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1 Source apportionment of PM_{2.5} oxidative potential in an East Mediterranean site

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12 Abstract:

13 This study aimed to evaluate the oxidative potential (OP) of PM_{2.5} collected for almost a year in
14 an urban area of the East Mediterranean. Two acellular assays, based on ascorbic acid (AA) and
15 dithiothreitol (DTT) depletion, were used to measure the OP. The results showed that the mean
16 volume normalized OP-AA_v value was $0.64 \pm 0.29 \text{ nmol} \cdot \text{min}^{-1} \cdot \text{m}^{-3}$ and the mean OP-DTT_v was
17 $0.49 \pm 0.26 \text{ nmol} \cdot \text{min}^{-1} \cdot \text{m}^{-3}$. Several approaches were adopted in this work to study the
18 relationship between the species in PM_{2.5} (carbonaceous matter, water-soluble ions, major and
19 trace elements, and organic compounds) or their sources and OP values. Spearman correlations
20 revealed strong correlations of OP-AA_v with carbonaceous subfractions as well as organic
21 compounds while OP-DTT_v seemed to be more correlated with elements emitted from different

22 anthropogenic activities. Furthermore, a multiple linear regression method was used to estimate
23 the contribution of PM_{2.5} sources, determined by a source-receptor model (Positive Matrix
24 Factorization), to the OP values. The results showed that the sources that highly contribute to the
25 PM_{2.5} mass (crustal dust and ammonium sulfate) were not the major sources contributing to the
26 values of OP. Instead, 69% of OP-AA_v and 62% of OP-DTT_v values were explained by three
27 local anthropogenic sources: Heavy Fuel Oil (HFO) combustion from a power plant, biomass
28 burning, and road traffic emissions. As for the seasonal variations, higher OP-AA_v values were
29 observed during winter compared to summer, while OP-DTT_v did not show any significant
30 differences between the two seasons. The contribution of biomass burning during winter was 33
31 and 34 times higher compared to summer for OP-AA_v and OP-DTT_v, respectively. On the other
32 hand, higher contributions were observed for HFO combustion during summer.

33 **Keywords:** PM oxidative potential, source apportionment, multiple linear regression, correlation
34 analysis with chemical composition, seasonal variations.

35

36 Introduction

37 Air pollution is considered as one of the major environmental challenges and poses a major
38 threat to health and climate. According to the World Health Organization, 99% of people
39 worldwide were living in areas where air quality exceeded the WHO guidelines in 2019 (WHO,
40 2021). It is estimated that the attributable excess mortality rate from ambient air pollution is
41 about 8.8 million per year (Lelieveld et al., 2019). Among the different air pollutants, particulate
42 matter with an aerodynamic diameter less than 2.5 μm (PM_{2.5}) can be easily inhaled into the
43 lungs and might cause diverse health effects especially cardiovascular and respiratory diseases
44 (Anderson et al., 2012; Lelieveld and Münzel, 2020; Xing et al., 2016). The exact mechanisms of
45 toxicity induced by exposure to PM are still poorly understood. Toxicological studies have
46 shown that the exposure to PM could induce oxidative stress by stimulating cells to produce
47 reactive oxygen species (ROS) in excess of the antioxidant capacity of the body (Ayres et al.,
48 2008; Bates et al., 2015). This imbalance triggers a cascade of effects such as inflammation,
49 DNA damage, and cell death (Becker et al., 2005; Wang et al., 2019). Additionally, the
50 toxicological effects due to the induction of oxidative stress by PM is related to their physico-
51 chemical characteristics such as surface properties and their chemical composition (Crobeddu et
52 al., 2017). Hence, the oxidative potential (OP) of PM has been found to be a practical indicator
53 for the evaluation of the oxidative capacity of PM components as a whole (Crobeddu et al.,
54 2017). According to Daellenbach et al. (2020) and Fakhri et al. (2023), if the OP is found to be
55 related to major health impacts, it might be more effective to control specific OP sources rather
56 than overall particulate mass. Recent papers showed that the correlation between acellular OP
57 and intracellular toxicity is site-dependent following the sources acting on a specific site

58 (Guascito et al., 2023; Weber et al., 2021; Xu et al., 2020). Therefore, further studies are needed
59 to investigate the impact of the emission sources on both aspects.

60 Recently, the development of different acellular assays has led to a rise in OP measurements
61 worldwide and their inclusion in epidemiological studies (Serafeim et al., 2023). The most
62 common ones include electron spin resonance (OP-ESR) that measures the generation of
63 hydroxyl radicals, dithiothreitol (OP-DTT), ascorbic acid (OP-AA) and glutathione (OP-GSH)
64 assays that measure the depletion rate of proxies for cellular reductants or antioxidants (Bates et
65 al., 2019; Guo et al., 2020). Among those, OP-AA and OP-DTT are widely used and are based
66 on spectrophotometric kinetic methods (Bates et al., 2019). The OP-DTT assay measures the
67 depletion rate of dithiothreitol, a chemical reactant used as a substitute of cellular reductants
68 owing to its sulfhydryl groups (Cho et al., 2005). While the OP-AA assay measures the ability of
69 PM to deplete antioxidants (ascorbic acid in this case) in the respiratory tract lining fluid (RTLFL)
70 (Mudway et al., 2004). These depletion rates are proportional to the generation rate of ROS and
71 the ability of PM to contribute to ROS overproduction. Up until today, there is no standard
72 methodology to measure oxidative potential in order to fully determine the ROS generation
73 variations (Janssen et al., 2014; Weber et al., 2021). This methodology should include different
74 tests due to their different sensitivities to PM components (Ayres et al., 2008). The current state
75 of knowledge regarding the correlation between species and the different OP assays is not
76 enough to reach a conclusion about the specificity of the tests to classes of compounds.
77 Nevertheless, an OP assessment based on the OP-AA and OP-DTT assays seems appropriate
78 when considering different families of PM components due to the complementarity between
79 these assays (Guo et al., 2020). However, the study of the relationship between OP values and
80 PM sources is sometimes limited since PM species and elements contributing to OP values can

81 be emitted by several sources. Additionally, few studies tried to determine OP values produced
82 by specific sources such as biomass burning and urban traffic (Bates et al., 2015; Saffari et al.,
83 2014). Therefore, assuming that OP is a predictive metric of the PM toxicity, it has become
84 increasingly important to link the OP values to PM sources in order to identify the sources with
85 the greatest possible impact. Bates et al. (2015) and Weber et al. (2018) developed
86 methodologies for the evaluation of the contributions of the sources using a multiple linear
87 regression approach in order to assign OP-AA and OP-DTT values for different sources obtained
88 by source apportionment application. More recently, Borlaza et al. (2021) compared a non-linear
89 modelling technique (Multilayer perceptron neural network analysis - MLP) to the multiple
90 linear regression model and showed similarities between the results of the two models with some
91 improvements in the OP prediction with the MLP model when local features or non-linear effects
92 occur.

93 In this context, the objectives of this research were to examine the oxidative potential of PM_{2.5}
94 measured using AA and DTT assays, to study the relationship between the PM_{2.5} chemical
95 components (carbonaceous, ionic, elemental, and organic) and OP results, and to conduct a
96 source apportionment of PM_{2.5} OP. The source apportionment of PM_{2.5} at the site was previously
97 presented in Fadel et al. (2023). This study will try to contribute to filling the lack of knowledge
98 regarding OP measurements and their attribution to common sources found in the East
99 Mediterranean and the Middle East region.

