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Source apportionment of the oxidative potential of fine ambient particulate matter (PM_{2.5}) in Athens, Greece

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Abstract

The main objective of this study was chemical characterization and source apportionment of the oxidative potential of ambient PM_{2.5} samples collected in an urban background area in Athens, Greece. Ambient PM_{2.5} samples were collected during the summer (June–September) of 2017 and winter (February–March) of 2018 at a residential, urban background site in the outlying neighborhood of the Demokritos National Laboratory in Athens, Greece. The collected PM samples were analyzed for their chemical constituents including metals and trace elements, water-soluble organic carbon (WSOC), elemental and organic carbon (EC/OC), and marker of biomass burning (i.e., levoglucosan). In addition, the DCFH *in vitro* assay was performed to determine the oxidative potential of the PM_{2.5} samples. We performed a series of statistical analyses, including Spearman rank-order correlation analysis, principal component analysis (PCA), and multi linear regression (MLR) to determine the most significant species (as source tracers) contributing to the oxidative potential of PM_{2.5}. Our findings revealed that the intrinsic (per PM mass) and extrinsic (per m³ of air volume) oxidative potentials of the collected ambient PM_{2.5} samples were significantly higher than those measured in many urban areas around the world. The results of the MLR analyses indicated that the major pollution sources contributing to the oxidative potential of ambient PM_{2.5} were vehicular emissions (characterized by EC) (44%), followed by secondary organic aerosol (SOA) formation (characterized by WSOC) (16%), and biomass burning (characterized by levoglucosan) (9%). The oxidative potential of the collected ambient PM_{2.5} samples was also higher in summer compared to the winter, mainly due to higher concentrations of EC and WSOC during this season. Results from this study corroborate the impact of traffic and SOA on the oxidative potential of ambient PM_{2.5} in greater Athens area, and can be helpful in adopting appropriate public health policies regarding detrimental outcomes of exposure to PM_{2.5}.

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Keywords

Ambient PM_{2.5}; Oxidative potential; Source apportionment; MLR; Athens

1. Introduction

Particulate matter (PM) is one of the most critical pollutants in the atmosphere, particularly in metropolitan areas that are heavily impacted by emissions from vehicles, industrial facilities, and other sources of urban air pollution. Among the different size fractions, ambient fine PM (i.e., air suspended particles with an aerodynamic diameter smaller than 2.5 µm, PM_{2.5}) is of great importance due to its distinct physico-chemical characteristics and diverse sources, as well as its adverse human health impacts due to acute and chronic exposures. Previous studies have indicated that exposure to PM_{2.5} is associated with several detrimental health impacts, including increased daily mortality as well as numerous cardiovascular, neurological, and respiratory diseases, such as chronic obstructive pulmonary disease (COPD) (Dockery and Stone, 2007; Gauderman et al., 2015). One of the main biological mechanisms believed to be contributing to the etiology of many of these detrimental health effects is the generation of reactive oxygen species (ROS) in cells, which triggers an oxidative stress response involving several proinflammatory cascades that ultimately result in pathology (Ayres et al., 2008; Jiang et al., 2016). When the intracellular ROS concentration exceeds an equilibrium threshold determined by available antioxidants within the cell, cellular oxidative stress and, in turn, adverse health outcomes ensue (Delfino et al., 2013; Li et al., 2009). Thus, several researchers have sought to develop biological and chemical assays to quantify the oxidative potential of particulate matter as indexed by this cellular oxidative stress response (Verma et al., 2015). The *in vitro* 2', 7'-dichlorodihydrofluorescein (DCFH) assay, which is conducted using alveolar macrophage cell cultures derived from rat lung tissue, is one of the most widely used measures of oxidative potential (Landreman et al., 2008; Shirmohammadi et al., 2017), which has also been linked to markers of airway and systemic inflammation (Delfino et al., 2010; Zhang et al., 2016).

It should be noted, however, that when evaluating the oxidative potential and adverse health effects of ambient PM, not all of the chemical components and size ranges could be considered equally toxic. Numerous studies have shown that some PM components, including redox active metals such as Fe, Cu, Mn and V (Akhtar et al., 2010; Charrier and Anastasio, 2012; Gasser et al., 2009), water-soluble organic carbon (WSOC) (Bae et al., 2017; Samara, 2017; Verma et al., 2012, 2009; Vreeland et al., 2017), elemental carbon (EC) (Cho et al., 2005; Kleinman et al., 2012; Samara, 2017; Shirmohammadi et al., 2017), organic carbon (OC) (Chirizzi et al., 2017; Samara, 2017; Styszko et al., 2017), and polycyclic aromatic hydrocarbons (PAHS) (Cho et al., 2005; Lundstedt et al., 2007; Shirmohammadi et al., 2016), are significantly associated with the oxidative potential of PM, while many other components, including secondary inorganic ions, are rather innocuous species, and while they may contribute significantly to PM mass concentrations, they do not have an appreciable impact on PM toxicity (Fang et al., 2016). In addition, particles emitted from various sources each have distinct chemical fingerprints, and many common chemical

PM species are released from a wide variety of sources (Hasheminassab et al., 2014; Manousakas et al., 2017b; Mousavi et al., 2018b; Port et al., 2017; Taghvaei et al., 2018). Therefore, it has become increasingly important to link the chemical species and sources of ambient PM with oxidative potential, which provides us with critical information to effectively reduce emissions from sources that release PM with greater toxicity.

