cdot\text{m}^3$) (Pietrogrande et al., 2019; Simonetti et al., 2018). Moreover, the winter-time DTT consumption rates in our study were higher than those reported in other European cities, including Athens and Lecce (0.40 ± 0.03 , and $0.26 \pm 0.03 \text{ nmol}/\text{min}\cdot\text{m}^3$, respectively) (Paraskevopoulou et al., 2019; Pietrogrande et al., 2018), as well as cities in the U.S., including Atlanta and Los Angeles (0.37 ± 0.09 , and $0.63 \pm 0.15 \text{ nmol}/\text{min}\cdot\text{m}^3$, respectively) (Shirmohammadi et al., 2017; Verma et al., 2014), but lower than DTT values measured in other highly polluted areas, such as the city of Thessaloniki, Greece, impacted heavily by biomass combustion in winter (DTT levels of $7.6 \pm 0.27 \text{ nmol}/\text{min}\cdot\text{m}^3$), Tehran ($9.0 \pm 0.47 \text{ nmol}/\text{min}\cdot\text{m}^3$), and coastal cities of Bohai Sea in China ($7.0 \pm 0.30 \text{ nmol}/\text{min}\cdot\text{m}^3$) (Al Hanai et al., 2019; Liu et al., 2018; Velali et al., 2016).

The higher wintertime DTT values observed in our sampling site are attributed to the significantly increased concentrations of organic compounds (i.e., PAHs and levoglucosan) as a result of biomass burning combustion for residential heating in the area. Similar observations have been previously reported in other European cities (Saffari et al., 2013; Simonetti et al., 2018; Velali et al., 2016) relating the enhanced PM oxidative potential to biomass burning activities particularly in the colder period of the year. Additionally, Decesari et al. (2017) reported that a significant portion of the toxicity of airborne PM during the winter in Po Valley is produced by environmental conditions favoring fog formation, which lead to the accumulation of redox-active compounds



b)

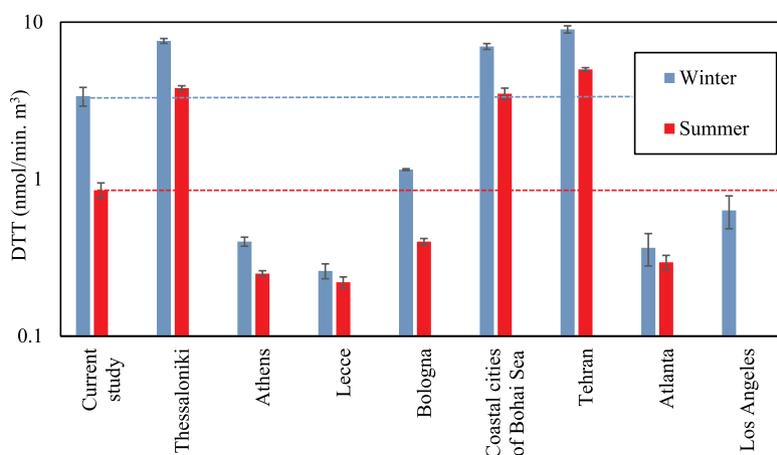
Site/city name	Site description	Country	Sampling year	Reference
Current Study	Urban background	Italy	2018 - 2019	-
Florence	Urban background	Italy	2009- 2010	(Martellini et al., 2012)
Thessaloniki	Urban background	Greece	2012 - 2012	(Manoli et al., 2016)
Brno	Urban city center	Czech Republic	2009-2010	(Křůmal et al., 2013)
Slapanice	Small suburban town	Czech Republic	2009-2010	(Křůmal et al., 2013)
Zaragoza city	Urban background; impacted by traffic and industrial activities	Spain	2009-2009	(Callén et al., 2011)
Monzon city	Urban background; impacted by various industrial activities	Spain	2009-2009	(Callén et al., 2011)
Monagrega (Teruel)	Regional background; located 7.6 km from a power plant	Spain	2009-2009	(Callén et al., 2011)
Torrelisa (Huesca)	Rural area; representative of biogenic sources	Spain	2009- 2009	(Callén et al., 2011)
Canoas*	Urban site; impacted by nearby roadway traffic	Brazil	2011-2013	(Agudelo-Castañeda and Teixeira, 2014)
Sapucaia do Su*	Urban site ; Impacted by nearby traffic and industrial zone	Brazil	2011-2013	(Agudelo-Castañeda and Teixeira, 2014)
Southeast Asia	Average representative of 11 background sites, 83 rural sites and 82 urban sites	Southeast Asia	2012-2013	(Hong et al., 2016)
Tehran	Average of 4 urban sites without direct impact of roadway traffic	Iran	2014-2014	(Hoseini et al., 2016)
Guangzhou	Urban site	China	2004	(Duan et al., 2007)
Los Angeles	Freeway	USA	2014-2016	(Shirmohammadi et al., 2017)

Fig. 4. a) Comparison of winter-time total PAHs concentrations in some urban, suburban and rural sites across the globe. b) Site characteristics of cited studies. Error bars correspond to standard error (SE). The SE for sites marked by * is not reported in the corresponding studies.

within the droplets, and not simply related to the emission and transport of pollutants in the area. In order to provide a more detailed insight into the comparative impact of different sources on PM_{2.5} oxidative potential, statistical analysis was performed to investigate the correlation between the DTT activity and mass concentrations of source specific species.