100

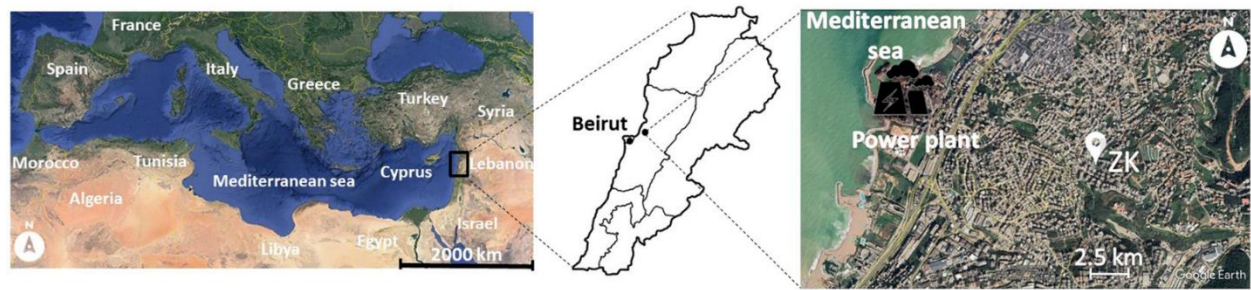
101 1 Materials and methods

102 1.1 PM_{2.5} sampling

103 PM_{2.5} sampling was conducted at Zouk Mikael (ZK), an urban site under industrial influence in
104 Lebanon. Detailed information about the sampling site and the sample collection were presented
105 in Fadel et al. (2021). The ZK site (33°57'57.07''N; 35°37'09.46''E) is highly urbanized with a
106 residential density of 4,200 inhabitants/km², located at 1.2 km of a congested highway linking
107 the capital Beirut to the North of Lebanon (**Figure 1**). This site also encompasses the biggest
108 power plant in the country which runs on Heavy Fuel Oil (HFO).

109 PM_{2.5} samples were collected for 24 hours on pre-cleaned Quartz microfibrils filters (150 mm,
110 Fiorini, France) every third day from 13th of December 2018 to 15th of October 2019, using a
111 high-volume sampler (CAV-A/mb, MCV S.A., Spain) operating at 30 m³/h. A total number of
112 98 loaded filters and 8 field blanks were collected.

113



114

115 **Figure 1:** Location of the sampling site at Zouk Mikael (ZK), Lebanon (modified from Google
116 Earth)

117

118 1.2 PM_{2.5} concentrations and chemical characterization

119 Detailed information regarding the determination of PM_{2.5} concentrations as well as the chemical
120 characterization can be found in the supplementary material and in our previous publications

121 (Fadel et al., 2023; 2022; 2021). Briefly, the PM_{2.5} concentration was determined based on the
122 standard gravimetric method EN 12341:2014 by weighing filters before and after sampling in a
123 temperature (20 ± 0.5°C) and humidity (50 ± 5%) controlled room.

124 Various analytical methods were used to analyze different chemical fractions of PM_{2.5}. The
125 carbonaceous sub-fractions (OC and EC) were analyzed by a Sunset Laboratory analyzer
126 implementing the EUSAAR2 temperature protocol (Cavalli et al., 2010). Organic compounds
127 such as Polycyclic Aromatic Hydrocarbons (PAHs), alkanes, hopanes, levoglucosan, carboxylic
128 acids, isoprene and α-pinene oxidation products were analyzed by gas chromatography coupled
129 to a mass spectrometer GC/MS (ISQ 7000, Thermo Scientific, United States of America) using
130 the method described in Fadel et al. (2021). The analysis of major and trace elements was
131 performed by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, iCAP
132 6000 series, Thermo Scientific, United Kingdom), and an ICP-Mass Spectrometry (ICP-MS,
133 Agilent 7900, Varian, United States of America), respectively using the method described in
134 Ledoux et al. (2006b) and Fadel et al. (2022). Finally, water-soluble ions were analyzed by ion
135 chromatography (Dionex™ ICS-900, Thermo Scientific, United Kingdom) following the method
136 presented by Ledoux et al. (2006a) and Fadel et al. (2023).

137

138 1.3 PM_{2.5} oxidative potential evaluation

139 The method used for the assessment of the oxidative potential using AA and DTT assays was
140 detailed in Moufarrej et al. (2020) and will be briefly presented here. The leaching agent used for
141 the PM_{2.5} extraction is the Gamble's solution (pH=7.4), a simulated lung fluid (SLF) that reflects
142 the composition of the interstitial fluid in the deep lung. The composition of the Gamble's

143 solution as well as the order of mixing of the components can be found in Colombo et al. (2008)
144 and in **Table S1**. For each sample, a punch of the filter (19 mm diameter) was extracted by 5 mL
145 of the Gamble's solution in a glass tube. The tubes were then placed in a heated orbital shaker
146 for 24 h at 37°C, at a speed of 250 oscillations per min. The extracted solutions were then filtered
147 on 0.45 µm nylon filters, and stored at -20°C until OP analysis.

148 The measurement of DTT depletion was carried out in 96 well black plates with clear flat
149 bottom. In each well of the plate, 40 µL of the PM leachate (or the Gamble's solution used as
150 blank or a filter field blank or 1,4-naphtoquinone used as positive control) was added to 120 µL
151 of phosphate buffer solution (pH = 7.4) before placing the plate under shaking for 10 min at
152 37°C. Then, the oxidation reaction was initiated by adding 25 µL of DTT (0.4 mM) and the
153 estimation of the remaining DTT was done by adding 15 µL of 5,5-dithio-bis-(2-nitrobenzoic
154 acid) (DTNB) in the wells at different times of reaction between the PM leachate and DTT at
155 37°C. The remaining DTT reacts with DTNB and is converted to 2-nitro-5-thiobenzoic acid
156 (TNB). The absorbance of TNB was measured 10 min after the last DTNB addition at 37°C and
157 at 412 nm.

158 The OP-AA assay was done in 96 well plates with UV-transparent flat bottom. In each well, 160
159 µL of PM extract were added and then the plate was incubated at 37°C for 10 min under shaking.
160 Then, 40 µL of the AA solution (1 mM) was added to the extract and incubated for 1 min before
161 placing it in the spectrophotometer. The absorbance of the remaining AA was measured at 265
162 nm every 2 min for 2 hours.

163 The AA or DTT depletion rates were determined by considering the slope of the linear
164 regression of the remaining AA or DTT, respectively versus time. For each PM_{2.5} sample, OP-
165 AA or OP DTT values (in nmol·min⁻¹) were corrected by subtracting the slope value of the field

166 blank filter. Then, the values were normalized to the mass of PM (OP-AA_m and OP-DTT_m
167 expressed in nmol·min⁻¹·μg⁻¹) and to the volume of air (OP-AA_v and OP-DTT_v expressed in
168 nmol·min⁻¹·m⁻³). For both assays, samples were analyzed in triplicates and the relative standard
169 deviation was below 7% for OP AA and below 10% for OP DTT.

170

171 1.4 Data processing

1.4.1 Source apportionment of PM_{2.5}

172 The identification and the quantification of the contribution of PM_{2.5} sources was done using the
173 USEPA PMF 5.0 model (Paatero and Tapper, 1994). The detailed results regarding the identified
174 sources at ZK site, the source profiles, and their contribution to PM_{2.5} can be found in our
175 previous publication (Fadel et al., 2023). Briefly, a selection of 32 species including the
176 carbonaceous sub-fractions (OC, EC), major ions (Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, and NH₄⁺), a set of
177 elements (Mg, Al, Ca, Fe, K, Ni, Ti, Cu, Sb, and Sn), and different organic tracers (levoglucosan,
178 hexa- and octadecanoic acids, isoprene and α-pinene oxidation products, 17α(H)-21β (H)-
179 hopane, C₂₀, C₂₁, C₂₄, C₂₅, C₂₇, C₂₉, and C₃₁ alkanes) were added into the model. A twelve-factor
180 solution was retained and the source categories were presented in **Table 1**.