Few studies have evaluated the adverse health effects and air quality deterioration associated with ambient PM in Athens, the capital of Greece, and one of Europe's largest metropolitan areas, with approximately 5 million residents (Economopoulou and Economopoulos, 2002; Karakatsani et al., 2003; Mantas et al., 2014). The economic crisis in Greece, starting in 2010, caused a great increase in the price of residential heating fuel oil, which in turn led to extensive and widespread burning of biomass, particularly wood, as an alternative fuel (Argyropoulos et al., 2016; Diapouli et al., 2017b). As a result, ambient wintertime PM_{2.5} and BC concentrations have increased remarkably over the past few years in Athens (Athanasopoulou et al., 2017; Paraskevopoulou et al., 2014) and are observed to be also spatially widespread across the Athens metropolitan area (Kalogridis et al., 2018). Previous studies in this city have indicated that local emission sources, including vehicular activities, secondary aerosols, and biomass burning, are the major contributors to PM_{2.5}. Additionally, the chemical composition of PM_{2.5} is highly dominated by secondary organic and inorganic compounds in Athens (Amato et al., 2016; Diapouli et al., 2017b; Pateraki et al., 2019). However, none of the studies have so far linked the chemical components and sources of ambient PM_{2.5} to its oxidative potential in this city.

The main objective of this study was to characterize chemically and toxicologically ambient PM_{2.5}, and to link individual chemical components and sources of PM_{2.5} to the measured oxidative potential in a suburban sampling site, approximately 7 km to the northeast of the city center of Athens, Greece. Ambient PM_{2.5} samples were collected in two seasons of the year, including a summer, or warm season (July–September), and a winter season (February–March). Collected PM samples were then analyzed for their chemical components, and the PM oxidative potential was determined using the DCFH *in vitro* assay. Principal component analysis (PCA) coupled with multiple linear regression (MLR) were used to link sources of ambient PM_{2.5} to the measured oxidative potential.

2. Experimental methodology

2.1 Sampling site

PM_{2.5} samples were collected at the Global Atmosphere Watch (GAW) Demokritos station (DEM_Athens) in Athens, Greece. The DEM_Athens station is located inside the National Center for Scientific Research “Demokritos” campus (37° 59' 25'' N, 23° 48' 34'' E, 270 meters above sea level (m.a.s.l.)). The campus is situated in a suburban region, approximately 7 km northeast of the metropolitan center of the city, and covers an area of 600 acres in a forest of pine trees, at the foot of Mount Hymettus. The site is not directly impacted by fresh urban PM emissions and is thus considered representative of the urban background air quality in Athens (Eleftheriadis et al., 2014; Triantafyllou et al., 2016).

2.2 Sample collection and analysis

Ambient PM_{2.5} samples were collected during two seasons of the year, including summer (June 5 to September 15, 2017), and winter (February 2 to March 16, 2018) campaigns. Weekly time-integrated PM_{2.5} samples were collected on 37 mm PTFE (Teflon) and Quartz filters (Pall Life Sciences, 2-mm pore, Ann Arbor, MI) using Sioutas Personal Cascade Impactor Samplers (PCISs, SKC Inc., Eighty-Four, PA, USA) (Misra et al., 2002; Singh et al., 2003) operating at a flow rate of 9 L/min. Therefore, the sampled air volume for each weekly time-integrated sample was 90.72 m³. In this study, since we aimed to collect the whole PM_{2.5} range without size segregation, we only used stage A of the PCIS to remove particles > 2.5 µm, and used 37-mm Teflon and Quartz filters in the “after-filter” stage of the PCIS to collect PM_{2.5}. In addition, the collection plate of stage A was covered with a thin layer of grease to prevent bouncing of coarse particles from stage A onto the after-filter stage. The Teflon filters collected with the PCISs were used for the DCFH *in vitro* assay, and water-soluble organic carbon (WSOC), while organic species (i.e., levoglucosan) analyses was performed on Quartz filters. The mass concentrations of PM_{2.5} samples on 37mm PTFE and Quartz filters were quantified gravimetrically by weighing these filters before and after sampling. This procedure was done using a high precision (± 0.001 mg) microbalance (MT5, Mettler Toledo Inc., Columbus, OH), following filter equilibration under controlled temperature (22–24 °C) and relative humidity (40–50%) conditions. Chemical analysis of the samples was carried out at the Wisconsin State Lab of Hygiene (WSLH) for levoglucosan and water-soluble organic carbon (WSOC). Gas Chromatography/Mass Spectrometry (GC/MS) was employed to determine levoglucosan concentrations (Schauer et al., 1999). Finally, a Sievers 900 Total Organic Carbon Analyzer was used to analyze the samples for water-soluble organic carbon (WSOC) following extraction and filtration (0.22 µm pore size) of the filters using ultrapure water (Stone et al., 2008).

