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1           **Assessment of the PM<sub>2.5</sub> oxidative potential in a coastal industrial city in Northern**  
2           **France: relationships with chemical composition, local emissions and long range sources**

3

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5

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10

11           Abstract

12           The objective of this work was to relate PM<sub>2.5</sub> Oxidative Potential (OP) data to PM  
13           composition and PM local and distant source contributions. PM<sub>2.5</sub> collected in Dunkerque, a  
14           coastal industrial city in North of France, was extensively characterized for major and minor  
15           chemical species. PM<sub>2.5</sub> filters were extracted using a synthetic pulmonary fluid to achieve OP  
16           estimation based on Ascorbic Acid (AA) and dithiothreitol (DTT) depletion assays. In order  
17           to evidence relationships between OP values, chemical composition and local and distant  
18           source contributions, correlation coefficient, Principal Component Analysis (PCA),  
19           concentration roses and polar plots and concentration weighted trajectories were used.  
20           Heterogeneous conclusions were drawn using the three first methods as the bivariate polar  
21           plots lead to dismiss some of the correlation evidenced using correlation coefficient and PCA.  
22           Both AA and DTT tests appeared complementary as they were not sensitive to the same  
23           species/source contribution. **The bivariate polar plot representation of OP values versus wind**  
24           **direction and wind speed revealed that PM<sub>2.5</sub> concentration and combustion sources were**  
25           **linked to OP-AA, whereas emissions from integrated steelworks, electric steelworks, heavy**

26 fuel oil combustion and traffic non-exhaust significantly contribute to OP-DTT. Sea-salts,  
27 aged sea-salts, crustal, secondary sulfates and secondary nitrates sources were not found to  
28 contribute to OP values. Constant weighted trajectories evidenced several source regions  
29 responsible for high OP values with Belgium, Germany and Netherland at the leader position.  
30 Contribution of inland regions appeared possibly related to the biomass and traffic related  
31 combustion while heavy fuel oil combustion could be also involved in the contribution of  
32 marine and coastal areas.

33

34 Keywords: PM<sub>2.5</sub>; source contribution; oxidative potential; dithiothreitol (DTT) assay; acid  
35 ascorbic (AA) assay, concentration weighted trajectories (CWT)

36

## 37 **Introduction**

38 Exposure to particulate matter (PM) is a major public health issue for all countries in  
39 the world. Air quality modelling has revealed that 91% of the global population lives in areas  
40 where annual average concentration of PM<sub>2.5</sub> (particulate matter with an equivalent  
41 aerodynamic diameter less than 2.5 µm) exceeds the corresponding WHO guideline limits  
42 (10 µg·m<sup>-3</sup>) (WHO, 2018). Exposure to the outdoor fine particles has been identified as an  
43 important risk factor of mortality with more than 4.2 million premature deaths in the World in  
44 2016 (WHO, 2018). Burnett et al. (2018) applied a new global exposure mortality model to  
45 study the association between PM<sub>2.5</sub> concentration and non-accidental mortality considering  
46 41 cohorts in 16 countries and estimated 8.9 million of PM<sub>2.5</sub> related deaths in 2015 (Burnett  
47 et al., 2018). It is consistent with the 8.8 million recently modelled by Lelieveld et al. (2020).  
48 A similar approach applied to the 250 most populates cities in the world predicted a median  
49 rate of PM<sub>2.5</sub>-related mortality reaching 39 per 100,000 people, with differences in the cities  
50 (13 to 125 deaths per 100,000 people) (Anenberg et al., 2019).

51 It is well established that particulate matter causes several diseases as lung cancers  
52 (Raaschou-Nielsen et al., 2013; Sax et al., 2013), cardiovascular diseases (Massamba et al.,  
53 2014), chronic obstructive pulmonary disease (COPD) (Li et al., 2016) and asthma (Bontinck  
54 et al., 2020; Hendryx et al., 2019). Toxicological studies have shown that PM has the ability  
55 to induce oxidative stress. This latter corresponds to an imbalance between the antioxidant  
56 defence and the overproduction of reactive oxygen species (ROS) triggered by an exposure to  
57 airborne PM. Oxidative stress appears as an early pathways potentially preceding severe  
58 damages to cell components (lipids, proteins and DNA) (Borm et al., 2007; Nel, 2005). The  
59 PM composition is a determinant of their ability to contribute to overproduce ROS, and both  
60 organic compounds and some metals appeared to be associated with ROS production (Kelly  
61 and Fussell, 2012).

62 Components that contribute mostly to PM mass were found to contribute the least to  
63 the toxicity (Borm et al., 2007). For this reason, the PM atmospheric concentration is not the  
64 only parameter to consider for assessing the impact of air pollution on human health. Indeed,  
65 water soluble major ions as ammonium sulfate, ammonium nitrate and sea-salts are relatively  
66 not correlated to the PM toxicity whereas trace elements as Pb, Cd, Ni, As and polycyclic  
67 aromatic hydrocarbons as benzo[a]pyrene are known for their high toxicity (Lippmann, 2014)  
68 and correspond to regulated species in Europe.

69 The assessment of toxicological effects of PM related to the oxidative stress is widely  
70 investigated considering *in vitro* lung cell exposure (Badran et al., 2020; Gualtieri et al., 2017;  
71 Jia et al., 2017). In parallel, acellular tests have been suggested over the last fifteen years to  
72 evaluate the PM oxidative potential (OP), which is a measure of the ability of PM to deplete  
73 certain antioxidant molecules in synthetic airway fluids (Ayres et al., 2008; Sauvain et al.,  
74 2013). The dithiothreitol (DTT) simulates reductant species in cells like Nicotinamide adenine  
75 dinucleotide or nicotinamide adenine dinucleotide phosphate. The DTT assay evaluates the  
76 ability of PM redox active species to transfer electrons to dissolved molecular oxygen  
77 (Kumagai et al., 2002; Li et al., 2003). In the absence of PM redox active species, DTT can  
78 act as a reducer of dissolved oxygen leading to formation of H<sub>2</sub>O<sub>2</sub>. PM components can act as  
79 catalyst to increase the reduction of oxygen species to ROS like superoxide anion and H<sub>2</sub>O<sub>2</sub>.  
80 The latter contribute to the overall level of ROS that could be responsible for an oxidative  
81 stress in cells. The ascorbic acid (AA) simulates antioxidants in the respiratory tract lining  
82 fluid (RTLFL) and the AA assay measures the ability of PM to deplete antioxidants in the  
83 RTLFL (Mudway et al., 2004). The application of DTT and AA assays in many studies showed  
84 that they were correlated to both common and different PM constituents. The OP assessed  
85 using DTT (OP-DTT) has been correlated not only with metals but also with oxygenated  
86 organic compounds (Charrier and Anastasio, 2012; Cho et al., 2005; Crobeddu et al., 2017;

87 Verma et al., 2015). The OP derived from AA assay (OP-AA) has been found correlated  
88 rather to metals (Fang et al., 2016; Pietrogrande et al., 2018). An OP assessment based on the  
89 use of several assays, as AA and DTT in the present study, appears as an appropriate  
90 approach for considering contributions of reactive species from several families of PM  
91 components. Information on the relationship between PM components and OP values are  
92 sometimes limited since the correlation is based on elements that are specific of a source but  
93 not always responsible for the OP response (Gao et al., 2020a). In addition, numerous  
94 elements and compounds are emitted by different sources and are not always considered at the  
95 analysis step. Therefore, several authors have suggested the investigation of PM source  
96 contribution to OP (Calas et al., 2019; Cesari et al., 2019; Yu et al., 2019) as a relevant  
97 indicator to identify the sources with high potential toxic effects on human health.

98 In this context, the objective of this study was to relate OP data to PM composition and PM  
99 source contribution in an industrial and urban area located in Northern France. The OP-DTT  
100 and OP-AA assays were used and relationships between OP results, PM<sub>2.5</sub> composition and  
101 emission sources contributions were investigated by methods including correlation, principal  
102 component analysis, bivariate polar plots, concentration roses and concentration weighted  
103 trajectories.

104

## 105 1. Materials and methods

### 106 1.1. PM<sub>2.5</sub> samples

#### 107 1.1.1. Study area and sampling.

108 PM<sub>2.5</sub> samples considered in this work were collected in Dunkerque (latitude:  
109 51°2'10"N; longitude: 2°22'46"E) in winter and spring 2010-2011. Since 2010-2011, the  
110 PM<sub>2.5</sub> samples have been stored at -18°C in the dark, in hermetically sealed boxes. This  
111 procedure ensures to prevent any volatilization or transformation of the organic compounds

112 over time. The detailed description of the sampling methodology and the study area is given  
113 in Kfoury et al. (2016). Briefly, Dunkerque, 210,000 inhabitants with its suburbs, is an  
114 industrialized city located in Northern France in the southern coast of the North-Sea. Due to  
115 its location, this site is significantly influenced by common sources as sea spray, marine  
116 traffic, domestic and road traffic emissions as well as more specific sources, notably industrial  
117 emissions in the field of metallurgy, cement production and organic chemistry. Between the  
118 industrial sources, an integrated steelworks (ISW) which is the biggest steel producer in  
119 Europe, and an electric steel plant (ESP) are noticeable and located in the 260–290° wind  
120 sector and east to the sampling site respectively (Figure S1). According to the European  
121 pollutant release and transfer register (E-PRTR), cumulatively in 2010, all the industries  
122 located in Dunkerque region emitted in the air 3,100 tons of total suspended particles  
123 including 8,117 kg of Zn, 6,962 kg of Pb, 1,398 kg of Ni, 1,241 kg of Cu, 1,194 kg of Cr, 175  
124 kg of Cd and 101 kg of As (E-PRTR, 2011). PM<sub>2.5</sub> was collected on a semi-daily basis  
125 (00:00–12:00 UTC and 12:00–24:00 UTC time period) using the high volume (30 m<sup>3</sup>·h<sup>-1</sup>)  
126 DA80 sampler (DA80, DIGITEL®, Switzerland). Two types of 150 mm diameter filters were  
127 used: cellulose (grade 41, Whatman®, GE Healthcare Life Sciences, United Kingdom) for  
128 major and trace elements analysis and OP determination, and high purity quartz microfiber  
129 filters (grade QM-A, Whatman®, GE Healthcare Life Sciences, United Kingdom) for carbon  
130 quantification.