181 The measured concentrations of PM_{2.5} as well as the added species and the values reconstructed
182 were strongly correlated with regression slopes higher than 0.85 and determination coefficients
183 (R²) higher than 0.83. Additionally, bootstrap analyses and DISP diagnostics indicated a good
184 model fit for the twelve-factor solution.

185

1.4.2 Correlation analysis

186 In order to analyze the correlations between OP data and PM_{2.5} components, statistical tests were
187 used after assessing the normality of the variables. The Shapiro-Wilk test was performed to
188 evaluate the normality of the distributions. Most of the variables were not normally distributed
189 ($p < 0.001$). Therefore, the Spearman correlation coefficient, a non-parametric test to study the
190 correlations was chosen. Two levels of significance were generally applied, $p < 0.05$ for 95%
191 confidence, and $p < 0.01$ for 99% confidence. The seasonal variability of the OP values was
192 analyzed using the Mann-Whitney statistical test.

193

1.4.3 Oxidative potential apportionment method

194 A multiple linear regression method has been used in order to estimate the contributions of PM
195 sources to OP. The method is based on the assumption that the OP values are linearly related to
196 the contributions of the sources using the following equation (Weber et al., 2018) (Eq.1):

$$197 \quad OP_{obs} = \sum_{i=1}^n C_{i-PM} \times \beta_i + \varepsilon \quad (Eq. 1)$$

198 Where OP_{obs} is the observed OP_v value matrix expressed in $\text{nmol} \cdot \text{min}^{-1} \cdot \text{m}^{-3}$, C_{i-PM} is the
199 concentration of PM attributed to the source i in the source contribution matrix expressed in
200 $\mu\text{g} \cdot \text{m}^{-3}$, β_i represents the intrinsic OP of the source ($\text{nmol} \cdot \text{min}^{-1} \cdot \mu\text{g}^{-1}$), and ε is a residual term (in
201 $\text{nmol} \cdot \text{min}^{-1} \cdot \text{m}^{-3}$) that accounts for the misfit between the observed and the modeled data. The
202 MLR was done by imposing the intercept equal to zero.

203 A weighted least square regression (WLS) was adopted in order to take into consideration the
204 uncertainties of the OP measurements. The input data for this model are the contributions of the

205 sources resulting from the PMF results for the ZK site, and the values of OP-AA_v and OP-DTT_v
206 along with their corresponding uncertainties. The latter were calculated at 2σ based on the RSD
207 of the triplicates, the uncertainty related with the sampling instrumentation, and the uncertainties
208 associated with the experimental procedures.

209 Once the initial run is done and values of intrinsic OP are calculated, sources with negative
210 intrinsic OP that are statistically insignificant at 5% level ($p > 0.05$) were removed from the
211 input data and the MLR was run again without these sources.

212 Afterwards, a bootstrap analysis on the MLR model is applied to evaluate the variability of the
213 obtained intrinsic OP results. This method creates sets of bootstrap data constructed by randomly
214 selecting blocks of observations from the initial dataset. The size of the blocks is calculated
215 according to Politis and White (2004) and was taken in this case as 5 samples per block. 100
216 bootstrap runs were randomly performed to ensure the robustness of the results. The obtained
217 intrinsic OP values were presented in a boxplot presenting the median and the percentiles 5, 25,
218 50, 75, and 90 (**Figure 2**).

219

220 2 Results and discussions

221 2.1 PM_{2.5} composition and source contribution

222 The concentrations of the different PM_{2.5} components (OC, EC, water-soluble ions, elements,
223 and organic compounds) for ZK were presented and discussed in details in our previous
224 publications (Fadel et al., 2023; Fadel et al., 2021), and are resumed in **Table S2** and **Table S3**.

225 PM_{2.5} average concentration for ZK was 33.6 µg.m⁻³. The major chemical components were OC,
226 EC, SO₄²⁻, Ca, NH₄⁺, and NO₃⁻ contributing to approximately 50% of the PM_{2.5} mass (**Table S2**).
227 As for the organic compounds, hexa- and octadecanoic acids, tracers of cooking emissions,
228 recorded the highest concentrations (259 and 175 ng/m³, respectively) between the identified
229 compounds, followed by levoglucosan (91 ng/m³), tracer of biomass burning. The total
230 concentrations of n-alkanes, PAHs, and hopanes were 26.7, 2.56, and 4.22, respectively (**Table**
231 **S3**).

232 Different organic and inorganic markers were used to estimate the contribution of the sources
233 using the PMF source receptor model (Fadel et al., 2023). The chemical markers of the sources
234 identified using PMF along with the average contributions of the sources to PM_{2.5} during the
235 entire sampling period as well as during winter and summer periods are presented in **Table 1**.

236 The average results show that 27.5% of PM_{2.5} was attributed to crustal dust that mainly originate
237 from the Arabian and Saharan deserts through long range transport (Fadel et al., 2023).
238 Additionally, high concentrations of carbonaceous matter (OC and EC) were reported to be of
239 long-range origins, possibly because of the abundance of oil fields and refineries in the
240 surrounding Arab countries.

241 The ammonium sulfate source, which was the second highest contributor (15.7%), can be either
242 of local (HFO combustion from the power plant) or distant origins (industrial areas of Europe
243 and Turkey). The site was also influenced by vehicular emissions (14% of PM_{2.5}) with three
244 PMF factors associated with exhaust and non-exhaust emissions (**Table 1**) since the site is close
245 to a congested highway. Traffic exhaust (1) source, characterized by high loadings of
246 17α(H)-21β(H)-hopane is mainly associated to unburned lubricating oils while traffic exhaust (2)
247 source is associated with high concentrations of OC and EC and is linked to fuel combustion.

248 **Table 1:** Markers of the identified sources at Zouk (ZK) site along with their average
 249 contribution to PM_{2.5} in percentages and in $\mu\text{g}\cdot\text{m}^{-3}$ retrieved from Fadel et al. (2023) during the
 250 entire sampling period (Dec. 2018 – Nov. 2019), winter (Dec. 2018 – Mar. 2019), and summer
 251 (Jun. 2019 – Sept. 2019) periods.

Sources	Markers	Total period		Winter		Summer	
		Contrib. to PM _{2.5} ($\mu\text{g}\cdot\text{m}^{-3}$)	Contrib. to PM _{2.5} (%)	Contrib. to PM _{2.5} ($\mu\text{g}\cdot\text{m}^{-3}$)	Contrib. to PM _{2.5} (%)	Contrib. to PM _{2.5} ($\mu\text{g}\cdot\text{m}^{-3}$)	Contrib. to PM _{2.5} (%)
Crustal dust	Al, Ca, Mg, Ti, K	8.19	27.5%	10.52	40.8%	4.90	16.2%
Ammonium sulfate	SO ₄ ²⁻ , NH ₄ ⁺	4.70	15.8%	2.10	8.2%	8.31	27.5%
HFO combustion	OC, EC, V, Ni	3.89	13.1%	1.39	5.4%	4.15	13.7%
Aged sea-salt	Na ⁺ , Cl ⁻ , NO ₃ ⁻	3.32	11.1%	2.27	8.8%	2.70	8.9%
Secondary biogenic	isoprene and α - pinene oxidation products	2.32	7.8%	0.40	1.5%	4.67	15.5%
Traffic exhaust (2)	OC, EC	1.83	6.1%	1.28	5.0%	2.15	7.1%
Traffic exhaust (1)	17 α (H)-21 β (H)- hopane	1.38	4.6%	2.12	8.2%	0.84	2.8%
Diesel generators	OC, EC, C ₂₀ , C ₂₁	1.33	4.5%	1.73	6.7%	0.57	1.9%
Biomass burning	OC, EC, levoglucosan	1.03	3.4%	2.32	9.0%	0.07	0.2%
Traffic non-exhaust	Cu, Sb, Sn	0.99	3.3%	0.79	3.1%	0.93	3.1%
Primary biogenic	C ₂₇ , C ₂₉ , C ₃₁	0.44	1.5%	0.50	2.0%	0.26	0.9%
Cooking	hexadecanoic and octadecanoic acids	0.42	1.4%	0.35	1.3%	0.67	2.2%

252

253 Furthermore, the industrial influence was highlighted by a relatively high contribution of HFO
 254 combustion from the power plant (13% of PM_{2.5} mass). Biogenic sources (primary and
 255 secondary pathways) were also identified with a combined contribution of 9.3%, and aged sea-

256 salts contributed 11.1%. Other anthropogenic sources such as diesel generators, biomass burning,
257 and cooking emissions contributed together to 9.3% of PM_{2.5} (**Table 1**).