In addition to PCIS sampling, a sequential low volume reference sampler equipped with a PM_{2.5} inlet (PM10/2.5 SEQ 47/50-CD with Peltier cooler, Sven Leckel GmbH) (2.3 m³/h) was used to collect daily 24-h samples on 47-mm Teflon filters (PTFE Watman, 1 µm pore size). 24-h PM_{2.5} concentrations were determined gravimetrically by a microbalance (Sartorius Model BP 211 D) of 0.01 mg accuracy. Prior to weighing, the filters were conditioned for 48 h at 19–21 °C and 45–50% RH. These filters were also analyzed by ED-XRF (Epsilon 5, PANalytical) for major and trace elements. Details on the analysis and QA/QC procedures may be found in Manousakas et. al (2017a). Furthermore, a model-4 semi-continuous OC/EC field analyzer (Sunset Laboratory Inc, USA) was used for the quantification of EC/OC by thermo-optical transmittance (TOT) analysis on a 3-hour basis. The instrument was sampling at a flow rate of 8 lpm, from a PM_{2.5} cut-off inlet and was equipped with an in-line parallel carbon denuder for the removal of organic gases. The EUSAAR2 protocol was applied for sample analysis (Cavalli et al., 2010).

2.3 Determination of PM oxidative potential via the DCFH assay

To determine the oxidative potential of the collected PM samples, the fluorogenic DCFH *in vitro* assay, which uses rodent alveolar macrophage cells (i.e., scavenging cells in the inner epithelial lining of the lung), was employed. For this assay, 1.00 ml sterilized Milli-Q water was used to extract PM from the Teflon filters while subjecting them to 16 hours of agitation

at room temperature in the absence of light, followed by 30 minutes of sonication. During the treatment phase of this assay, cultures of the NR8383 rat alveolar cell line (American Type Culture Collection) were exposed to the suspended PM aqueous phase slurries derived from filter extraction along with 15 μM concentrations of 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA) in 96-well cell culture plates. As soon as it enters a cell, DCFH-DA is converted to the non-fluorescent DCFH through a process of de-acetylation by intracellular esterase enzymes. The non-fluorescent DCFH is then converted to the highly fluorescent dichlorofluorescein (DCF) due to oxidation by reactive species produced in the cytoplasm of the cells. DCF production was monitored spectrophotometrically using a microplate reader, which provides a reliable index of PM oxidative potential in fluorescence units per mass of PM ($\text{FU}\cdot\mu\text{g}^{-1}$ PM). Moreover, since the Toll-like receptors (TLR-2) of macrophage cells are able to identify Zymosan, this glucan was used in the assay as a positive control for observation of a potent response. The intrinsic PM oxidative potential can be obtained in units of μg Zymosan. μg^{-1} PM by normalizing the fluorescence data (reported in $\text{FU}\cdot\mu\text{g}^{-1}$ PM) to the response of a unit of Zymosan. The intrinsic PM oxidative potential can then be multiplied by the ambient PM mass concentration for the corresponding samples to obtain the extrinsic PM induced toxicity (i.e., in units of μg Zymosan. m^{-3} air) (Landreman et al., 2008).

2.4 Source Apportionment of PM_{2.5} and its associated oxidative potential

In this study, the principal component analysis (PCA) was done using daily 24-h samples of EC, OC, trace, and metal elements to identify the major source factors that contribute to PM_{2.5} concentrations. Assuming that correlated chemical species have similar emission sources, PCA was performed to find out the clusters of chemical components, each representing specific PM_{2.5} sources. Varimax orthogonal rotation method was utilized to better fit the data and provide optimized factor loadings, allowing for the matching of each component with a single factor. In addition, source factors having eigenvalues greater than unity were considered to be significant sources (Argyropoulos et al., 2016). The Kaiser-Meyer-Olkin (KMO) value we also set to above 0.5 to ensure the suitability of the data for the PCA procedure (Pechenizkiy et al., 2004).

Volumetric concentrations of weekly sampled WSOC, OC, EC, levoglucosan, trace and metal elements, and the corresponding PM_{2.5} oxidative potential were used to perform bivariate correlation analysis by calculating Spearman's rho (non-parametric) coefficients. The correlation coefficients provide us with preliminary data, allowing us to identify species that are highly correlated with measured PM oxidative potential. We then employed the MLR analysis between these species (as independent variables and chemical markers of various PM_{2.5} sources) and PM oxidative potential (as dependent variable) to determine the source factors most responsible for driving the PM_{2.5} oxidative potential. According to the approach suggested by previous studies (Argyropoulos et al., 2016; Shirmohammadi et al., 2018), we ran MLR using various combinations of source markers, and kept the statistically significant ($p\text{-value} < 0.05$) species that led to the highest R^2 regression values. Then, the standardized regression coefficient (Beta) of each chemical marker was used along with the derived R^2 value of the regression line to determine the relative contribution of each source to PM_{2.5} oxidative potential. Additionally, the standard error (std. error) for both