131

## 132 1.2. PM<sub>2.5</sub> composition and source contribution

133 PM<sub>2.5</sub> samples were analyzed for their content in major and trace species as Ag, Al,  
134 As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Rb, Sb, Sn, Sr, Ti, V, Zn, NH<sub>4</sub><sup>+</sup>,  
135 Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and total carbon (TC) using Inductively Coupled Plasma-Mass spectrometry  
136 (ICP-MS), Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES), ion

137 chromatography and a CHNS/O elemental analyzer. The detailed protocols are described in  
138 Kfoury et al. (2016) and Ledoux et al. (2017).

139 In a previous study, constrained weighted-non-negative matrix factorization (CW-  
140 NMF) was applied to the whole PM<sub>2.5</sub> composition dataset (173 PM<sub>2.5</sub> samples) and led to the  
141 identification of 11 contributing sources (Kfoury et al., 2016). The eight first ones can be  
142 considered as sources typically encountered at an urban coastal site: sea salts, aged sea salts,  
143 crustal, heavy fuel oil combustion, combustion 2 (mix between biomass and road traffic  
144 combustion) and traffic non-exhaust (related to wear of the car mobile parts such as brakes,  
145 tires, clutch ...) for which both a local and distant origin can be considered, and secondary  
146 sulfates and secondary nitrates which are typically related to long range transport. Three other  
147 source profiles were related to the local steelmaking activities located close to the sampling  
148 site (less than 7 km): one for the ESP emissions and two for the ISW sources with a  
149 distinction for the latter between the sintering stack (ISW-Sintering Stack) and the fugitive  
150 emissions from the whole ISW site (ISW-Fugitive).

151 In this work, 57 out of the 173 PM<sub>2.5</sub> samples were considered for studying their oxidative  
152 potential. The sample selection was made based on PM<sub>2.5</sub> concentrations and source  
153 contributions. PM<sub>2.5</sub> samples showing higher relative contribution for each of the eleven  
154 sources were included in addition to the high (> 50 µg·m<sup>-3</sup>) and low (<10 µg·m<sup>-3</sup>) PM<sub>2.5</sub>  
155 concentration samples.

156

### 157 1.3. Oxidative potential measurements

158 OP was assessed by using two a-cellular methods based on the depletion rate of DTT  
159 (OP-DTT) and AA (OP-AA) in the presence of the PM constituent. When performing these  
160 tests, an important issue is first related to the choice of the leaching agent that will be used for  
161 the PM extraction. The latter has to be representative of the physiological conditions



162 occurring in the PM target organs (Calas et al., 2017; Pietrogrande et al., 2019). As well, the  
163 extraction procedure has also an important influence on the OP results and the review of the  
164 literature showed large differences between the methods used (Bates et al., 2019). The fact  
165 there is no standardized method for OP measurements leads to consider a compromise  
166 between all the critical parameters such as solvent, extraction procedure and solid/liquid (S/L)  
167 ratio (Hernandez-Pellon et al., 2018).

168

### 169 1.3.1. Sample preparation for OP tests

170 The Gamble's solution (pH=7.4) is one of the most used simulated lung fluids (SLF)  
171 and represents the interstitial fluid in the deep lung. Therefore, it was chosen as a leaching  
172 agent for the PM<sub>2.5</sub> extraction. The Gamble's solution was daily freshly prepared according to  
173 the specifications given in Colombo et al. (2008), using ultrapure water and mixing the stock  
174 solutions following the order given in Table S1 (see supplementary materials) to avoid salt  
175 precipitation. The citrate was used to simulate proteins that can be found in the lung lining  
176 fluid and acetate instead of organic acids (Hedberg et al., 2010; Marques et al., 2011). All  
177 chemicals were of analytical grades. The pH of the Gamble's solution was adjusted to 7.4 by  
178 adding drop-wise HCl 10% (Wragg and Klinck, 2007) or NaOH 1M (Caboche et al., 2011).

179 For each of the 57 PM<sub>2.5</sub> samples, about 1/10 of the cellulose filter, containing an  
180 average of 1.40 mg of PM<sub>2.5</sub>, was placed in a 15 mL glass tube with 14 mL of Gamble's  
181 solution. The volume was chosen in accordance with real human exposure conditions with  
182 respect to the ambient concentration of particles, the inhaled air volume and the pulmonary  
183 fluid volume. In these conditions, the S/L ratio was in the 1/500 - 1/50000 range avoiding any  
184 risk of saturation and competition between the soluble compounds (Caboche et al., 2011).

185 The extraction tubes were covered with aluminum foil and placed in a heated orbital shaker  
186 for 24 h at 37°C, at a speed of 250 oscillations·min<sup>-1</sup>. Solutions were then filtered on 0.45 µm

187 nylon filters, and the filtrates were placed in flasks, and stored at -20°C until OP analyses.  
188 Blanks were considered by treating several field blank filters with the same protocol as  
189 applied on PM<sub>2.5</sub> filters.

190

### 191 1.3.2. Dithiothreitol OP test

192 Redox-active species in PM have the ability to oxidize DTT to DTT disulfide, and  
193 catalyze the reduction of oxygen species to ROS like superoxide anion and H<sub>2</sub>O<sub>2</sub>. When  
194 5,5-dithio-bis-(2-nitrobenzoic acid) (DNTB) is added, the remaining DTT reacts with DTNB,  
195 generating DTT-disulfide and 2-nitro-5-thiobenzoic acid (TNB) (Figure S2). The latter is  
196 quantified, by measuring its absorbance at 412 nm, which is also proportional to the  
197 remaining quantity of DTT (Visentin et al., 2016).

198 The DTT protocol was optimized in a microplate version which makes easier the  
199 consideration of several points (i.e. 7 points in this work) for evaluation of the DTT depletion.  
200 DTT and DNTB stock solutions were prepared at a concentration of 0.4 mM and 1.5 mM,  
201 respectively, in a phosphate buffer (pH=7.4). Since both solutions are sensitive to light and  
202 temperature (Damodaran, 1985; Eyer et al., 2003), they were kept in amber glass vials in the  
203 dark at -20°C until use. The OP-DTT measurement was carried out in 96 well black plates  
204 with clear flat bottom (Coastar® 3631, Corning Incorporated Life Sciences, USA). 120 µL of  
205 potassium phosphate buffer (pH=7.4), and 40 µL of the PM leachate (or blank or positive  
206 control) were added in each well. The plate was then placed at 37°C for 10 min under  
207 shaking. 25 µL of DTT (0.4 mM) was then added to initiate the oxidation reaction.

208 The remaining DTT concentration was estimated after 0, 5, 10, 20, 30, 45 and 60  
209 minutes of reaction between PM leachate components and DTT, at 37°C. After each time of  
210 reaction, 15 µL DTNB were then added to each well to convert remaining DTT to TNB. After  
211 10 min at 37°C, the absorbance of TNB was measured at 412 nm (spectrophotometer

212 Multiskan Go, Thermo Fisher Scientific, Finland), and converted to DTT remaining quantity.  
213 The DTT depletion rate was calculated using the slope of the curve (linear regression) of  
214 remaining DTT versus time. 1,4-naphthoquinone (1,4-NQ), 100  $\mu\text{M}$ , was used as a positive  
215 control and obtained values ( $1.23 \mu\text{M}\cdot\text{min}^{-1}$ ) were in the range of those obtained in the  
216 literature.

217 For each  $\text{PM}_{2.5}$  sample, OP-DTT values were obtained by correcting the  $\text{PM}_{2.5}$  filter  
218 slope values with the blank filter one. Samples were analyzed in triplicates and the given OP-  
219 DTT values correspond to the arithmetic mean. The relative standard deviation was below 4.1  
220 %. The OP-DTT values were finally expressed per unit of mass of PM (OP-DTT<sub>m</sub> in  
221  $\text{pmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$ ) and per unit of air volume (OP-DTT<sub>v</sub> in  $\text{nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$ ). The first unit can  
222 be related to the intrinsic OP of 1  $\mu\text{g}$  of emitted PM and will be used to compare OP of the  
223 sources. The second one can be related to the intrinsic OP of 1  $\text{m}^3$  of the air people breathe  
224 and is more adapted for studying the situation (wind direction and air mass origin...) in which  
225 the impact on health could be high.