258

259 2.2 Oxidative potential of PM_{2.5}

260 The average volume and mass-normalized OP-AA and OP-DTT values at ZK are presented in
261 **Table 2** for the entire study period along with the values for winter and summer periods.
262 Additionally, time series for the different variables (OP-AA_v, OP-AA_m, OP-DTT_v, OP-DTT_m)
263 are presented in **Figure S1**. The mass-normalized OP corresponds to the intrinsic OP value
264 related to the oxidative properties of PM per unit mass while volume-normalized OP takes into
265 account the dilution of PM in the atmosphere and was considered to have a closer relation to
266 human exposure (Hakimzadeh et al., 2020).

267 The mean OP-AA_v value at ZK was $0.64 \pm 0.29 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$, varying between 0.15 and 1.49
268 $\text{nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$ while the mean OP-DTT_v value was $0.49 \pm 0.26 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$ with a minimum
269 of 0.12 and a maximum of $1.93 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$. The values in our study for OP-AA_v were in the
270 range of values reported for different urban and industrial sites in France such as Grenoble, Nice,
271 Talence, and Dunkirk ($0.2\text{-}1.6 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$) (Calas et al., 2019; Moufarrej et al., 2020).
272 Additionally, our values were higher than the ones reported for a Central Mediterranean
273 suburban site of the flat Salento's peninsula where OP-AA_v average reported value was 0.29
274 $\text{nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$ (Pietrogrande et al., 2018) but in the same range of values reported for a
275 Mediterranean urban site in Spain ($0.91 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$) (Clemente et al., 2023).

276

277 **Table 2** : Average volume ($\text{nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$) (OP-AA_v and OP-DTT_v) and mass ($\text{nmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$)
 278 1) (OP-AA_m and OP-DTT_m) normalized OP-AA and OP-DTT measured for $\text{PM}_{2.5}$ with their
 279 standard deviations for the total period, winter, and summer at Zouk (ZK) site.

	ZK site		
	Total Period	Winter	Summer
Periods	Dec. 2018 - Nov. 2019	Dec. 2018 - Mar. 2019	Jun. - Sept. 2019
OP-AA_v ($\text{nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$)	0.64 ± 0.29	0.70 ± 0.28	0.49 ± 0.14
OP-AA_m ($\text{nmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$)	0.03 ± 0.02	0.04 ± 0.02	0.02 ± 0.01
OP-DTT_v ($\text{nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$)	0.49 ± 0.26	0.43 ± 0.22	0.52 ± 0.21
OP-DTT_m ($\text{nmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$)	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01

280
 281 As for DTT, the results of our study for OP-DTT_v (**Table 2**) were in the range of values observed
 282 over the southern United States ($0.1\text{-}1.5 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$), for French sites ($0.36\text{-}4.12 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$), and for Chinese sites ($0.19\text{-}1.1 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$) (Calas et al., 2019; Verma et al., 2014;
 283 Wang et al., 2020). The average OP-AA_m and OP-DTT_m were 0.03 ± 0.02 and 0.02 ± 0.01
 284 $\text{nmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$, and were also comparable to the values reported in the above-mentioned
 285 studies. Despite the closeness in the average values of OP-AA_v and OP-DTT_v , a different
 286 temporal evolution is observed (**Figure S1**). This might be due to the specificity of each assay
 287 towards certain $\text{PM}_{2.5}$ components.
 288

289
 290 **2.3 Correlation between OP-AA_v , OP-DTT_v and $\text{PM}_{2.5}$ chemical components**

291 To investigate the relationships between OP values and species concentrations, Spearman
 292 correlation coefficients between volume-normalized OP-AA or OP-DTT values and $\text{PM}_{2.5}$
 293 components concentrations were calculated (**Table 3**). The species include the carbonaceous

294 matter (OC, EC), water-soluble ions, elements, and different classes of organic compounds
295 among which alkanes, polycyclic aromatic hydrocarbons (PAHs), hopanes, levoglucosan,
296 carboxylic acids, and secondary compounds. This approach allows us to give insights into the
297 species that might contribute to oxidative properties of PM.

298 OP-AA_v did not show a significant correlation with PM_{2.5} concentration while OP-DTT_v is
299 significantly correlated with PM_{2.5} (**Table 3**). Similar observations were done by Calas et al.
300 (2019) and Yang et al. (2014) stressing on the idea that the OP values correlate more with
301 specific species rather than PM_{2.5} mass as a whole.

302 Both assays appeared sensitive to elements as observed in **Table 3**. However, organic
303 compounds including hopanes, levoglucosan, alkanes, and PAHs were not found to correlate
304 with OP-DTT_v. This is likely due to the fact that these water insoluble species may not serve as
305 actual reactants in an aqueous solution (such as the Gamble's solution) to oxidize DTT (Bates et
306 al., 2019; Fang et al., 2016). The same observations were presented by Liu et al. (2020) when
307 examining the oxidative potential of PM in different areas in China. On the other hand, organic
308 compounds showed significant correlations with OP-AA_v especially n-alkanes, PAHs,
309 levoglucosan, and hopanes (**Table 3**). As for elements associated with crustal dust such as Al,
310 Mg, K, and Ti, weak correlations were found for both assays. High concentrations of these
311 crustal elements are usually predictive of long-range transport of dust from deserts in the
312 Mediterranean region (Borgie et al., 2016). The occurrence of these phenomena were verified by
313 the evaluation of the HYSPLIT backtrajectories showing air masses coming from Saharan and
314 Arabian deserts to the sampling site (Fadel et al., 2023). A special attention was given to samples
315 that verify these above-mentioned criteria in order to further understand the influence of dust
316 storm episodes on OP values. For that purpose, samples that showed high concentrations of

317 crustal elements (or high contribution of the crustal dust source to $PM_{2.5}$) were reported in **Table**
318 **S4** as well as their respective OP values with the comparison to the rest of the sampling period.
319 OP-DTT_v average value for samples collected during dust storm episodes from Arabian or
320 Saharan deserts (0.54 and 0.38 $nmol \cdot min^{-1} \cdot m^{-3}$, respectively) are not very different from the
321 average of DTT_v of PM observed in the remaining sampling days (0.49 $nmol \cdot min^{-1} \cdot m^{-3}$) (**Table**
322 **S4**). Similar conclusions were given by Chirizzi et al. (2017) that studied the influence of
323 Saharan dust outbreaks on OP-DTT_v and did not find any significant differences between the
324 average OP-DTT_v of PM in the area and the one from Saharan dust particles. Regarding OP-
325 AA_v, the average value for samples collected during a Saharan dust outbreak (0.43 $nmol \cdot min^{-1}$
326 $\cdot m^{-3}$) was slightly lower than the one reported for the remaining sampling days (0.62 $nmol \cdot min^{-1}$
327 $\cdot m^{-3}$). However, a remarkable difference was observed when examining OP-AA_v values for
328 samples under the influence of long-range transport from Arabian deserts presenting values
329 (average of 1.05 $nmol \cdot min^{-1} \cdot m^{-3}$) that were 1.7 times higher than the average OP-AA_v for the rest
330 of the sampling days. This might be explained by the higher concentrations of carbonaceous
331 matter in $PM_{2.5}$ for the samples that were under the influence of Arabian deserts outbreaks (OC +
332 EC: 10.2 $\mu g \cdot m^{-3}$) in comparison with the samples under the influence of Saharan deserts (4.7
333 $\mu g \cdot m^{-3}$) and the remaining sampling days (5.4 $\mu g \cdot m^{-3}$) since it has been shown that the
334 carbonaceous matter is well correlated with OP (Chirizzi et al., 2017; Moufarrej et al., 2020). It
335 has been previously reported that in Fadel et al. (2023) that the higher concentrations of
336 carbonaceous matter in these samples is due to their transportation with the dust from the
337 numerous oil fields and refineries in Arab countries.