unstandardized (B) and standardized coefficient (Beta) was calculated. The following equation was used for deriving the standard error for unstandardized coefficients of a multiple linear regression estimate:

$$\sigma_{est} = \sqrt{\frac{\sum (Y - Y')^2}{N}} \quad (1)$$

where, σ_{est} refers to the standard error of the regression estimate; Y is the actual score (sample); Y' is the predicted score from the MLR estimation; and N is the number of samples (Everitt and Skrondal, 2010). In order to calculate the standard error for standardized coefficient (Beta), samples should be standardized by converting the values into the Z-score, using the equation below:

$$Z = \frac{\sigma - Y}{\bar{Y}} \quad (2)$$

where, Z-score is the standardized format of score (sample), σ is the standard deviation of score (sample), and $\bar{Y}$ refers to the mean of samples (Kreyszig, 2011). Finally, the standard error of Beta can be obtained by substituting the derived Z-score and their corresponding mean (instead of Y and Y') in equation (1).

3. Results and Discussion

3.1. Mass concentration and chemical composition of PM_{2.5}

3.1.1. Concentrations of PM_{2.5} mass and carbonaceous species—Figure 1(a) and Table S1 presents the average PM_{2.5} mass concentrations of collected samples using PCIS during the summer and winter seasons as well as during the whole study period (i.e., average of warm and cold seasons). Based on this figure, comparable PM_{2.5} mass concentrations (P -value = 0.890) were observed in the cold ($11.8 \pm 6.0 \mu\text{g}/\text{m}^3$) and summer seasons ($11.2 \pm 3.3 \mu\text{g}/\text{m}^3$). Typically, stable meteorological conditions, lower wind speed, and lower mixing heights result in higher PM_{2.5} levels in cold periods of the year (Sowlat et al., 2016). However, as can be seen in Table S2, in the present study, the wind speeds are comparable during the cold and warm season, leading to similar degrees of atmospheric instability and horizontal dispersion of the emissions, which could be one of the reasons for observing comparable PM_{2.5} concentrations in cold and warm seasons. Consistent with our results, previous studies in suburban areas of Athens have also indicated comparable PM_{2.5} concentrations in both seasons (Diapouli et al., 2017b; Vasilatou et al., 2017). In addition, the significant contribution of SOA to PM_{2.5} mass concentrations during warm period counterbalances the impact of meteorological conditions that increase PM_{2.5} concentrations during cold period, leading to comparable PM_{2.5} levels in both phases of the sampling. Furthermore, the average PM_{2.5} mass concentration during the whole study period ($11.4 \pm 4.4 \mu\text{g}/\text{m}^3$) is in agreement with the results from the recent studies of Amato et al. (2016) (at the same sampling site) and Diapouli et al. (2017b). This agreement also corroborates the fact that our sampling has been representative of a whole-year sampling,

and that the average PM_{2.5} level measured in this study can be considered as the annual average of PM_{2.5} in the study area.

The seasonal average concentrations of carbonaceous compounds, including elemental (EC) and organic carbon (OC), measured on a 3-h basis, and water soluble organic carbon (WSOC), measured on a weekly basis, are illustrated in Figure 1(b). According to this figure, higher concentrations were observed for EC in warm season ($0.44 \pm 0.1 \mu\text{g}/\text{m}^3$) compared to the cold season ($0.26 \pm 0.06 \mu\text{g}/\text{m}^3$), and the difference was statistically significant (P -value = 0.004) according to the independent sample T-test. This could be attributed to the fact that our sampling site is downwind of the city center, so vehicular emissions from the abundant traffic sources in the city center reach the study area to a higher extent in the summertime due to the enhanced atmospheric dispersion and mixing during that period (Toro Araya et al., 2014). The average EC concentration for the whole study period ($0.36 \pm 0.12 \mu\text{g}/\text{m}^3$) was also within the range of values reported by previous studies carried out in the area (Amato et al., 2016; Paraskevopoulou et al., 2014).

Investigating the seasonal trend of OC concentrations also revealed comparable concentrations (P -value = 0.403) in cold ($1.8 \pm 0.3 \mu\text{g}/\text{m}^3$) and warm ($2.0 \pm 0.4 \mu\text{g}/\text{m}^3$) periods, with summertime values being only slightly higher. In addition to primary sources (i.e., biomass burning and traffic activities), OC can be originated from secondary sources and photochemical activities, leading to the formation of SOA. Therefore, while the contribution of some primary sources (such as biomass burning for residential heating) to OC concentrations are expected to be higher during the cold season, their impact is counterbalanced by SOA contributions due to peak photochemical activities in the summer, which increase OC concentrations to levels higher than those observed in the cold season (Paraskevopoulou et al., 2014). In addition, the average OC concentration observed for the whole study period ($1.93 \pm 0.39 \mu\text{g}/\text{m}^3$) is in good agreement with the OC values reported in the previous studies performed in urban background sites near Athens (Amato et al., 2016; Paraskevopoulou et al., 2014). WSOC (a chemical marker of SOA (Arhami et al., 2017; Snyder et al., 2009)) levels were enhanced during the summer ($1.4 \pm 0.5 \mu\text{g}/\text{m}^3$) compared to the winter ($0.7 \pm 0.3 \mu\text{g}/\text{m}^3$), due to the photochemical formation of secondary organic compounds (Hasheminassab et al., 2014; Heo et al., 2009) and the winter vs. summer difference was statistically significant (P -value = 0.012).