226

### 227 1.3.3. Ascorbic acid OP test

228 AA is present in the lung epithelial lining fluid (ELF), along with other antioxidants  
229 like reduced glutathione (GSH), and uric acid (UA). Since AA has the same response,  
230 whether in a mixture of these antioxidants or alone, it can be used as a simplified model of the  
231 synthetic respiratory tract lining fluid (Zielinski et al., 1999). As for DTT, the redox active  
232 species in PM have the ability to oxidize AA to dehydroascorbic acid (Figure S2), and  
233 catalyze the formation of ROS by transferring an electron to oxygen molecules. AA stock  
234 solution (1 mM) was prepared in ultrapure water, and stored at  $-20^\circ\text{C}$  due to its instability at  
235 room temperature (Bode et al., 1990). The OP-AA measurement was done in 96 well plates  
236 with UV-transparent flat bottom (UV-Star® 655801, Greiner bio-one, Austria). 160  $\mu\text{L}$  of PM

237 leachate was placed in each well of the plate, and the latter was heated to 37°C (5 min), before  
238 adding 40 µL of AA solution and shaking for 1 min. Finally, the plate was placed in the  
239 spectrophotometer (Multiskan Go, Thermo Fisher Scientific, Finland), at 37°C and the  
240 absorbance was measured at 265 nm every 2 minutes for 2 h (Jung and Wells, 1998) with a  
241 30 s shaking step before each measurement (Yang et al., 2014). OP-AA values were deduced  
242 from the AA depletion curve versus time considering the slope of the linear part of the curve,  
243 where AA depletion rate is maximal. Samples were analyzed in triplicates (RSD < 3.7 %),  
244 blank filters were considered, 1.4 NQ was used as positive control (2.74 µM·min<sup>-1</sup>) and OP-  
245 AA values were expressed per unit of mass of PM and volume (OP-AA<sub>m</sub> and OP-AA<sub>v</sub>  
246 respectively).

247

248

#### 249 1.4. Data handling and processing

250 Relationships between OP results, PM<sub>2.5</sub> composition and source contributions were  
251 investigated by using several methods including correlation, principal component analysis  
252 (PCA), bivariate polar plots, concentration roses, OP roses and concentration weighted  
253 trajectories (CWT). The R software was used in addition to FactomineR (Lê et al., 2008) and  
254 openair (Carslaw and Ropkins, 2012) packages to perform these calculations.

255

##### 256 1.4.1. Correlation

257 Prior the determination of the correlation coefficient between the variables under  
258 study, the Shapiro-Wilk test was performed to assess the normality of the data distribution. As  
259 the normality was not verified ( $p < 0.001$ ) for most of the variables, the Spearman correlation  
260 coefficient was used. Two levels of significance were considered,  $p < 0.05$  and  $p < 0.001$ ,

261 allowing to conclude about the correlation with 95% and 99.9% of confidence respectively. In  
262 addition, correlations were also investigated by using PCA after data normalization.

263

264 1.4.2. Bivariate polar plots and concentrations roses.

265 Bivariate polar plots and OP and concentration roses were used to investigate the  
266 relationships between OP values and contribution of local sources.

267 Bivariate polar plots represent the variation of a quantitative parameter (concentration, OP  
268 value, source contribution) versus the wind direction and wind speed. For each PM<sub>2.5</sub> sample,  
269 the parameter values obtained for the 12 h period were distributed in front of the 12  
270 corresponding hourly wind speed and directions. The data set used to draw each polar plot  
271 counts 57x12 lines. The OP and concentration roses, which give the average value in a  
272 particular wind direction, were calculated using the same dataset after averaging the values at  
273 45° intervals.

274

275 1.4.3. Concentration weighted trajectories

276 The concentration weighted trajectories (CWT) (Cheng et al., 2013; Dimitriou et al.,  
277 2015) were used to investigate relationships between OP and distant sources. The CWT  
278 methods assume that when an air mass is passing through a polluted area, the material can be  
279 transported along the trajectory to the receptor site. By using air mass back-trajectories and  
280 affecting values observed at the receptor site along the trajectories, it is possible, by the end  
281 after averaging, to locate areas responsible for high values (Carslaw, 2019).

282 Air mass back-trajectories were calculated using the hybrid single particles Lagrangian  
283 integrated trajectory (HYSPLIT) model (Rolph et al., 2017; Stein et al., 2015) considering the  
284 Gridded Meteorological Data Archives (GDAS 0.5 degrees) and a height of 100 meters above  
285 ground level at receptor site. For each PM<sub>2.5</sub> sample, four 72 h backward trajectories were

286 assigned (one trajectory every 3 hours) and OP and source contribution values obtained for  
287 the 12 hours period were merged with the 4 corresponding trajectories. The dataset used for  
288 CWT calculation count 72x4x57 lines.

289

## 290 2. Results and discussion

### 291 2.1. PM<sub>2.5</sub> composition et sources contribution

292 Table 1 regroups the average composition of the PM<sub>2.5</sub> samples and Table 2  
293 summarizes the chemical markers that were used for identifying the sources as well as their  
294 average contributions (Kfoury et al., 2016). The PM<sub>2.5</sub> average concentration of the selected  
295 samples was 29.2  $\mu\text{g}\cdot\text{m}^{-3}$ , which is similar to the average concentration typically encountered  
296 during the winter-spring period in the studied area (Kfoury et al., 2016). Among the PM  
297 components,  $\text{NO}_3^-$ , TC,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and Na showed the highest average concentrations  
298 ( $> 300 \text{ ng}\cdot\text{m}^{-3}$ ) representing together about 67% of the PM<sub>2.5</sub> mass. These elements appeared  
299 characteristics of the secondary nitrate and sulfate source profiles as well as the combustion  
300 and the marine sources (Table 2).  $\text{NH}_4^+$  and  $\text{Cl}^-$  are also characteristic elements of the ISW  
301 sintering stack emissions (Hleis et al., 2013). Fe, K, Ca, Mg and Al were found with  
302 concentrations between 26 and 155  $\text{ng}\cdot\text{m}^{-3}$ . These elements are known to belong to the  
303 aluminosilicates category. Nevertheless, at Dunkerque urban-industrial site, they were shown  
304 to be also associated with emissions from the ISW (Hleis et al., 2013) and notably dusts from  
305 the sintering unit. Among the trace metals, Zn (67.6  $\text{ng}\cdot\text{m}^{-3}$ ), Pb (14.8  $\text{ng}\cdot\text{m}^{-3}$ ) and Mn  
306 (13.7  $\text{ng}\cdot\text{m}^{-3}$ ) stand out and were mainly associated with the metallurgical activities occurring  
307 in the ESP and the ISW (Table 2).

308

### 309 2.2. OP-AA and OP-DTT average values

310 The average mass- and volume-normalized OP-DTT and OP-AA values at Dunkerque  
311 site are presented together with values published for other European and world sites in  
312 Table 3, together with the leaching agents used for extracting PM samples. Ultrapure water,  
313 ethanol, methanol, water, phosphate buffer and Gamble solution were used for leaching in  
314 addition to ultrasonic treatment or shaking for various times. In one study only , the solution  
315 was not filtered after extraction (Janssen et al., 2014). The heterogeneity of the methodologies  
316 used could influence the obtained values and could make the comparison not reliable. As the  
317 leaching agent is different, the response could also be different as published by Calas et al.  
318 (2017) who compared responses in OP\_DTT test on extracts obtained by using artificial  
319 lysosomal fluid (ALF), ultrapure water, Gamble solution and Gamble solution implemented  
320 with dipalmitoylphosphatidylcholine. Based on the analysis of 5 different PM samples,  
321 including four real PM samples, it was shown that OP values observed using the ultrapure  
322 water were always slightly higher than those obtained using the Gamble solution.  
323 Nevertheless, focusing on the real PM samples, the difference was not exceeding 13% which  
324 make reliable the comparison between values obtained using ultrapure water and Gamble  
325 solution. In most of the comparison studies included in table 3, ultrapure water was used as  
326 leaching agent. Solubility is also highly dependent of the pH of the leaching agent  
327 (Hernandez-Pellon et al., 2018). As the phosphate buffer has the same pH value as the  
328 Gamble solution (7.4), we can assume that OP values could be compared without severe bias.  
329 However, Jedynska et al. (2017) used methanol as leaching agent and the leachate probably  
330 concentrates more organic constituents than leachates obtained using Gamble, water or  
331 phosphate buffer. In contrast to the other studies, Janssen et al. (2014) did not filter extracts  
332 before testing OP which leads to the inclusion of the contributions of insoluble species in OP  
333 values. Consequently, except for Jedynska et al. (2017), who used methanol and Janssen et al.

334 (2014), we can be confident with the reliability of the comparison between values from the  
335 cited papers.

336 Focusing on values related to PM<sub>2.5</sub> concentration, the average  $\pm$  standard deviation  
337 OP-DTTv value,  $0.36 \pm 0.24 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$ , appeared in accordance with values observed in  
338 urban and urban background sites such as Paris (France), Atlanta (USA), Lecce (Italy),  
339 Athens (Greece) (Chirizzi et al., 2017; Gao et al., 2020b; Jedynska et al., 2017;  
340 Paraskevopoulou et al., 2019). On the other hand, OP-DTTv value is lower than the one  
341 determined in Beijing and Hangzhou (China) or in Patalia (India) (Patel and Rastogi, 2018;  
342 Wang et al., 2019; Yu et al., 2019). Except for the Netherlands, the corresponding PM<sub>2.5</sub>  
343 concentrations are also far higher ( $> 113 \mu\text{g}\cdot\text{m}^{-3}$ ) than Dunkerque one. The average OP-  
344 DTTm,  $17.7 \pm 15.4 \text{ pmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$ , OP-AAv,  $1.12 \pm 1.15 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{m}^{-3}$  and OP-AAm  
345 values,  $55 \pm 66 \text{ pmol}\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$  were also comparable to the range published for European,  
346 Asian and American sites.