338 A strong correlation was found between OP-DTT_v and elements originating from different
339 anthropogenic sources namely V, Ni, Zn, Cu, Sn, and Sb (**Table 3**). Elements such as Cu, V, and

340 Ni are known to be involved in the production of radicals via the Fenton reaction involving the
341 reduction of H₂O₂ by a transition metal (Visentin et al., 2016) and control the DTT oxidation.
342 Additionally, good and moderate correlations were found between OP-DTT_v and OC, and OP-
343 DTT_v and EC, respectively. OC and EC were mainly attributed to vehicular emissions at the
344 sampling site.

345 Cu, Sb, and Sn mainly originate from resuspension of road dust (non-exhaust vehicular
346 emissions), while V and Ni are emitted by HFO combustion. Similar correlations were observed
347 between OP-DTT_v and elements in Moufarrej et al. (2020) in Dunkirk, a coastal industrial city in
348 Northern France. Moreover, OP-DTT_v did not show any significant correlation with PAHs that
349 might be linked to vehicular emissions, in agreement with Vreeland et al. (2017).

350 On the other hand, OC, EC, many PAHs, and levoglucosan showed good correlations with OP-
351 AAv. These results are in agreement with previous studies that showed a high sensitivity of OP-
352 AAv assay to biomass burning and also to road traffic exhaust chemical markers (OC, EC,
353 fluoranthene, pyrene, chrysene, benzo[a]pyrene) (Calas et al., 2018; Janssen et al., 2014;
354 Moufarrej et al., 2020; Weber et al., 2021).

355 A strong correlation was also observed between OP-AA_v and indeno[1,2,3-c,d]pyrene that was
356 linked to the HFO combustion from the power plant at ZK in our previous study (Fadel et al.,
357 2021). OP-AA_v showed significant correlation with levoglucosan suggesting that biomass
358 burning contributes to the value of OP-AA_v.

359

360

361 **Table 3:** Spearman correlation coefficient (r) between Oxidative Potential derived from AA and
 362 DTT depletion measurements (OP-AA_v and OP-DTT_v), PM_{2.5} concentrations, and PM_{2.5}
 363 components (carbonaceous fraction, water-soluble ions, elements, and organic species) –
 364 Correlation coefficients for which p-value <0.05 are reported (*p<0.01; bold r>0.5).

	Species	OP-AA _v	OP-DTT _v		Species	OP-AA _v	OP-DTT _v
	OP-AA _v		0.41*		C ₁₉ – nonadecane	0.28	
	PM _{2.5}		0.42*		C ₂₀ – eicosane	0.29	
Carbonaceous sub-fraction	OC	0.53*	0.51*		C ₂₁ - heneicosane	0.41*	
	EC	0.53*	0.43*		C ₂₂ - docosane	0.41*	
Water-soluble ions	Cl ⁻			n-alkanes	C ₂₃ - tricosane	0.43*	
	NO ₃ ⁻	0.28	0.21		C ₂₄ - tetracosane	0.43*	
	SO ₄ ²⁻		0.46*		C ₂₅ - pentacosane	0.39*	
	Na ⁺				C ₂₆ – hexacosane	0.39*	
	NH ₄ ⁺		0.38*		C ₂₇ - heptacosane	0.33*	
	K ⁺	0.31	0.53*		C ₂₈ – octacosane	0.34*	
	Mg ²⁺				C ₂₉ – nonacosane	0.25	
	Ca ²⁺	0.21	0.26	C ₃₀ - triacontane	0.32		
	Mg		0.23	C ₃₁ - hentriacontane		0.21	
	Mn	0.42*	0.31	C ₃₂ - dotriacontane	0.25	0.29	
Elements	Al				acenaphthylene	0.40*	
	Ba	0.35*	0.24		acenaphthene	0.35*	
	Ca	0.22	0.23		fluorene	0.25	
	Fe	0.22	0.29		anthracene	0.46*	
	K	0.26	0.39*		phenanthrene	0.51*	
	Ni	0.47	0.76*		fluoranthene	0.50*	
	P	0.30	0.52*	PAHs	pyrene	0.51*	
	V	0.29	0.69*		benz[a]anthracene	0.52*	
	Pb	0.52*	0.47*		chrysene	0.56*	
	Sr		0.23		benzo[b]fluoranthene	0.50*	
	Ti		0.23		benzo[k]fluoranthene	0.43*	
	Zn	0.46	0.67*		benz[a]pyrene	0.52*	
	Sc				dibenz[a,h]anthracene	0.52*	
	Cr				benzo[g,h,i]perylene	0.45*	
	Co	0.42*	0.46*		indeno[1,2,3-c,d]pyrene	0.57*	
	Cu	0.38*	0.50*		Anhydrosugar	levoglucosan	0.50*
	As		0.47*	Carboxylic acids	hexadecanoic acid		
	Rb		0.31		octadecanoic acid		
	Nb			Secondary compounds	isoprene oxidation products		
	Cd	0.31	0.41*		α-pinene oxidation products		
Sb	0.48*	0.65*					
La			Hopanes	trisnorneohopane	0.23		
Ce				17α(H)-trisnorhopane	0.32		
Tl		0.48*		17α(H)-21β(H)-norhopane	0.32	0.26	
Bi		0.50*		17α(H)-21β(H)-hopane	0.36*	0.25	
				17α(H)-21β(H)-22S-homohopane	0.26	0.24	
				17α(H)-21β(H)-22R-homohopane		0.28	

365

366 2.4 Apportionment of OP sources

2.4.1 Accuracy of the model

367 Once the initial MLR run was done, sources presenting negative intrinsic OP values and that
368 were statistically insignificant ($p < 0.05$) were removed from the initial input data and the MLR
369 was done again. This was the case in our study for the “Cooking” source in OP-AA_v ($p = 0.547$)
370 and for the “diesel generators” source in OP-DTT_v ($p = 0.07$). By that, the “cooking” source for
371 OP-AA_v and the “diesel generators” source for OP-DTT_v will not be used in the source
372 apportionment of OP.

373 The MLR was run again considering 11 sources instead of 12 for both assays. All the remaining
374 sources for both assays showed positive intrinsic OP. A significant correlation was observed
375 between the reconstructed and observed OP ($R^2 > 0.8$) with a regression line close to unity for
376 both assays (**Figure S2**). The residuals between the observed and the modeled OP values were
377 close to zero for low OP values and slightly increased for higher OP values (**Figure S3**).
378 Moreover, the distribution of the residuals is normal (Shapiro Wilk test, $p < 0.05$) for both OP-AA
379 and OP-DTT with a slight increase towards the underestimation for the highest OP values. All of
380 these findings show that the modeling method is valid (Weber et al., 2021), and the results of
381 intrinsic OP can be presented.