3.1.2 Levoglucosan Concentrations—The average concentrations of levoglucosan, one of the most widely used tracers of biomass burning (Simoneit et al., 1999), during the whole study period, as well as by season, are illustrated in Figure 2. According to the figure, the average concentration of levoglucosan was significantly higher during the cold season ($44.8 \pm 39.8 \text{ ng}/\text{m}^3$) as opposed to the warm season ($5.5 \pm 0.8 \text{ ng}/\text{m}^3$) (P -value = 0.039). This trend clearly reveals the higher wood burning activities, particularly for domestic heating purposes, in colder months of the year, as observed in previous studies (Diapouli et al., 2017a, 2017b; Gratsea et al., 2017). In addition, the average levoglucosan concentrations for the whole sampling period ($24.8 \pm 33.54 \text{ ng}/\text{m}^3$) is quite comparable with previously reported value by Amato et al. (2016) ($37 \text{ ng}/\text{m}^3$).

3.1.3. Metals and trace elements—Previous studies have indicated that major and trace elements can be originated from a wide variety of sources such as resuspension of road dust, tire and break ware, road abrasion, and soil dust emissions (Adamiec et al., 2016; Harrison et al., 2012). Figure 3 presents the average concentrations of metal and trace elements during the warm and cold seasons. As can be seen in the figure, crustal elements including Ca, Si, Ti, and Fe, that are typical chemical markers of soil dust activities (Hasheminassab et al., 2014; Zhang et al., 2013), had significantly higher concentrations (P -value < 0.05) during the summer, due mainly to drier atmospheric conditions (i.e., lower relative humidity in the summer (Table S2)) that facilitate particle resuspension from the loose soil open surfaces in the city of Athens and the surrounding region (Athanasopoulou et al., 2010). Furthermore, comparable concentrations were observed for Cu, and Pb (with P -values of 0.351, and 0.605 respectively), that are used as tracers of road dust and non-tail pipe traffic emissions (Adamiec et al., 2016; Hjortenkranz et al., 2007) during both phases of the sampling campaign. Comparable concentrations of Na (P -value = 0.64) a chemical tracer of sea salt (Zong et al., 2016), were observed during the summer and winter period, with slightly higher concentrations in the warm phase. Generally, Na concentrations are expected to be higher in the summer time due to higher wind speeds that facilitate the dispersion of sea salt particles further inland. However, strong northeasterly winds experienced during the winter time in the Athens area (Diapouli et al., 2017b) also bring sea salt to the area, which lead to observing comparable Na concentrations during the warm and cold seasons. This is consistent with the meteorological data presented in Table S2, showing comparable wind speeds during both seasons.

Overall, S, Al, Si, Ca, and Fe were among the most abundant elemental species in the collected PM_{2.5} samples. Additionally, concentrations of the measured trace elements and metals were consistently within the range of reported values in previous studies (Amato et al., 2016; Diapouli et al., 2017b; Paraskevopoulou et al., 2014). For example, in this study, the average concentration of Fe and Si were 103.8 ng/m³ and 213.0 ng/m³, respectively. These levels are in good agreement with the results from the study of Amato et al. (2016) at the same sampling location, reporting Fe and Si concentrations of 112.0 ng/m³ and 234.0 ng/m³, respectively.

3.2 Oxidative potential of PM_{2.5}

Figure 4 presents the intrinsic (per PM mass) and extrinsic (per air volume) levels of PM_{2.5} oxidative potential in the warm and cold seasons. In addition, the average values of intrinsic and extrinsic PM_{2.5} oxidative potential are shown in Table S1 during the two sampling campaigns as well as the whole study period. While the mass-normalized oxidative potential (in units of μg Zymosan/mg PM) is indicative of the intrinsic PM-induced toxicity and used in conventional toxicology, the volumetric oxidative potential (in units of μg Zymosan/m³ of air) is a more suitable measure for PM population exposure and inhalation assessment studies (Shirmohammadi et al., 2018, 2017). As can be seen in Figure 4(a), the mass-based oxidative potential of the collected ambient PM_{2.5} samples was higher in summer (12910.7 ± 4898.6 μg Zymosan/mg PM) as compared to winter (8549.3 ± 4388.1 μg Zymosan/mg PM), although the differences were marginally significant (P -value = 0.151). Similar temporal trends were observed for the volumetric PM oxidative potential, indicating