Table 1 shows the results of Spearman rank regression analysis between the extrinsic DTT activity and PM_{2.5} chemical compounds. As shown in Table 1, DTT was highly correlated with WSOC_{nb}, organic SOA

compounds, Al, and to some extent EC during the warm season. Previous studies have reported Al and EC as surrogates of re-suspended road dust and vehicular emissions, respectively (Hasheminassab et al., 2014; Pun et al., 2017; Schauer et al., 2003), while WSOC_{nb} is a chemical marker for secondary aerosols in the warm season, as discussed earlier. The correlation analysis therefore suggested that secondary organic compounds, and to lesser degree, vehicular emissions, are the main sources of the extrinsic oxidative potential of PM_{2.5} during the warm season. Winter-time Spearman correlation results showed that DTT levels were



a)

Site name	Site description	Country	Sampling year	Reference
Current Study	Urban background	Italy	2018 -2019	-
Thessaloniki	Urban background	Greece	2013	(Velali et al., 2016)
Athens	Urban	Greece	2016-2017	(Paraskevopoulou et al., 2019)
Lecce	Suburban	Italy	2014-2015	(Pietrogrande et al., 2018)
Bologna	Urban	Italy	2015	(Pietrogrande et al., 2019)
Coastal cities of Bohai Sea	Urban	China	2015-2016	(Liu et al., 2018)
Tehran	Urban (impacted by traffic)	Iran	2014-2015	(Al Hanai et al., 2019)
Atlanta (Urban)	Urban	USA	2012-2013	(Verma et al., 2014)
Los Angeles	Freeway	USA	2014-2016	(Shirmohammadi et al., 2017)

Fig. 5. a) Oxidative potential measured by DTT in the current study and comparison with sites from previous studies using the same assay. Error bars correspond to standard error (SE). b) Site characteristics of cited studies.

Table 1

Spearman correlation coefficients (R) between the DTT activity (nmol/min.m³ air) and mass concentration (µg/m³) of different chemical species. Correlation coefficients in bold are statistically significant (P_{value}<0.05).

Species	DTT (nmol/min.m ³)	
	Winter	Summer
WSOC _{nb}	-	0.89
WSOC _{bb}	0.71	-0.14
Levoglucosan	0.70	-0.14
K ⁺ /K	0.40	0.36
Total PAHs	0.70	-0.64
SOA tracers	-0.37	0.79
V	0.68	-0.75
Mn	0.57	-0.68
Ni	0.57	-0.29
Cu	0.57	-0.11
Zn	0.71	-0.64
Al	0.70	0.80
EC	0.64	0.50

highly correlated with WSOC_{bb}, levoglucosan, PAHs, and redox-active metals, illustrating the predominant effect of biomass burning, and to a lesser degree vehicular emissions and re-suspended road dust in PM_{2.5} toxicity during the cold season. The correlation between the oxidative potential of PM_{2.5} and individual chemical species was used as a guideline for the selection of specific PM_{2.5} source markers that were employed in the MLR model discussed in the following paragraph.

The results of the MLR analysis between the extrinsic DTT values and chemical species used as source-specific markers are shown in Table 2. Based on the output of Spearman correlation analysis, and after trying different combinations of source tracers in the MLR model, the best

Table 2

Multiple linear regression (MLR) analysis between DTT (as dependent parameter) and source specific chemical markers (independent parameters).

Source chemical marker	Unstandardized coefficients (±std. error)	Standardized coefficients (Beta)	Partial R	P-value	R ²
(Constant)	-0.442 ±0.453	-	-	-	0.95
WSOC _{nb}	0.432 ±0.174	0.459	0.68	0.042	
WSOC _{bb}	0.373 ±0.065	0.914	0.91	0.001	
EC	0.706 ±0.302	0.351	0.66	0.052	
Al	0.001 ±0.001	0.399	0.82	0.007	

linear regression fit resulting in the highest R² value is comprised of DTT as the dependent variable and WSOC_{nb}, WSOC_{bb}, EC, and Al as independent variables. Based on the R² value, the MLR model explained 95% of the total variance in DTT activity. The following equation shows the best linear fit between predicted DTT and statistically significant (P_{value}< 0.05) source tracers:

$$DTT = 0.432 \times WSOC_{nb} + 0.373 \times WSOC_{bb} + 0.706 \times EC + 0.001 \times Al - 0.442 \quad (2)$$

where DTT is in units of nmol/min. m³, Al is in ng/m³, and the units of other species (i.e., WSOC_{nb}, WSOC_{bb}, and EC) are all in µg/m³. The modeled DTT activity was plotted with respect to measured DTT in Fig. 6 (a).