347

### 348 2.3. Correlation of OP with chemical species and source contributions

349 In order to study the contribution of PM chemical components to the DTT and AA  
350 oxidation activity, the correlation between OP-DTTv and OP-AAv values and the chemical  
351 species was investigated based on the Spearman correlation coefficients (Table 4) and PCA  
352 (Figure 1 and Table S2).

353

#### 354 2.3.1. Spearman correlation

355 OP-DTTv and OP-AAv showed statistically significant correlation ( $p < 0.05$ ) with  
356 almost all the species under study (Table 4). However, they were not correlated with Ca and  
357 Cl<sup>-</sup>, while Al, Co, V were only correlated with OP-DTTv, and Sr only with OP-AAv. Stronger  
358 correlations were globally observed between the PM components and OP-DTTv compared to



359 OP-AAv. This latter observation is consistent with results from other research groups (Calas  
360 et al., 2019; Fang et al., 2016). In particular, Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, K, Mn,  
361 Ni, Pb, Rb, Sb, Sn, Zn,  $\text{NO}_3^-$  and TC showed correlation coefficient higher than 0.6 with OP-  
362 DTTv. Such a correlation level was observed only for As, Ba, Cu, Na, Pb, Sb, Sn and TC with  
363 OP-AAv. A very strong correlation was found between OP-DTTv and Cu ( $r = 0.85$ ), Cd  
364 ( $r = 0.82$ ) and Sn ( $r = 0.82$ ).

365 The major PM components TC,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  appeared more correlated with  
366 OP-DTTv than OP-AAv. This is consistent with the stronger correlation found between  $\text{PM}_{2.5}$   
367 concentrations and OP-DTTv in comparison with OP-AAv ( $r = 0.67$  versus  $r = 0.45$   
368 respectively). Our results are in agreement with other observations showing that secondary  
369 inorganic aerosols (SIA) components were correlated with OP-DTT (Ma et al., 2018;  
370 Paraskevopoulou et al., 2019; Wang et al., 2019). On the contrary, Mg, Na and Sr showed  
371 negative correlation coefficients with OP values. These elements are mainly related to the  
372 marine influence at the study site. Finally a moderate correlation ( $r = 0.46$ ,  $p < 0.001$ ) was  
373 found between OP-DTTv and OP-AAv which indicates that the two tests do not exactly  
374 respond to the same species and prove the complementarity between both.

375 AA and DTT tests respond to the oxidative species solubilized in the gamble solution  
376 after leaching of the collected PM. The leachate includes not only the PM components that  
377 were identified and quantified, but also unanalyzed PM species. These latter, such as water  
378 soluble organic carbon (WSOC) including humic-like substances (HULIS) or oxygenated  
379 PAH, are an integral part of the leachate and also contribute to the OP values as well (Bates et  
380 al., 2019; Gao et al., 2020a; Jiang et al., 2020; Lin and Yu, 2019; Ma et al., 2018). In this  
381 study, the inorganic PM composition has been investigated and, based on this, the CW-NMF  
382 model allowed to determine the source contributions. Consequently, studying the correlation

383 between OP values and source contributions allows indirectly to consider all the species  
384 including the WSOC related to a specific source whether they have been analyzed or not.  
385 Strong correlations ( $r \geq 0.6$ ) were found between the "traffic non-exhaust", "secondary  
386 nitrates", "ISW fugitive", "ISW sintering stack" and "electric steel plant" sources contribution  
387 and OP-DTT values. The three industrial sources are known to emit metals with redox  
388 properties (E-PRTR, 2011; Hleis et al., 2013; Kfoury et al., 2016) able to potentiate ROS  
389 overproduction. "Secondary sulfates" and "heavy fuel oil combustion" were moderately  
390 correlated ( $0.4 \leq r < 0.6$ ) with only OP-DTTv. Considering the mass normalized data (Table  
391 S3 in supplementary materials), OP-DTTm appeared strongly correlated with "ISW fugitive",  
392 moderately correlated with "traffic non exhaust", "heavy fuel oil combustion", "crustal" and  
393 "ISW sintering stack" while no correlation was found with secondary nitrates and only poor  
394 correlation with secondary sulfates ( $r=0.35$ ). Except for "aged sea-salts" ( $r = -0.67$ ) and  
395 "traffic non-exhaust" ( $r = 0.66$ ), OP-AAv only showed, at best, moderate correlations with the  
396 contribution of each of the 11 sources. Interestingly "sea-salts" and "aged sea-salts" sources  
397 show negative correlations with OP-DTTv and OP-AAv values. However, it would be wrong  
398 to conclude that emissions related to these sources are able to decrease the OP values. Indeed,  
399 in the urban coastal area under study, high marine contributions are associated with high  
400 speed winds and favorable condition of dispersion (Ledoux et al., 2006). Consequently, when  
401 the marine origin is predominant, the  $PM_{2.5}$  concentration tends to be relatively low (Figure  
402 S3 and Figure S4) and metal concentration values as well, which could explain the low OP  
403 values. Finally, no significant correlation was found with the "crustal" source suggesting that  
404 this latter does not significantly contribute to the OP values.

405

406 2.3.2. Principal Component Analysis

407 Unlike Spearman correlation which tests the correlation between pairs of variables, the  
408 PCA is a multivariate analysis. It also allows to evidence discrete relationships between  
409 variables that will be regrouped as components. PCA was applied to the composition data of  
410 the 57 PM<sub>2.5</sub> samples for the 29 studied species concentration. The source contributions and  
411 OP values were considered as supplementary variables.

412 The 5 first obtained axes explain 71.7% of the data variability. As OP-AAv and OP-  
413 DTTv showed only significant correlation coefficients with the two first principal  
414 components, the focus was only done on these latter (Figure 1 and Table S2). The variable  
415 factor map of the two major axes which represent together 47.1% of the total variance is  
416 presented in Figure 1c. Axis 1 is highly positively associated with metals (from high to low r  
417 value with  $r > 0.6$ : Bi, K, Rb, Ag, Sn, As, Fe, Al, Ti, Pb, Mn, Ba, Co, TC and Ni) and  
418 negatively associated with Na. So the first axis evidenced that several metals are correlated  
419 and that when a concentration is high for one these elements, all the concentrations tends to  
420 be also high for the others. From lower to higher values, axis 1 makes the distinction between  
421 the typical sea components and the typical metals emitted by anthropogenic and industrial  
422 activities. NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and TC are negatively correlated with the second axis while Na,  
423 Sr, Ca and Mg are positively correlated. Hence, the second axis makes the distinction between  
424 the typical sea components (positive part of the axis) and the SIA (negative part of the axis).  
425 In the region where the study takes place, SIA are mainly associated with winds blowing from  
426 the East (continent) and long range transport while marine aerosol are mainly originates from  
427 the North and western direction. When the marine contribution is high, the secondary aerosol  
428 contribution tends to be low (Figure S3). This explains why SIA are placed against sea-salts  
429 components on the second axis. NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and TC contribute the most to the PM<sub>2.5</sub>  
430 mass, and a strong correlation ( $r = -0.70$ ) was found between the PM<sub>2.5</sub> concentration and the  
431 second axis.

432 OP-DTTv was very strongly correlated ( $r = 0.84$ ) with the first axis as a consequence  
433 of the clear relationships between DTT test values and metal concentrations while OP-AAv  
434 appeared only moderately anticorrelated ( $r = -0.48$ ) with the second axis. Considering now  
435 both dimensions but only 47.1% of the data variability, OP-AAv was related to the  
436 "secondary nitrates", "secondary sulfates" and "combustion 2" (road traffic and biomass  
437 combustion) sources. OP-AAv was also very strongly anticorrelated with "sea-salts" and  
438 "aged sea-salts" sources. This result was not so well evidenced considering the whole data  
439 variability by studying the correlation coefficient. Then for OP-DTTv, PCA findings were  
440 mixed as it was only correlated with axis 1. Considering axes 1 and 2, only one clear  
441 relationship appeared with the ISW sintering stack while several ones were evidenced from  
442 the correlation coefficient study. A deepest investigation will be done hereafter.

443

#### 444 2.4. OP values and relationship with local and distant sources

445 Concentration roses and bivariate polar plots were used to study the link between OP  
446 observed values and local sources contribution while CWT was used to search for regional  
447 influences.

448

##### 449 2.4.1. Mass-normalized and volume-normalized OP

450 Roses representing OP value versus wind direction and bivariate polar plots  
451 considering OP expressed in the two units (per  $m^3$  or per  $\mu g PM_{2.5}$ ) are given in Figure 2.  
452 OP-AA and OP-DTT did not exhibit exactly the same behavior regarding the wind direction.  
453 The maximum for mass-normalized OP-AAm and OP-DTTm was obtained when the wind  
454 blew from the northwest (NW) wind sector, while the maximum for volume-normalized OP  
455 was related to the southeast (SE) wind direction for OP-AAm, and SE, west (W) and  
456 northeast (NE) direction for OP-DTTm. The W-NW and the SE sectors correspond to the

457 industrial park including the ISW and the urban sector, respectively, while in the northeast  
458 direction is located the electric steel plant.