higher per-volume oxidative potential in the summer ($150.6 \pm 84.4 \mu\text{g Zymosan}/\text{m}^3$) than in the winter ($83.3 \pm 35.8 \mu\text{g Zymosan}/\text{m}^3$) (Figure 4(b)) with marginally significant statistical difference between seasonal levels (P -value = 0.113). Comparison of the mass-based oxidative potential levels measured in this study ($11041.6 \pm 5034.3 \mu\text{g Zymosan}/\text{mg PM}$) with those of earlier studies carried out in different metropolitan areas around the world indicated higher oxidative potential levels compared to those of many other cities, including Denver (with the average of $2006.6 \mu\text{g Zymosan}/\text{mg PM}$), Thessaloniki (around $738.0 \mu\text{g Zymosan}/\text{mg PM}$), and Los Angeles (with the average of $748.5 \mu\text{g Zymosan}/\text{mg PM}$). It is noteworthy that the mass-normalized oxidative potential of the ambient $\text{PM}_{2.5}$ samples in this study are even higher than those measured inside major freeways in the Los Angeles County, including I-110 ($3660 \pm 1743 \mu\text{g Zymosan}/\text{mg PM}$) and I-710 freeways ($3439 \pm 3058 \mu\text{g Zymosan}/\text{mg PM}$) (Shirmohammadi et al., 2017). In addition, the mass-based oxidative potential of the ambient $\text{PM}_{2.5}$ samples collected in this study are also higher than that of the ultrafine PM (UFP) samples collected in central Los Angeles ($9424 \pm 3703 \mu\text{g Zymosan}/\text{mg PM}$) (Mousavi et al., 2018a), and near the Los Angeles international airport (i.e., LAX) ($4600.93 \pm 1516.98 \mu\text{g Zymosan}/\text{mg PM}$) (Shirmohammadi et al., 2018). These results underscore the very high oxidative potential of the ambient $\text{PM}_{2.5}$ in the metropolitan area of Athens and its nearby suburban areas, which we believe is one of the most notable observations of our study. Similar trends were also observed for the volume-based oxidative potential of $\text{PM}_{2.5}$, indicating much higher (by 3–5 fold) levels in our sampling site ($120.5 \pm 80.7 \mu\text{g Zymosan}/\text{m}^3$) compared to other urban environments, including Denver (with the average of $20.9 \mu\text{g Zymosan}/\text{m}^3$), Thessaloniki (around $28.0 \mu\text{g Zymosan}/\text{m}^3$), and Los Angeles (with the average of $35.8 \mu\text{g Zymosan}/\text{m}^3$) (Saffari et al., 2014). The higher oxidative potential level observed in our sampling site is of particular significance because the elevated PM toxicity pertains to an urban background area in Athens, compared with the heavily impacted traffic and metropolitan areas investigated in previous studies.

3.3. Source apportionment of ambient $\text{PM}_{2.5}$ and its associated oxidative potential

3.3.1. Source apportionment of $\text{PM}_{2.5}$ mass concentration using the PCA approach—Table 1 illustrates the results of the PCA analysis performed on the daily EC, OC, as well as trace elements and metal concentrations during the whole study period. Our analysis indicates that the PCA was able to identify four source factors, explaining about 95% of total variance in the data. The identified factors were named as soil dust emissions (due to significant loadings of Ca, Si, and Ti as crustal elements (Sowlat et al., 2012; Taghvaei et al., 2018)), vehicular emissions (due to high loadings of EC, and Ni (Hasheminassab et al., 2014; Zong et al., 2016)), road dust and non-tail pipe traffic emissions (due to high loadings of Cu, and Pb (Adamiec et al., 2016; Pant and Harrison, 2013)), and a fourth factor with a very high loadings of OC (and to a lesser extent EC). The fourth factor cannot be attributed to a unique source, as OC originates from a multitude of sources, including both primary (i.e., traffic and biomass burning), and secondary (i.e., SOA) sources. Therefore, as will be discussed in Section 3.3.3., we performed an additional MLR analysis to apportion OC concentrations to its contributing sources.

3.3.2. Correlation analysis between individual chemical species and PM oxidative potential—Bivariate correlation analysis was carried out between the volume-

based PM oxidative potential and weekly sampled concentrations of WSOC, OC, EC, levoglucosan, and trace elements and metals to find species that are highly correlated with PM-induced toxicity. Table 2 shows the Spearman's rho coefficient (R); in which the highly (with $R > 0.7$) and relatively highly (with $R > 0.6$) correlated species are bolded. Based on the table, OC was strongly correlated with PM oxidative potential (with $R > 0.7$). This result was well in agreement with the results of previous studies, introducing OC as a significant fraction of PM with notable toxicity (Samara, 2017; Styszko et al., 2017). Moderate-to-strong associations were also observed between oxidative potential and EC, as well as with WSOC, in accordance with results from previous studies demonstrating the oxidative potential of these toxic species (Shirmohammadi et al., 2017; Vreeland et al., 2017). In addition, a moderate association was also observed between PM-induced oxidative potential and Ni as tracer of traffic emissions (Querol et al., 2007).

3.3.3. Source apportionment of PM oxidative potential using MLR approach

—As mentioned in the Methodology section (Section 2.4), based on the results of the correlation analysis between individual chemical components and the oxidative potential of ambient PM_{2.5} samples, we performed an MLR analysis to determine the most significant sources responsible for the PM-induced toxicity, using oxidative potential as the dependent variable and weekly sampled individual species as source markers and independent variables; the results of which are presented in Table 3(b). As can be seen in the table, EC and OC were the most important species contributing to PM oxidative potential, with the standardized regression coefficients (Beta) of 0.497 and 0.451, respectively. Finally, the coefficient of statistical determination for the model indicates that 73% of variation in the oxidative potential of ambient PM_{2.5} samples was explained by EC (a tracer of vehicular emissions) and OC.