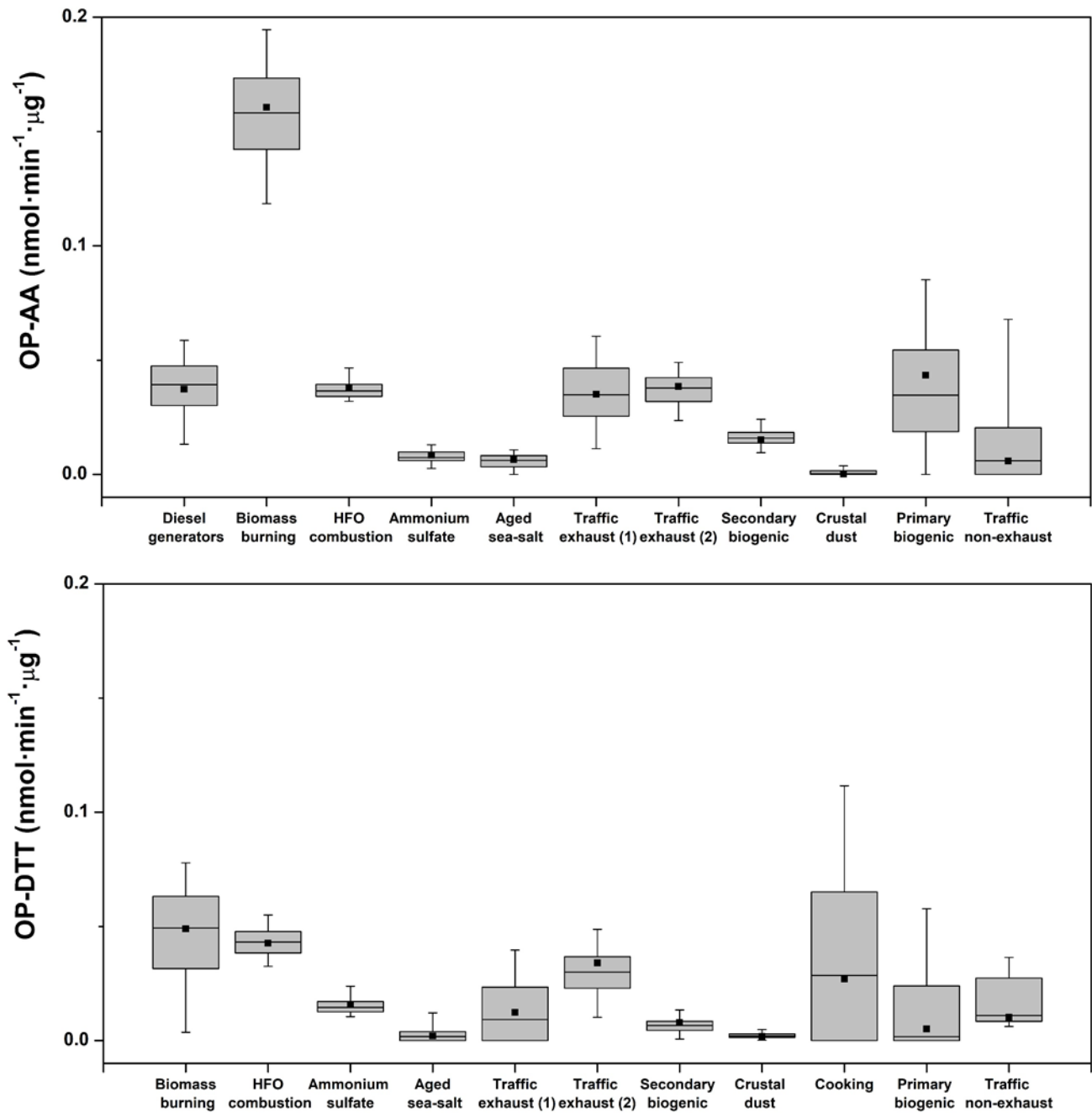
382

2.4.2 Intrinsic OP values

383 The values of intrinsic OP obtained from the base run as well as the median, 5th, 25th, 75th, and
384 95th percentile values of OP obtained from the bootstrap analysis are presented in **Figure 2**. The
385 use of a boxplot representation allows to quickly evaluate the stability of the results: a certain
386 confidence could be set on the intrinsic OP values showing low variability during the bootstrap
387 procedure (25th and 75th percentile close to the median value). On the other hand, when 25th et
388 75th percentile values are far from the median values (high interquartile range), conclusions
389 should be carefully drawn regarding the obtained intrinsic OP value for the considered sources.

390 For OP-AA_v, the bootstrap procedure evidenced few variabilities in the intrinsic OP for most of
391 the sources. Additionally, the intrinsic OP values from the base run and median values from the
392 bootstrap analysis were close (**Figure 2**). For the majority of the identified sources, positive
393 average intrinsic OP-AA values were observed stressing on the significant oxidative properties
394 of PM. From the calculations, the biomass burning source showed the highest intrinsic OP with a
395 value of 0.161 nmol·min⁻¹·μg⁻¹, followed by primary biogenic source (0.043 nmol·min⁻¹·μg⁻¹),
396 HFO combustion (0.038 nmol·min⁻¹·μg⁻¹), traffic exhaust (2) (0.039 nmol·min⁻¹·μg⁻¹), diesel
397 generators (0.037 nmol·min⁻¹·μg⁻¹), traffic exhaust (1) (0.035 nmol·min⁻¹·μg⁻¹), and then
398 secondary biogenic source (0.015 nmol·min⁻¹·μg⁻¹). Biomass burning is one of the few sources
399 that shows a considerably significant redox activity. Ammonium sulfate, aged sea-salt, and
400 traffic non-exhaust sources showed considerably lower mean intrinsic OP-AA values (0.006 -
401 0.008 nmol·min⁻¹·μg⁻¹), and crustal dust source presented the lowest intrinsic OP-AA value
402 (0.0002 nmol·min⁻¹·μg⁻¹) (**Figure 2**).

403



404

405 **Figure 2:** Boxplots of intrinsic OP values obtained from the bootstrap analysis for both AA and

406 DTT values expressed in nmol·min⁻¹·μg⁻¹ (5th, 25th, 50th, 75th, and 95th percentiles) and the OP

407 value obtained from the base run for the identified sources by PMF at ZK (black squares).

408 For OP-DTT_v, the bootstrap method applied to the MLR results showed few variabilities for
409 intrinsic OP values for most of the sources. The different sources also show close values between
410 the obtained OP values from the base run and median values from the bootstrap analysis (**Figure**
411 **2**). The highest variability of intrinsic OP-DTT values was observed for the cooking source.
412 However, due to its low contribution to PM_{2.5} (1.4%), it will not highly affect the apportionment
413 results.

414 Biomass burning source showed the highest intrinsic OP-DTT_v value (0.049 nmol·min⁻¹·μg⁻¹),
415 followed by HFO combustion (0.043 nmol·min⁻¹·μg⁻¹), traffic exhaust (2) (0.034 nmol·min⁻¹·μg⁻¹)
416 ¹), cooking (0.027 nmol·min⁻¹·μg⁻¹) ammonium sulfate (0.016 nmol·min⁻¹·μg⁻¹), traffic exhaust
417 (1) (0.012 nmol·min⁻¹·μg⁻¹), and traffic non-exhaust (0.01 nmol·min⁻¹·μg⁻¹). Primary and
418 secondary biogenic sources as well as crustal dust and aged sea-salt showed considerably lower
419 intrinsic OP-DTT values (0.008-0.002 nmol·min⁻¹·μg⁻¹).