459 Especially when considering the OP-AA values, 1  $\mu\text{g}$  of PM coming from the wind  
460 sector including the industrial park showed the maximum intrinsic oxidative potential  
461 compared to an equivalent mass of PM sampled from the others wind sectors. By normalizing  
462 OP values to the air volume, this sector no longer exhibited the highest value. This is  
463 important information derived from this study. Considering 1  $\text{m}^3$  of air that people breathe,  
464 emissions from the industrial park do not appear as the most impacting on OP values. At our  
465 study site, emissions from the SE sector corresponding locally to the urban sector or long  
466 range transport influence (as it will be seen in section 2.4.3) appear to be the most  
467 problematic, considering OP-AAv values. However, the OP-DTTv values showed not only a  
468 maximum under the urban sector but also when the winds blew from the west direction  
469 suggesting a high OP-DTTv potential for a source located in the industrial park.

470

#### 471 2.4.2. OP relationships with the 11 identified CW-NMF sources

472 Figure 3 represents the volume-normalized source contributions bivariate polar plots  
473 of the 11 identified  $\text{PM}_{2.5}$  emission sources in addition to the one for  $\text{PM}_{2.5}$  concentrations, for  
474 comparison with the corresponding OP-DTTv and OP-AAv one. The use of bivariate polar  
475 plots gives an additional strong criterion for validating the relationships between OP values  
476 and PM source contribution evidenced with the Spearman correlation and PCA mathematical  
477 tools. By using this, OP and source contribution values are distributed versus the wind  
478 direction and wind speed. The geographical position of the sources as well the characteristics  
479 of the emission (ie: resuspension or blowing back of chimney emission to ground level under  
480 the effect of wind speed) are directly and indirectly considered when bivariate polar plots are  
481 investigated (Carslaw et al., 2006; Ledoux et al., 2018). It makes possible to deepen

482 investigation and strengthen conclusions regarding relationships between OP values and  
483 source contributions.

484         Clearly OP-AAv showed a pattern similar to that of PM<sub>2.5</sub> and road traffic and biomass  
485 combustion ("combustion 2"). HULIS could be the reason of the relationship between OP and  
486 combustion sources as they are highly redox active species known to participate to the OP  
487 values and mainly emitted by combustion processes (Dou et al., 2015; Ma et al., 2018). This  
488 observation is also consistent with the one of Yu et al. (2019), who found that vehicle  
489 emissions (traffic exhaust and non-exhaust as a whole) highly contribute to ROS production.  
490 Based on the polar plot patterns, traffic non-exhaust could also participate to OP-AAv but the  
491 absence of correlation between both would suggest to reject the idea. These first observations  
492 are in agreement with the PCA findings (Figure 1). However, PCA was suggesting a  
493 relationship between OP-AAv and the secondary inorganic aerosols for 47.1% of the data.  
494 The bivariate polar plots tend to discredit this as the corresponding plots are quite different  
495 (Figure 2 and Figure 3). Except with the PM<sub>2.5</sub>, combustion 2 and possibly traffic non-exhaust  
496 source, OP-AAv pattern do not show any similarity with other sources, which could be  
497 contradictory with partial conclusion done from the correlation coefficient study. This tends  
498 to demonstrate that investigations using only the correlation coefficient between sources  
499 contribution (or species concentrations) and OP are not enough to conclude about  
500 relationships.

501         Unlike OP-AAv, OP-DTTv bivariate polar plot showed similarities and compatibilities  
502 with several sources. Between them, the ISW sintering stack seems to be responsible for the  
503 spot observed in the west direction at a wind speed close to 5 m·s<sup>-1</sup>. In the same direction, the  
504 ISW fugitive and the heavy-fuel oil combustion source are also possible contributors. In  
505 addition, in the east-northeast wind direction, the OP-DTTv concentration spot overlap the  
506 one observed for the electric steel plant making emissions relate to this source another

507 OP-DDTv influencing factor. Relatively high values observed in the SE quarter could be the  
508 fact of combustion 2 or traffic non-exhaust sources. In this case, observations matched quite  
509 well those done from PCA study but also contradict again some conclusions done using the  
510 correlation coefficient. For example strong correlation was found between secondary nitrates  
511 and OP-DDTv ( $r = 0.67$ ,  $p < 0.001$ ), but their respective bivariate polar plots could challenge  
512 it. Finally, our observation made possible to definitely dismiss the contribution of the sea-  
513 salts, aged sea-salts, crustal and secondary sulfates to the OP values.

514 Up to our knowledge, this is the first time that bivariate polar plots of OP and sources  
515 contributions were compared to study and validate the influence of source emission on OP  
516 values. In most of the published works, only correlation coefficients are used to conclude on  
517 relationships between OP and species /sources. This could be inadequate in light of our results  
518 which clearly demonstrate the interest to use bivariate polar plots as additional information.

519

#### 520 2.4.3. Regional influence

521 The computing of OP-AAV and OP-DDTv with the air-mass back trajectories using the CWT  
522 method allowed to study the impact of regional emissions on OP values (Figure 4). Regions  
523 contributing the most to OP-DDTv are inland, including the upper part of the western  
524 continental Europe notably France, Belgium, Germany and Poland. For OP-AAV, the main  
525 hotspot is located in Belgium and the center of Germany. Long range transport from these  
526 source regions located east to the study site could also explain the high OP values locally  
527 observed for eastern and southeastern wind on the bivariate polar plots. The North-Sea, the  
528 English Channel and the coastal part of the Atlantic Ocean appears also as source region  
529 especially for the OP-DDTv. This is in agreement with the relationships previously found  
530 between OP-DDTv and heavy fuel oil combustion source and the CWT obtained for the latter  
531 is also consistent with this. To be mentioned here that the English Channel and the North Sea

532 are among the most used shipping routes for marine transportation (EEA, 2013b; Ledoux et  
533 al., 2018).

534 CWT results for secondary nitrates evidenced mainly Belgium and southern part of  
535 Netherlands as source regions which is consistent with Pay et al. (2010) and Pay et al. (2012)  
536 who identify these countries as important NO<sub>x</sub> emitters. Secondary sulfates were originated  
537 from Belgium, North of Germany and Poland who also showed exceedances of the SO<sub>2</sub> limit  
538 value (EEA, 2012). In both cases, the similarity with the OP-AA<sub>v</sub> and OP-DTT<sub>v</sub> CWT is  
539 poor.

540 The highest concentrations of PM<sub>2.5</sub> were traced back to North of France, Belgium,  
541 Luxembourg, Netherlands and Germany also. This is consistent with the potential source  
542 contribution results obtained by Waked et al. (2018) and Pay et al. (2012) who evidenced  
543 these countries as important source of PM<sub>10</sub> in relation with industrial and shipping related  
544 emissions especially for Belgium and Netherlands. Combustion 2 and traffic non-exhaust  
545 CWT patterns showed higher concentrations on the continent which is totally in agreement  
546 with the definition of the sources. Source regions of biomass and traffic related combustion  
547 traffic-non-exhaust emissions match quite well the OP-DTT<sub>v</sub> and OP-AA<sub>v</sub> CWT confirming  
548 the relationships suggested at a local scale. Eastern Europe, especially Bulgaria, Czech  
549 Republic and Poland, was also identified as an important source of PM in Europe (EEA,  
550 2013a). Nevertheless, we were unable to observe their influence as there were no air masses  
551 coming from these regions during the sampling period.

552

## 553 Conclusion

554 PM<sub>2.5</sub> collected in a coastal industrial city in Northern France was responsible for OP  
555 values in the same order of magnitude as those encountered in other world locations. PM<sub>2.5</sub>  
556 concentrations, some PM<sub>2.5</sub> components and PM<sub>2.5</sub> sources were found to be specifically



557 correlated with one of the two tests (AA and DTT). For one of the first time, bivariate polar  
558 plots drawn for OP and source contributions were considered together to investigate their  
559 relationships. Conclusions deduced from correlation coefficient studies and PCA were  
560 challenged after using the OP and source contribution bivariate polar plots suggesting the  
561 importance to use such a methodology. Ascorbic acid assay results appeared clearly linked to  
562 the PM<sub>2.5</sub> concentrations and combustion sources. Dithiothreitol assay was clearly related to  
563 sources emitting metals, in our case ISW diffuse and sintering stack, electric steel plant  
564 emissions, heavy fuel oil combustion and possibly other combustion sources. Sea-salts, aged  
565 sea-salts, crustal, secondary sulfates and secondary nitrates sources do not seem to contribute  
566 to OP values. Some high OP values source regions have also been identified (Germany,  
567 Belgium and Netherlands) showing that long range transport is also a parameter to consider  
568 when studying OP of particulate matter.