Although EC is a tracer of vehicular emissions (Hasheminassab et al., 2014; Heo et al., 2009; Zong et al., 2016), OC is not a unique tracer of a specific pollution source. Previous studies have indicated that a combination of primary combustion sources (i.e., biomass burning, industrial emissions, airport, port and vehicular activities) as well as secondary formation mechanisms (e.g., photochemistry producing SOA) contribute to OC concentrations (Arhami et al., 2018; Paraskevopoulou et al., 2014). As a result, it is vital to identify the relative contribution of these primary and secondary sources to OC and, in turn, to PM_{2.5} oxidative potential. Therefore, we performed another set of MLR analysis using OC as the dependent variable and individual marker species as independent variables. According to the standardized regression coefficients presented in Table 3, the majority of OC was associated with WSOC (Beta=0.75) which is a tracer of SOA (Arhami et al., 2017; Liu et al., 2018) and levoglucosan (Beta=0.42) which is a tracer of biomass burning (Simoneit et al., 1999). The remaining loading was also due to OC from traffic sources (Beta=0.27), represented by EC (Zong et al., 2016). Finally, this model was able to explain 88% of total variance in the OC concentrations. It should be noted that since WSOC also comes from primary biomass burning sources, we estimated the biomass burning fraction of WSOC (i.e., WSOC_{bb}) to support our choice of WSOC as a tracer for SOA in this study, employing a technique used in previous studies. Based on this approach, the concentration of levoglucosan, a well-known tracer of biomass burning (Simoneit et al., 1999), was

divided by 0.135, the ratio of levoglucosan/OC derived from the wood smoke profiles (Fine et al., 2004), to derive the concentration of biomass burning originated OC. Furthermore, assuming that 71% of biomass burning fraction of OC is water soluble (Sannigrahi et al., 2005), the OC originating from biomass burning was multiplied by 0.71 to estimate the $WSOC_{bb}$. The $WSOC$ from non-biomass burning sources (i.e., $WSOC_{nb}$) was then derived by subtracting $WSOC_{bb}$ from total $WSOC$. The results from this analysis indicated that $WSOC_{bb}$ (with the average of $0.12 \mu\text{g}/\text{m}^3$) is a very small fraction (i.e. 11%) of total $WSOC$ (with the average of $1.1 \mu\text{g}/\text{m}^3$), while majority of $WSOC$ is composed of $WSOC_{nb}$ which can be regarded as a metric of SOA formation (Snyder et al., 2009). These results confirmed the suitability of using $WSOC$ as a tracer of SOA in this study.

Using the standardized coefficients and R^2 values obtained from the MLR models described above, we calculated the relative contributions of EC (i.e. of vehicular emissions) and OC to PM induced toxicity, the results of which are shown in Figure 5(a). As illustrated in the figure, EC and OC contributed to 38% and 35% of oxidative potential, respectively. Similarly, Figure 5(b) illustrates the relative contribution of different sources to OC mass concentrations. According to this figure, $WSOC$ (a tracer of SOA) had the highest contribution to OC concentrations, accounting for 45% of its concentrations. Vehicular emissions (as represented by EC) and biomass burning (as represented by levoglucosan) contributed to 26% and 17% of OC concentrations, respectively. The relative contribution of each source to OC can then be multiplied by the relative contribution of OC to PM oxidative potential (i.e., 35%) to obtain an estimate of the relative contribution of that individual source to PM induced toxicity. Combining the data presented in Figures 5(a) and 5(b), the relative contributions of vehicular emissions, secondary sources, and biomass burning to PM oxidative potential were calculated, the results of which are presented in Figure 5(c). As shown in the figure, traffic activities were responsible for approximately 44% of PM-induced toxicity, followed by SOA (16%), and biomass burning (9%). These results also explain the higher oxidative potential of the ambient $PM_{2.5}$ samples that were collected during the summer, which can be attributed to the higher concentrations of EC and $WSOC$ during that sampling period. Finally, according to previous studies in suburban Athens, road dust (i.e., brake and tire wear) and oil combustion were also identified as sources of $PM_{2.5}$ (Amato et al., 2016; Diapouli et al., 2017b). The undetermined portion of PM oxidative potential might therefore be attributable to these sources.