420 The examination of the intrinsic OP values reveals the sensitivity of the OP whether by AA or
421 DTT measurements to PM sources and their chemical composition. Biomass burning source
422 showed the highest intrinsic OP-AA value, that is at least three times higher than the value
423 obtained for the HFO combustion and traffic exhaust sources. On the other hand, OP-DTT test
424 seems to be multi-source influenced with close intrinsic values for biomass burning, HFO
425 combustion, and traffic exhaust (2). Similar results were observed by Weber et al. (2018) when
426 applying the method to the Chamonix site in France.

427 Furthermore, as observed earlier, sources with a high organic profile contribution show higher
428 intrinsic values for AA test compared to DTT, namely biomass burning, secondary biogenic,
429 diesel generators, and traffic exhaust (1) (having high loading of 17α(H)-21β(H)-hopane). As for
430 HFO combustion source characterized by elements such as Ni and V, intrinsic OP values were

431 similar for both tests since AA and DTT are sensitive to elements, in line with the findings of
432 Bates et al. (2019).

433 On the other hand, traffic non-exhaust characterized by high content of Cu, Sb, and Sn showed a
434 strong variability in the MLR bootstrap results and its corresponding OP intrinsic values are
435 relatively low compared to other sources (**Figure 2**). Weber et al. (2018); (2021) presented
436 intrinsic OP for elements associated to non-exhaust emissions in PM₁₀, but they were either
437 combined to sea-salts or to carbonaceous matter related to exhaust vehicular emissions that
438 largely contribute to the values of OP. The same observation was made in this study for the
439 traffic exhaust (2) source, characterized by high loadings of OC and EC, and showed an intrinsic
440 OP value for both assays. On the other hand, Shen et al. (2022) has highlighted the important
441 contribution of brake and tire wear emissions to OP-DTT_v as the emitted elements could be
442 redox-active. The low intrinsic OP values observed in our study for traffic non-exhaust might be
443 linked to the PM fraction considered. Giannossa et al. (2022) have showed that resuspended dust
444 mainly contributes to the OP of the coarse fraction rather than the fine one.

445 The ammonium sulfate source showed a significant intrinsic OP-DTT_v value as previously
446 showed by Weber et al. (2018).

447

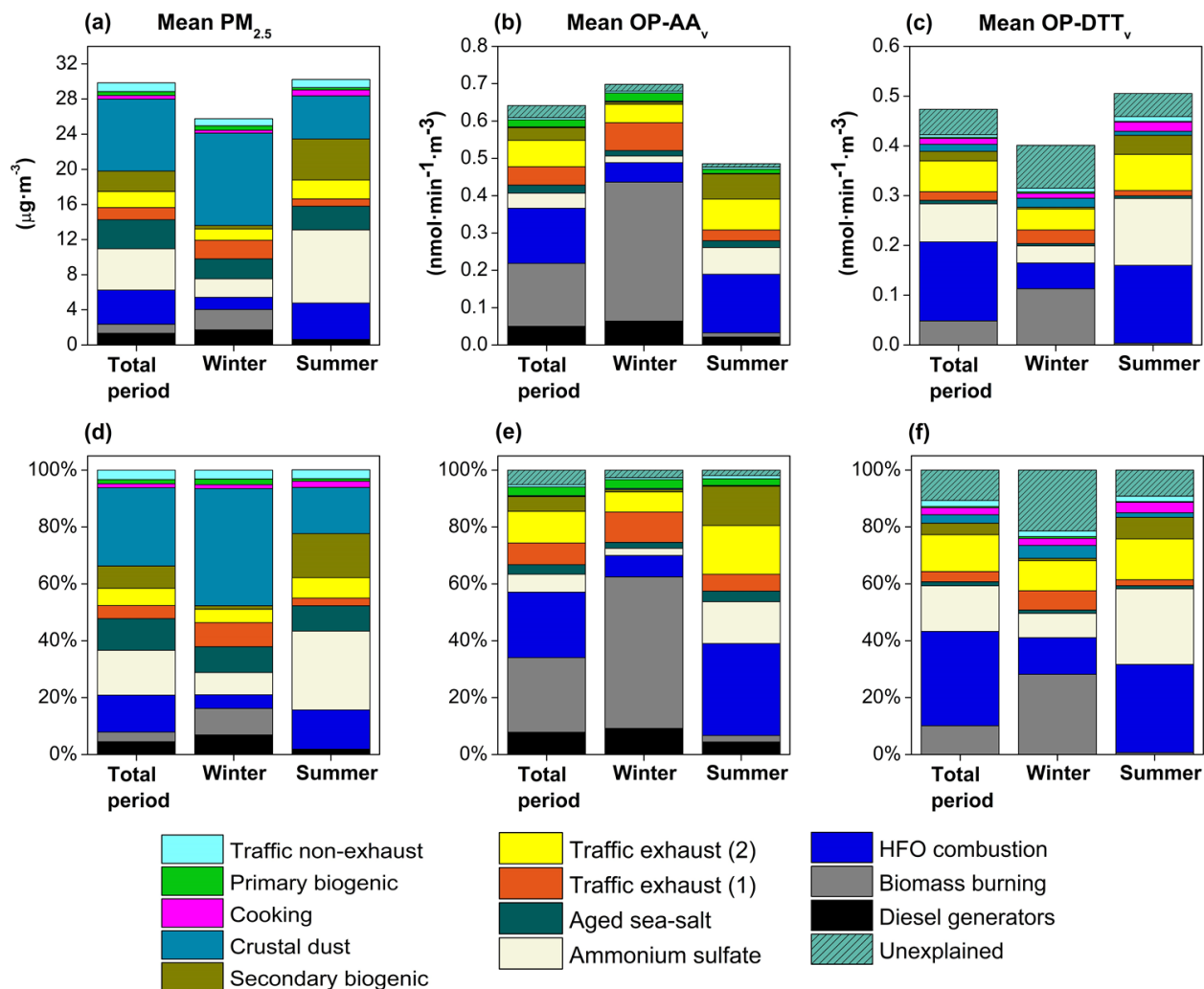
2.4.3 Contribution of the sources to the OP values

448 The average and normalized contribution of the sources to PM_{2.5} concentration, OP-AA_v, and
449 OP-DTT_v for the total period as well as for winter and summer periods are presented in **Figure 3**.
450 Source contribution was calculated for all the sources except for the “cooking” source for OP-
451 AA_v and the “diesel generators” source for OP-DTT_v. The “unexplained” category corresponds

452 to the difference between the observed OP and the sum of the contributions of all the sources.
453 For the total period, 95% of OP-AA_v and 88% of OP-DTT_v observed values could be explained
454 by the identified sources.

455 It can be directly observed that the sources that largely contribute to PM_{2.5} in the total period
456 were not the ones contributing the most to the OP values. Specifically, crustal dust source, that
457 contributes to 27.5% of PM_{2.5}, only contributes to 3.3% of OP-DTT_v and to 0.3% of OP-AA_v.

458 The second contributor to PM_{2.5} is the ammonium sulfate source (15.8% of PM_{2.5}) that
459 contributes to 6.3% of OP-AA_v and 15.4% of OP-DTT_v. In different studies, it has been reported
460 that secondary inorganic sources, such as ammonium sulfate and ammonium nitrate, are
461 commonly associated with low toxicity in PM, and their ions do not exhibit any sensitivity
462 towards both AA and DTT assays (Borlaza et al., 2021; Calas et al., 2019; Cesari et al., 2019;
463 Verma et al., 2014). However, the contribution of the ammonium sulfate source to OP-DTT_v
464 might be attributed to the formation of redox active SOA at the same time as the inorganic ions.
465 In this study, the ammonium sulfate factor identified by PMF is mainly associated with the HFO
466 combustion from the power plant in addition to distant sources (through long-range transport)
467 from Turkey and Western Europe during late spring and summer seasons (Fadel et al., 2023).
468 This source represents by that a regional secondary factor with an anthropogenic influence that
469 could explain its contribution to OP, particularly OP-DTT. Weber et al. (2021) have also
470 reported a considerable intrinsic OP value for the ammonium sulfate source, identified through
471 7500 samples, in the DTT assay due to the presence of organic carbon in the chemical profile.