As shown in Table 2, WSOC_{bb} was the dominant contributor to the extrinsic PM_{2.5} oxidative potential, with a corresponding Beta of 0.914, followed by WSOC_{nb}, EC, and Al (Beta values = 0.459, 0.351, and 0.399, respectively). As previously mentioned, WSOC_{nb}, WSOC_{bb}, EC, and Al were treated as chemical source tracers of SOA, biomass burning,

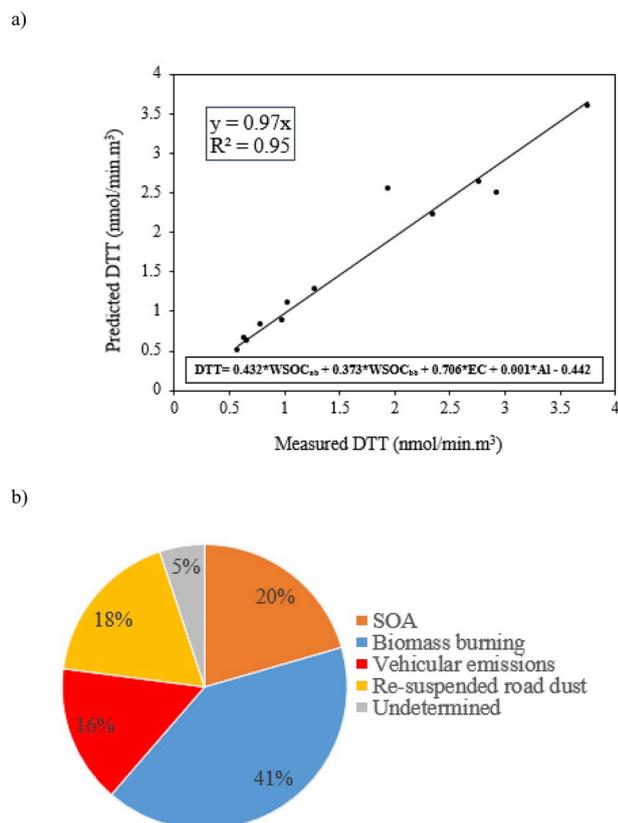


Fig. 6. a) Linear regression between measured and predicted DTT activity using multilinear regression (MLR) analysis. b) Relative source contributions to the oxidative potential measured by DTT at the sampling site.

vehicular emissions, and re-suspended road dust, respectively. Based on the derived beta values and the model coefficient of determination, the percent contributions of the four identified sources to the oxidative potential of $PM_{2.5}$ are presented in Fig. 6(b). Biomass burning emissions contributed to 41% of the overall extrinsic oxidative potential of $PM_{2.5}$, followed by SOA (20%), re-suspended road dust (18%), and vehicular emissions (16%). These results further underscore the dominant role of biomass burning emissions to the overall toxicity of $PM_{2.5}$ in the metropolitan area of Milan.

4. Summary and conclusions

The main goal of this study was to identify and quantify the $PM_{2.5}$ major sources contributing to its oxidative potential in the metropolitan area of Milan. Total $PM_{2.5}$ mass concentrations, as well as the concentrations of major carbonaceous PM species (i.e., EC, and OC), increased from the warm to the cold period. Of particular note were the concentration levels of PAHs, which increased by an approximate 150-fold, from $0.40 \pm 0.07 \text{ ng/m}^3$ during the warm period to $72.81 \pm 16.59 \text{ ng/m}^3$ in the cold season. These PAHs concentrations were among the highest reported in recent studies conducted globally. Increased biomass burning activities combined with meteorological stability resulted in high extrinsic $PM_{2.5}$ oxidative potential values in the wintertime in the study area, significantly higher than those reported in most of European cities, and even inside freeways in Los Angeles. Our statistical analysis indicated that biomass burning, SOA, re-suspended road dust, and vehicular emissions were the major contributing sources to the oxidative potential of $PM_{2.5}$, with corresponding contributions of 41%, 20%, 18%, and 16%, respectively, altogether explaining 95% of the measured DTT activity. Our results underscore the significant role of biomass burning emissions to $PM_{2.5}$ toxicity in the Milan metropolitan area and call for

pressing actions by policy makers to mitigate these emissions in order to protect the public against their adverse health effects.

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.

CRedit authorship contribution statement

Maryam Hakimzadeh: Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft. **Ehsan Soleimanian:** Methodology, Formal analysis, Data curation, Validation. **Amirhosein Mousavi:** Methodology, Data curation, Validation. **Alessandro Borghini:** Investigation, Data curation, Resources. **Cinzia De Marco:** Investigation, Data curation, Resources. **Ario A. Ruprecht:** Project administration, Supervision, Investigation, Writing - review & editing. **Constantinos Sioutas:** Conceptualization, Project administration, Funding acquisition, Supervision, Resources, Writing - review & editing.

Acknowledgments

This study was supported by the National Institutes of Health (NIH) (grants numbers: 5R01AI065617-18). We would also like to acknowledge the support of the PhD fellowship award from the USC Viterbi School of Engineering.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2020.117328>.

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