569

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- 582 Anenberg, S.C., Achakulwisut, P., Brauer, M., Moran, D., Apte, J.S., Henze, D.K., 2019.  
583 Particulate matter-attributable mortality and relationships with carbon dioxide in 250  
584 urban areas worldwide. *Sci Rep* 9, 11552. (10.1038/s41598-019-48057-9)
- 585 Ayres, J.G., Borm, P., Cassee, F.R., Castranova, V., Donaldson, K., Ghio, A., Harrison, R.M.,  
586 Hider, R., Kelly, F., Kooter, I.M., Marano, F., Maynard, R.L., Mudway, I., Nel, A.,  
587 Sioutas, C., Smith, S., Baeza-Squiban, A., Cho, A., Duggan, S., Froines, J., 2008.  
588 Evaluating the toxicity of airborne particulate matter and nanoparticles by measuring  
589 oxidative stress potential--a workshop report and consensus statement. *Inhal. Toxicol.*  
590 20, 75-99. (10.1080/08958370701665517)
- 591 Badran, G., Verdin, A., Grare, C., Abbas, I., Achour, D., Ledoux, F., Roumié, M., Cazier, F.,  
592 Courcot, D., Lo Guidice, J.-M., Garçon, G., 2020. Toxicological appraisal of the  
593 chemical fractions of ambient fine (PM<sub>2.5-0.3</sub>) and quasi-ultrafine (PM<sub>0.3</sub>) particles in  
594 human bronchial epithelial BEAS-2B cells. *Environ. Pollut.* 263, 114620.  
595 (10.1016/j.envpol.2020.114620)
- 596 Bates, J.T., Fang, T., Verma, V., Zeng, L., Weber, R.J., Tolbert, P.E., Abrams, J.Y., Sarnat,  
597 S.E., Klein, M., Mulholland, J.A., Russell, A.G., 2019. Review of Acellular Assays of  
598 Ambient Particulate Matter Oxidative Potential: Methods and Relationships with  
599 Composition, Sources, and Health Effects. *Environ. Sci. Technol.* 53, 4003-4019.  
600 (10.1021/acs.est.8b03430)
- 601 Bode, A.M., Cunningham, L., Rose, R.C., 1990. Spontaneous decay of oxidized ascorbic acid  
602 (dehydro-L-ascorbic acid) evaluated by high-pressure liquid chromatography. *Clin.*  
603 *Chem.* 36, 1807-1809.
- 604 Bontinck, A., Maes, T., Joos, G., 2020. Asthma and air pollution: recent insights in  
605 pathogenesis and clinical implications. *Curr. Opin. Pulm. Med.* 26, 10-19.  
606 (10.1097/mcp.0000000000000644)
- 607 Borm, P.J.A., Kelly, F., Künzli, N., Schins, R.P.F., Donaldson, K., 2007. Oxidant generation  
608 by particulate matter: from biologically effective dose to a promising, novel metric.  
609 *Occup. Environ. Med.* 64, 73-74. (10.1136/oem.2006.029090)
- 610 Burnett, R., Chen, H., Szyszkowicz, M., Fann, N., Hubbell, B., Pope, C.A., Apte, J.S., Brauer,  
611 M., Cohen, A., Weichenthal, S., Coggins, J., Di, Q., Brunekreef, B., Frostad, J., Lim,  
612 S.S., Kan, H., Walker, K.D., Thurston, G.D., Hayes, R.B., Lim, C.C., Turner, M.C.,  
613 Jerrett, M., Krewski, D., Gapstur, S.M., Diver, W.R., Ostro, B., Goldberg, D., Crouse,  
614 D.L., Martin, R.V., Peters, P., Pinault, L., Tjepkema, M., van Donkelaar, A.,  
615 Villeneuve, P.J., Miller, A.B., Yin, P., Zhou, M., Wang, L., Janssen, N.A.H., Marra, M.,  
616 Atkinson, R.W., Tsang, H., Quoc Thach, T., Cannon, J.B., Allen, R.T., Hart, J.E.,  
617 Laden, F., Cesaroni, G., Forastiere, F., Weinmayr, G., Jaensch, A., Nagel, G., Concin,  
618 H., Spadaro, J.V., 2018. Global estimates of mortality associated with long-term  
619 exposure to outdoor fine particulate matter. *Proceedings of the National Academy of*  
620 *Sciences* 115, 9592. (10.1073/pnas.1803222115)
- 621 Caboche, J., Esperanza, P., Bruno, M., Alleman, L.Y., 2011. Development of an in vitro  
622 method to estimate lung bioaccessibility of metals from atmospheric particles. *Journal*  
623 *of environmental monitoring: JEM* 13, 621-630. (10.1039/c0em00439a)
- 624 Calas, A., Uzu, G., Besombes, J.L., Martins, J.M.F., Redaelli, M., Weber, S., Charron, A.,  
625 Albinet, A., Chevrier, F., Brulfert, G., Mesbah, B., Favez, O., Jaffrezo, J.L., 2019.  
626 Seasonal variations and chemical predictors of oxidative potential (OP) of particulate  
627 matter (PM), for seven urban French sites. *Atmosphere* 10. (10.3390/atmos10110698)
- 628 Calas, A., Uzu, G., Martins, J.M.F., Voisin, D., Spadini, L., Lacroix, T., Jaffrezo, J.L., 2017.  
629 The importance of simulated lung fluid (SLF) extractions for a more relevant evaluation

630 of the oxidative potential of particulate matter. *Sci. Rep.* 7, 11617. (10.1038/s41598-  
631 017-11979-3)

632 Carslaw, D., 2019. The openair manual - open-source tools for analysing air pollution data.  
633 Manual for version 2.6-6, University of York, p. 229.

634 Carslaw, D., Ropkins, K., 2012. openair - An R package for air quality data analysis. *Environ.*  
635 *Modell. Softw.* 27-28, 52-61. (10.1016/j.envsoft.2011.09.008)

636 Carslaw, D.C., Beevers, S.D., Ropkins, K., Bell, M.C., 2006. Detecting and quantifying  
637 aircraft and other on-airport contributions to ambient nitrogen oxides in the vicinity of a  
638 large international airport. *Atmos. Environ.* 40, 5424-5434.  
639 (<https://doi.org/10.1016/j.atmosenv.2006.04.062>)

640 Cesari, D., Merico, E., Grasso, F.M., Decesari, S., Belosi, F., Manarini, F., de Nuntii, P.,  
641 Rinaldi, M., Volpi, F., Gambaro, A., Morabito, E., Contini, D., 2019. Source  
642 apportionment of PM<sub>2.5</sub> and of its oxidative potential in an industrial suburban site in  
643 South Italy. *Atmosphere* 10. (10.3390/ATMOS10120758)

644 Charrier, J.G., Anastasio, C., 2012. On dithiothreitol (DTT) as a measure of oxidative  
645 potential for ambient particles: evidence for the importance of soluble transition metals.  
646 *Atmos. Chem. Phys.* 12, 11317-11350. (10.5194/acpd-12-11317-2012)

647 Cheng, I., Zhang, L., Blanchard, P., Dalziel, J., Tordon, R., 2013. Concentration-weighted  
648 trajectory approach to identifying potential sources of speciated atmospheric mercury at  
649 an urban coastal site in Nova Scotia, Canada. *Atmos. Chem. Phys.* 13, 6031-6048.  
650 (10.5194/acp-13-6031-2013)

651 Chirizzi, D., Cesari, D., Guascito, M., Dinoi, A., Giotta, L., Donateo, A., Contini, D., 2017.  
652 Influence of Saharan dust outbreaks and carbon content on oxidative potential of water-  
653 soluble fractions of PM<sub>2.5</sub> and PM<sub>10</sub>. *Atmos. Environ.* 163.  
654 (10.1016/j.atmosenv.2017.05.021)

655 Cho, A.K., Sioutas, C., Miguel, A.H., Kumagai, Y., Schmitz, D.A., Singh, M., Eiguren-  
656 Fernandez, A., Froines, J.R., 2005. Redox activity of airborne particulate matter at  
657 different sites in the Los Angeles Basin. *Environ. Res.* 99, 40-47.  
658 (10.1016/j.envres.2005.01.003)

659 Colombo, C., Monhemius, A.J., Plant, J.A., 2008. Platinum, palladium and rhodium release  
660 from vehicle exhaust catalysts and road dust exposed to simulated lung fluids.  
661 *Ecotoxicol. Environ. Saf.* 71, 722-730. (10.1016/j.ecoenv.2007.11.011)

662 Crobeddu, B., Aragao-Santiago, L., Bui, L.-C., Boland, S., Baeza Squiban, A., 2017.  
663 Oxidative potential of particulate matter 2.5 as predictive indicator of cellular stress.  
664 *Environ. Pollut.* 230, 125-133. (<https://doi.org/10.1016/j.envpol.2017.06.051>)

665 Damodaran, S., 1985. Estimation of disulfide bonds using 2-nitro-5-thiosulfobenzoic acid:  
666 limitations. *Anal. Biochem.* 145, 200-204.

667 Dimitriou, K., Remoundaki, E., Mantas, E., Kassomenos, P., 2015. Spatial distribution of  
668 source areas of PM<sub>2.5</sub> by Concentration Weighted Trajectory (CWT) model applied in  
669 PM<sub>2.5</sub> concentration and composition data. *Atmos. Environ.* 116, 138-145.  
670 (<https://doi.org/10.1016/j.atmosenv.2015.06.021>)

671 Dou, J., Lin, P., Kuang, B.-Y., Yu, J.Z., 2015. Reactive Oxygen Species Production Mediated  
672 by Humic-like Substances in Atmospheric Aerosols: Enhancement Effects by Pyridine,  
673 Imidazole, and Their Derivatives. *Environ. Sci. Technol.* 49, 6457-6465.  
674 (10.1021/es5059378)

675 E-PRTR, 2011. The European Pollutant Release and Transfer Register. European  
676 Environment Agency. <http://prtr.ec.europa.eu>. Assessed June 09, 2020.