472

473

474 **Figure 3:** Mean contribution of the sources to the (a) PM_{2.5} concentration, (b) OP-AA_v, and (c)
 475 OP-DTT_v for the total (Dec 2018-Nov 2019), winter (Dec 2018-March 2019), and summer (June
 476 2019-September 2019) periods; their respective normalized contributions are presented for (d)
 477 PM_{2.5} concentration, (e) OP-AA_v, and (f) OP-DTT_v for the different periods.

478

479 Biomass burning which was only responsible for 3.4% of PM_{2.5} also shows a low contribution to
 480 OP-DTT_v (10.3%), but the highest share of OP-AA_v between the sources (26.3%). Traffic

481 exhaust and non-exhaust emission sources contribute to both OP-AA_v and OP-DTT_v with a share
482 of 19.5% and 18.4%, respectively. As for the industrial typology of the site, HFO combustion
483 attributed to the power plant showed high shares to both assays with a contribution of 23.1% for
484 OP-AA_v and 32.7% for OP-DTT_v (**Figure 3**).

485 We can conclude that common sources contribute the most to the values of OP, namely biomass
486 burning, traffic emissions, and HFO combustion explaining 69% of OP-AA_v value and 62% of
487 OP-DTT_v. These results were consistent with several literature studies that report dominant
488 contribution of biomass burning to OP-DTT_v and OP-AA_v, (Fang et al., 2016; Perrone et al.,
489 2019; Verma et al., 2014), traffic emissions as well as fuel oil combustion (Crobeddu et al.,
490 2017; Moreno et al., 2017; Yang et al., 2014). Primary and secondary biogenic sources
491 contribute to 8.2% of OP-AA_v value and 4.4% of OP-DTT_v while aged sea-salts contribute to
492 3.4% of OP-AA_v and 1.4% of OP-DTT_v. Diesel generator contributed to 7.8% of OP-AA_v and
493 the cooking emissions source contribute to 2.4% of OP-DTT_v.

494

495 2.5 Seasonal variations

496 When comparing winter and summer periods, the overall OP-DTT_v did not show any significant
497 variability ($p > 0.05$). However, a different scenario was observed for OP-AA_v since the values
498 were significantly higher ($p < 0.001$) during winter period compared to summer (**Table 2**).
499 According to the literature, there is not a unique trend for the seasonal variations either for OP-
500 DTT or OP-AA. Several papers have reported a strong seasonality of OP with higher values
501 during winter compared to summer (Borlaza et al., 2021; Calas et al., 2019; Calas et al., 2018;
502 Verma et al., 2014) while others have presented the opposite seasonal trend (Charrier et al.,

503 2015; Fang et al., 2016; Perrone et al., 2016). In the same context, Pietrogrande et al. (2019)
504 have reported that observed OP-DTT values were independent from seasonality in different rural
505 and urban sites. Additionally, different seasonal trends might be observed for different PM
506 fractions. For instance, Giannossa et al. (2022) showed that higher OP-DTT_v were observed
507 during summer for PM_{10-2.5} fraction while higher values were observed during winter for PM_{2.5},
508 suggesting that different sources with different seasonality might influence OP-DTT_v.

509 These observations might lead to the conclusion that the OP is significantly correlated with the
510 chemical composition of PM and its temporal variability is linked to the emission sources and
511 their intensities that are different across sampling sites.

512 In this work, the results presented in **Figure 3** revealed significant differences in the
513 contributions of the sources especially for biomass burning and HFO combustion between winter
514 and summer periods. The biomass burning source, contributing only to 9.0% of PM_{2.5} during
515 winter, was found to be the major contributor to both OP-AA_v (53.3%) and OP-DTT_v (26.5%).
516 These contributions were 33 and 34 times higher than the ones observed during summer for OP-
517 AA_v (2.3%) and OP-DTT_v (0.7%), respectively (**Figure 3**). This predominance of biomass
518 burning source to OP values during cold months has been previously reported in the literature by
519 Borlaza et al. (2021) and Verma et al. (2014) and highlights the severity of biomass burning
520 emissions from residential heating during the winter. On the other hand, the HFO combustion
521 source from the power plant demonstrated higher contributions during the warm period for OP-
522 AA_v (32.3%) and for OP-DTT_v (31%) compared to the cold period (7.5% for OP-AA_v and
523 14.2% for OP-DTT_v). This might be attributed to the increase in electricity production during the
524 summer months, which leads to a higher contribution of this source to PM_{2.5} (13.7% during
525 summer vs. 5.4% during winter). In contrast, the contributions from traffic sources were found to

526 be relatively consistent throughout the year, with variations of less than 6% (**Figure 3**).
527 Additionally, secondary biogenic source was found to have at least 10 times higher contribution
528 to both OP assays during the summer compared to winter. Ammonium sulfate sources showed
529 considerably higher contribution to OP-DTT_v during summer (26.6% vs. 8.0% during winter)
530 due to the higher contribution of the source to PM_{2.5} (**Table 1**).

531 As previously mentioned, the ammonium sulfate is mainly emitted from the HFO combustion
532 from the power plant in addition to distant anthropogenic sources that arrive to the site through
533 long range transport especially during summer (Fadel et al., 2023).

534

535 3 Conclusion

536 This work represents a significant advancement in the field of air quality research in the East
537 Mediterranean and the Middle East region. Specifically, this work focused on evaluating the
538 oxidative potential (OP) of PM_{2.5} samples collected for almost a year (December 2018 - October
539 2019) using two acellular assays: ascorbic acid (AA) and dithiothreitol (DTT), correlating OP
540 values with a wide range of chemical species in PM_{2.5}, and on apportioning OP on different
541 emission sources. The mean OP-AA_v value was $0.64 \pm 0.29 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$ and the mean OP-
542 DTT_v was $0.49 \pm 0.26 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$. Spearman correlations showed that OP-AA_v showed
543 strong correlations with the carbonaceous subfractions, and organic compounds while OP-DTT_v
544 showed a strong correlation with elements emitted from anthropogenic activities such as V, Ni,
545 Zn, Cu, Sn, and Sb.

546 A multiple linear regression method was applied in order to estimate the contribution of PM
547 sources to the OP values. The results showed that crustal dust and ammonium sulfate sources

548 that largely contribute to PM_{2.5} mass were not the major sources contributing to the values of OP.
549 However, 69% of OP-AA_v and 62% of OP-DTT_v values were explained by three local
550 anthropogenic sources: Heavy Fuel Oil (HFO) combustion from a power plant, biomass burning,
551 and road traffic emissions. Seasonal variations showed that biomass burning is the largest
552 contributor to OP during winter (53.3% for OP-AA_v and 26.5% for OP-DTT_v) while HFO
553 combustion contributes the most during summer (32.3% for OP-AA_v, and 31% for OP-DTT_v). In
554 contrast, the contributions from traffic sources were found to be relatively consistent throughout
555 the year (18% and 24% of OP-AA_v and 18% and 19% of OP-DTT_v during winter and summer,
556 respectively). Following the obtained results, air quality plans should be prioritizing these three
557 sources to limit the impact of air pollution on human health. Overall, this study has provided
558 insight into the relationship between PM sources and oxidative potential in an urban site in the
559 East Mediterranean.

560

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