4. Summary and Conclusions

This study sought to identify pollution sources that contribute to the oxidative potential of ambient $PM_{2.5}$ in the metropolitan area of Athens, Greece. Our results indicated significantly higher mass-normalized and volumetric oxidative potential of the ambient $PM_{2.5}$ collected in the study area as compared to those collected in many urban areas around the world. It is of particular note that the oxidative potential of the $PM_{2.5}$ samples in Athens was even higher than that measured inside major freeways in Los Angeles, California. In addition, the significantly higher PM toxicity in our sampling site is one of the most notable observations of this study, since the measured oxidative potential pertains to a site which is not directly impacted by fresh urban PM emissions. Our attempt to apportion sources of $PM_{2.5}$ indicated that vehicular emissions were responsible for approximately 44% of PM-

induced oxidative potential of the samples, followed by secondary organic aerosol (SOA) (16%) and biomass burning (9%) as the next major contributors. Overall, our findings highlight the importance of traffic emissions and photochemical reactions in deriving PM-induced toxicity in Athens, Greece, and can be used by policy makers to prioritize the required public health actions and policies to mitigate the adverse health effects of PM by controlling the emissions from sources that are causing most of the PM toxicity in the area of Athens.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights:

- Sources of the PM_{2.5} oxidative potential (OP) were determined in a suburban site in Athens.
- We used a combination of PCA and MLR to perform OP source apportionment.
- Vehicular emissions was found to be the major contributor to PM_{2.5} OP
- SOA and biomass burning were the next major contributors to PM_{2.5} OP.

(a)

(b)

Fig. 1. The average mass concentrations of a) PM_{2.5} during the entire study period, and by season; b) carbonaceous components (elemental carbon (EC), organic carbon (OC), and water soluble organic carbon (WSOC)) by season. Error bars correspond to one standard deviation (SD).

Fig. 2. Average levoglucosan concentrations during the entire study period, and by season. Error bars correspond to one standard deviation (SD).

Fig. 3. Average concentrations of metal and trace elements by season. Error bars correspond to one standard deviation (SD).

Fig. 4. PM_{2.5} oxidative potential for warm and cold phases: a) Mass-normalized oxidative potential; b) Volume-based oxidative potential. Error bars correspond to one standard deviation (SD).

(a)

(b)

(c)

Fig. 5. Relative contribution of: a) EC and OC to $PM_{2.5}$ oxidative potential b) different sources to OC mass concentrations; and c) different sources to $PM_{2.5}$ oxidative potential.

Table 1.

Loadings of chemical species in the factors resolved by the principal component analysis (PCA). Loadings > 0.6 are bolded.

Species	Source factors			
	Soil dust emissions	Vehicular emissions	Road dust emissions	OC factor
OC	0.03	0.12	0.01	0.97
EC	-0.29	0.75	-0.08	0.47
Ni	-0.04	0.95	-0.03	0.01
Cu	-0.38	0.51	0.63	-0.38
Pb	0.21	-0.16	0.95	0.07
Ca	0.98	-0.06	0.04	-0.08
Si	0.98	-0.16	0.06	0.04
Ti	0.98	-0.13	0.04	0.07
%Variance	44.56	20.81	18.12	11.99
%Cumulative variance	44.56	65.37	83.50	95.49

Table 2.

Spearman bivariate correlation analyses between volume-based oxidative potential ($\mu\text{g Zymosan}/\text{m}^3$) and weekly sampled concentrations of individual chemical species. Highly correlated species are bolded, and significant values are marked with an asterisk (*).

Species	R	Species	R
WSOC	0.66 *	Ti	-0.01
OC	0.78 *	Mn	-0.24
EC	0.66 *	Na	-0.25
Levoglucosan	0.03	K	0.20
S	0.48	Zn	0.06
Al	-0.03	Cu	-0.17
Si	0.03	Pb	-0.11
Ca	-0.14	Ni	0.47
Fe	-0.07	Br	0.31

* $P < 0.05$

Table 3.

Results of the multiple linear regression (MLR) analysis between a) PM_{2.5} oxidative potential (as the dependent variable) and selected chemical species (as independent variables); b) OC (as the dependent variable) and selected chemical species (as independent variables).

Volumetric PM-induced oxidative potential($N_{\text{cold}}=6$, $N_{\text{warm}}=9$)							
Species	Source	Unstandardized coefficient ($\pm$ std. error)	Standardized coefficient ($\pm$ std. error)	P-value	Partial R	VIF	R ²
Constant		-188.74		0.017			0.73
EC	Vehicular emissions	325.63 $\pm$ 125.32	0.50 $\pm$ 0.19	0.023	0.60	1.60	
OC	Multiple sources	101.33 $\pm$ 42.95	0.45 $\pm$ 0.19	0.036	0.56	1.60	
(a)							
Organic Carbon ($N_{\text{cold}}=6$, $N_{\text{warm}}=9$)							
Species	Source/Formation Mechanism	Unstandardized coefficient ($\pm$ std. error)	Standardized coefficient($\pm$ std. error)	P- value	Partial R	VIF	R ²
Constant		1.05		0.000			0.88
WSOC	Secondary organic aerosol (SOA)	0.54 $\pm$ 0.09	0.75 $\pm$ 0.13	0.000	0.87	1.44	
Levoglucosan	Biomass burning	0.01 $\pm$ 0.00	0.42 $\pm$ 0.11	0.003	0.76	1.04	
EC	Vehicular emissions	0.57 $\pm$ 0.26	0.27 $\pm$ 0.13	0.055	0.54	1.43	
(b)							