677 EEA, 2012. European Environmental Agency - Air Quality in Europe - Report No 4/2012.  
678 Office for Official Publications of the European Union, 2012, Luxembourg, 108 p.

679 EEA, 2013a. European Environmental Agency - Air Quality in Europe - 2013 Report.  
680 Technical Report No 09/2013. EEA, Copenhagen. Publications Office of the European  
681 Union, 112 p.

682 EEA, 2013b. European Environmental Agency. The impact of international shipping on  
683 European air quality and climate forcing. Technical report No 4/2013. Publications  
684 Office of the European Union, 2013, Luxembourg, 84 p.

685 Eyer, P., Worek, F., Kiderlen, D., Sinko, G., Stuglin, A., Simeon-Rudolf, V., Reiner, E., 2003.  
686 Molar absorption coefficients for the reduced Ellman reagent: reassessment. *Anal.*  
687 *Biochem.* 312, 224-227.

688 Fang, T., Verma, V., Bates, J.T., Abrams, J., Klein, M., Strickland, M.J., Sarnat, S.E., Chang,  
689 H.H., Mulholland, J.A., Tolbert, P.E., Russell, A.G., Weber, R.J., 2016. Oxidative  
690 potential of ambient water-soluble PM<sub>2.5</sub> in the southeastern United States: contrasts in  
691 sources and health associations between ascorbic acid (AA) and dithiothreitol (DTT)  
692 assays. *Atmos. Chem. Phys.* 16, 3865-3879. (<https://doi.org/10.5194/acp-16-3865-2016>)

693 Gao, D., Godri Pollitt, K.J., Mulholland, J.A., Russell, A.G., Weber, R.J., 2020a.  
694 Characterization and comparison of PM<sub>2.5</sub> oxidative potential assessed by two acellular  
695 assays. *Atmos. Chem. Phys.* 20, 5197-5210. (10.5194/acp-20-5197-2020)

696 Gao, D., Mulholland, J.A., Russell, A.G., Weber, R.J., 2020b. Characterization of water-  
697 insoluble oxidative potential of PM<sub>2.5</sub> using the dithiothreitol assay. *Atmos. Environ.*  
698 224. (10.1016/j.atmosenv.2020.117327)

699 Gualtieri, M., Ledoux, F., Verdin, A., Billet, S., Martin, P.J., Courcot, D., 2017. Particulate  
700 matter physico-chemical characterization and *in vitro* toxicological effects, Chapter 12,  
701 in: Kumar, D.P. (Ed.), *Airborne Particles: Origin, Emissions and Health Impacts*. Nova  
702 Science Publisher, pp. 241-292.

703 Hedberg, Y., Gustafsson, J., Karlsson, H.L., Möller, L., Odnevall Wallinder, I., 2010.  
704 Bioaccessibility, bioavailability and toxicity of commercially relevant iron- and  
705 chromium-based particles: in vitro studies with an inhalation perspective. *Particle and*  
706 *fibre toxicology* 7, 23-23. (10.1186/1743-8977-7-23)

707 Hendryx, M., Luo, J., Chojenta, C., Byles, J.E., 2019. Air pollution exposures from multiple  
708 point sources and risk of incident chronic obstructive pulmonary disease (COPD) and  
709 asthma. *Environ. Res.* 179, 108783. (10.1016/j.envres.2019.108783)

710 Hernandez-Pellon, A., Nischkauer, W., Limbeck, A., Fernandez-Olmo, I., 2018. Metal(loid)  
711 bioaccessibility and inhalation risk assessment: A comparison between an urban and an  
712 industrial area. *Environ. Res.* 165, 140-149. (10.1016/j.envres.2018.04.014)

713 Hleis, D., Fernández-Olmo, I., Ledoux, F., Kfoury, A., Courcot, L., Desmots, T., Courcot,  
714 D., 2013. Chemical profile identification of fugitive and confined particle emissions  
715 from an integrated iron and steelmaking plant. *J. Hazard. Mater.* 250-251, 246-255.  
716 (10.1016/j.jhazmat.2013.01.080)

717 Janssen, N.A.H., Yang, A., Strak, M., Steenhof, M., Hellack, B., Gerlofs-Nijland, M.E.,  
718 Kuhlbusch, T., Kelly, F., Harrison, R., Brunekreef, B., Hoek, G., Cassee, F., 2014.  
719 Oxidative potential of particulate matter collected at sites with different source  
720 characteristics. *Sci. Total Environ.* 472, 572-581.  
721 (<http://dx.doi.org/10.1016/j.scitotenv.2013.11.099>)

722 Jedynska, A., Hoek, G., Wang, M., Yang, A., Eeftens, M., Cyrus, J., Keuken, M., Ampe, C.,  
723 Beelen, R., Cesaroni, G., Forastiere, F., Cirach, M., de Hoogh, K., De Nazelle, A.,  
724 Nystad, W., Akhlaghi, H.M., Declercq, C., Stempfelet, M., Eriksen, K.T.,  
725 Dimakopoulou, K., Lanki, T., Meliefste, K., Nieuwenhuijsen, M., Yli-Tuomi, T.,  
726 Raaschou-Nielsen, O., Janssen, N.A.H., Brunekreef, B., Kooter, I.M., 2017. Spatial  
727 variations and development of land use regression models of oxidative potential in ten

728 European study areas. *Atmos. Environ.* 150, 24-32.  
729 (<https://doi.org/10.1016/j.atmosenv.2016.11.029>)

730 Jia, Y.Y., Wang, Q., Liu, T., 2017. Toxicity Research of PM(2.5) Compositions In Vitro. *Int.*  
731 *J. Environ. Res. Public. Health* 14, 232. (10.3390/ijerph14030232)

732 Jiang, H., Ahmed, C.M.S., Zhao, Z., Chen, J.Y., Zhang, H., Canchola, A., Lin, Y.H., 2020.  
733 Role of functional groups in reaction kinetics of dithiothreitol with secondary organic  
734 aerosols. *Environ. Pollut.* 263. (10.1016/j.envpol.2020.114402)

735 Jovanovic, M.V., Savic, J.Z., Salimi, F., Stevanovic, S., Brown, R.A., Jovasevic-Stojanovic,  
736 M., Manojlovic, D., Bartonova, A., Bottle, S., Ristovski, Z.D., 2019. Measurements of  
737 oxidative potential of particulate matter at belgrade tunnel; comparison of BPEAnit,  
738 DTT and DCFH assays. *Int. J. Environ. Res. Public. Health* 16.  
739 (10.3390/ijerph16244906)

740 Jung, C.-H., Wells, W.W., 1998. Spontaneous Conversion of l-Dehydroascorbic Acid to  
741 Ascorbic Acid and l-Erythroascorbic Acid. *Arch. Biochem. Biophys.* 355, 9-14.  
742 (10.1006/abbi.1998.0713)

743 Kelly, F.J., Fussell, J.C., 2012. Size, source and chemical composition as determinants of  
744 toxicity attributable to ambient particulate matter. *Atmos. Environ.* 60, 504-526.  
745 (<https://doi.org/10.1016/j.atmosenv.2012.06.039>)

746 Kfoury, A., Ledoux, F., Roche, C., Delmaire, G., Roussel, G., Courcot, D., 2016. PM<sub>2.5</sub>  
747 source apportionment in a French urban coastal site under steelworks emission  
748 influences using Constrained Non-Negative Matrix Factorization receptor model. *J.*  
749 *Environ. Sci. (China)* 40, 114-128. (10.1016/j.jes.2015.10.025)

750 Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T., Shimojo, N., 2002.  
751 Oxidation of Proximal Protein Sulfhydryls by Phenanthraquinone, a Component of  
752 Diesel Exhaust Particles. *Chem. Res. Toxicol.* 15, 483-489. (10.1021/tx0100993)

753 Lê, S., Josse, J., Husson, F., 2008. FactoMineR: An R Package for Multivariate Analysis. *J.*  
754 *Stat. Softw.* 25, 1-18. (10.18637/jss.v025.i01)

755 Ledoux, F., Courcot, L., Courcot, D., Aboukaïs, A., Puskarić, E., 2006. A summer and winter  
756 apportionment of particulate matter at urban and rural areas in Northern France. *Atmos.*  
757 *Res.* 82, 633-642. (<http://dx.doi.org/10.1016/j.atmosres.2006.02.019>)

758 Ledoux, F., Kfoury, A., Delmaire, G., Roussel, G., El Zein, A., Courcot, D., 2017.  
759 Contributions of local and regional anthropogenic sources of metals in PM<sub>2.5</sub> at an urban  
760 site in Northern France. *Chemosphere* 181, 713-724.  
761 (<https://doi.org/10.1016/j.chemosphere.2017.04.128>)

762 Ledoux, F., Roche, C., Cazier, F., Beaugard, C., Courcot, D., 2018. Influence of ship  
763 emissions on NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub> and PM concentrations in a North-Sea harbor in France.  
764 *Journal of Environmental Sciences* 71, 56-66.  
765 (<https://doi.org/10.1016/j.jes.2018.03.030>)

766 Lelieveld, J., Pozzer, A., Pöschl, U., Fnais, M., Haines, A., Münzel, T., 2020. Loss of life  
767 expectancy from air pollution compared to other risk factors: a worldwide perspective.  
768 *Cardiovasc. Res.* (10.1093/cvr/cvaa025)

769 Li, J., Sun, S., Tang, R., Qiu, H., Huang, Q., Mason, T.G., Tian, L., 2016. Major air pollutants  
770 and risk of COPD exacerbations: a systematic review and meta-analysis. *Int. J. Chron.*  
771 *Obstruct. Pulmon. Dis.* 11, 3079-3091. (10.2147/copd.s122282)

772 Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wang, M., Oberley, T.,  
773 Froines, J., Nel, A., 2003. Ultrafine particulate pollutants induce oxidative stress and  
774 mitochondrial damage. *Environ. Health Perspect.* 111, 455-460. (10.1289/ehp.6000)

775 Lin, M., Yu, J.Z., 2019. Effect of metal-organic interactions on the oxidative potential of  
776 mixtures of atmospheric humic-like substances and copper/manganese as investigated

777 by the dithiothreitol assay. *Sci. Total Environ.* 697, 134012.  
778 (<https://doi.org/10.1016/j.scitotenv.2019.134012>)

779 Lippmann, M., 2014. Toxicological and epidemiological studies of cardiovascular effects of  
780 ambient air fine particulate matter (PM<sub>2.5</sub>) and its chemical components: Coherence and  
781 public health implications. *Crit. Rev. Toxicol.* 44, 299-347.  
782 (10.3109/10408444.2013.861796)

783 Ma, Y., Cheng, Y., Qiu, X., Cao, G., Fang, Y., Wang, J., Zhu, T., Yu, J., Hu, D., 2018.  
784 Sources and oxidative potential of water-soluble humic-like substances (HULIS<sub>WS</sub>) in  
785 fine particulate matter (PM<sub>2.5</sub>) in Beijing. *Atmos. Chem. Phys.* 18, 5607-5617.  
786 (<https://doi.org/10.5194/acp-18-5607-2018>)

787 Marques, M.R.C., Loebenberg, R., Almukainzi, M., 2011. Simulated Biological Fluids with  
788 Possible Application in Dissolution Testing. *Dissolution Technology* 18, 15-28.  
789 (10.14227/DT180311P15)

790 Massamba, V.K., Coppieters, Y., Mercier, G., Collart, P., Levêque, A., 2014. Particle  
791 pollution effects on the risk of cardiovascular diseases. *Ann. Cardiol. Angeiol.* 63, 40-  
792 47. (10.1016/j.ancard.2013.08.017)

793 Mudway, I.S., Stenfors, N., Duggan, S.T., Roxborough, H., Zielinski, H., Marklund, S.L.,  
794 Blomberg, A., Frew, A.J., Sandström, T., Kelly, F.J., 2004. An in vitro and in vivo  
795 investigation of the effects of diesel exhaust on human airway lining fluid antioxidants.  
796 *Arch. Biochem. Biophys.* 423, 200-212. (10.1016/j.abb.2003.12.018)

797 Nel, A., 2005. Air Pollution-Related Illness: Effects of Particles. *Science* 308, 804.

798 Paraskevopoulou, D., Bougiatioti, A., Stavroulas, I., Fang, T., Lianou, M., Liakakou, E.,  
799 Gerasopoulos, E., Weber, R., Nenes, A., Mihalopoulos, N., 2019. Yearlong variability  
800 of oxidative potential of particulate matter in an urban Mediterranean environment.  
801 *Atmos. Environ.* 206, 183-196. (<https://doi.org/10.1016/j.atmosenv.2019.02.027>)

802 Patel, A., Rastogi, N., 2018. Oxidative potential of ambient fine aerosol over a semi-urban  
803 site in the Indo-Gangetic Plain. *Atmos. Environ.* 175, 127-134.  
804 (10.1016/j.atmosenv.2017.12.004)

805 Pay, M.T., Jiménez-Guerrero, P., Baldasano, J.M., 2012. Assessing sensitivity regimes of  
806 secondary inorganic aerosol formation in Europe with the CALIOPE-EU modeling  
807 system. *Atmos. Environ.* 51, 146-164. (<https://doi.org/10.1016/j.atmosenv.2012.01.027>)

808 Pay, M.T., Piot, M., Jorba, O., Gassó, S., Gonçalves, M., Basart, S., Dabdub, D., Jiménez-  
809 Guerrero, P., Baldasano, J.M., 2010. A full year evaluation of the CALIOPE-EU air  
810 quality modeling system over Europe for 2004. *Atmos. Environ.* 44, 3322-3342.  
811 (<https://doi.org/10.1016/j.atmosenv.2010.05.040>)

812 Perrone, M.R., Bertoli, I., Romano, S., Russo, M., Rispoli, G., Pietrogrande, M.C., 2019.  
813 PM<sub>2.5</sub> and PM<sub>10</sub> oxidative potential at a Central Mediterranean Site: Contrasts between  
814 dithiothreitol- and ascorbic acid-measured values in relation with particle size and  
815 chemical composition. *Atmos. Environ.* 210, 143-155.  
816 (10.1016/j.atmosenv.2019.04.047)

817 Pietrogrande, M.C., Bertoli, I., Manarini, F., Russo, M., 2019. Ascorbate assay as a measure  
818 of oxidative potential for ambient particles: Evidence for the importance of cell-free  
819 surrogate lung fluid composition. *Atmos. Environ.* 211, 103-112.  
820 (<https://doi.org/10.1016/j.atmosenv.2019.05.012>)

821 Pietrogrande, M.C., Dalpiaz, C., Dell'Anna, R., Lazzeri, P., Manarini, F., Visentin, M.,  
822 Tonidandel, G., 2018. Chemical composition and oxidative potential of atmospheric  
823 coarse particles at an industrial and urban background site in the alpine region of  
824 northern Italy. *Atmos. Environ.* 191, 340-350. (10.1016/j.atmosenv.2018.08.022)

825 Raaschou-Nielsen, O., Andersen, Z.J., Beelen, R., Samoli, E., Stafoggia, M., Weinmayr, G.,  
826 Hoffmann, B., Fischer, P., Nieuwenhuijsen, M.J., Brunekreef, B., Xun, W.W.,

827 Katsouyanni, K., Dimakopoulou, K., Sommar, J., Forsberg, B., Modig, L., Oudin, A.,  
828 Oftedal, B., Schwarze, P.E., Nafstad, P., De Faire, U., Pedersen, N.L., Ostenson, C.G.,  
829 Fratiglioni, L., Penell, J., Korek, M., Pershagen, G., Eriksen, K.T., Sorensen, M.,  
830 Tjonneland, A., Ellermann, T., Eeftens, M., Peeters, P.H., Meliefste, K., Wang, M.,  
831 Bueno-de-Mesquita, B., Key, T.J., de Hoogh, K., Concin, H., Nagel, G., Vilier, A.,  
832 Gioni, S., Krogh, V., Tsai, M.Y., Ricceri, F., Sacerdote, C., Galassi, C., Migliore, E.,  
833 Ranzi, A., Cesaroni, G., Badaloni, C., Forastiere, F., Tamayo, I., Amiano, P.,  
834 Dorronsoro, M., Trichopoulou, A., Bamia, C., Vineis, P., Hoek, G., 2013. Air pollution  
835 and lung cancer incidence in 17 European cohorts: prospective analyses from the  
836 European Study of Cohorts for Air Pollution Effects (ESCAPE). *Lancet Oncol.* 14, 813-  
837 822. (10.1016/S1470-2045(13)70279-1)

838 Rolph, G., Stein, A., Stunder, B., 2017. Real-time Environmental Applications and Display  
839 sYstem: READY. *Environ. Modell. Softw.* 95, 210-228.  
840 (<https://doi.org/10.1016/j.envsoft.2017.06.025>)

841 Sauvain, J.-J., Rossi, M.J., Riediker, M., 2013. Comparison of Three Acellular Tests for  
842 Assessing the Oxidation Potential of Nanomaterials. *Aerosol Sci. Technol.* 47, 218-227.  
843 (10.1080/02786826.2012.742951)

844 Sax, S.N., Zu, K., Goodman, J.E., 2013. Air pollution and lung cancer in Europe. *Lancet*  
845 *Oncol.* 14, e439-e440. (10.1016/s1470-2045(13)70438-8)

846 Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015.  
847 NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bull.*  
848 *Am. Meteorol. Soc.* 96, 2059-2077. (10.1175/bams-d-14-00110.1)

849 Verma, V., Fang, T., Xu, L., Peltier, R.E., Russell, A.G., Ng, N.L., Weber, R.J., 2015.  
850 Organic aerosols associated with the generation of reactive oxygen species (ROS) by  
851 water-soluble PM<sub>2.5</sub>. *Environ. Sci. Technol.* 49, 4646-4656. (10.1021/es505577w)

852 Visentin, M., Pagnoni, A., Sarti, E., Pietrogrande, M.C., 2016. Urban PM<sub>2.5</sub> oxidative  
853 potential: Importance of chemical species and comparison of two spectrophotometric  
854 cell-free assays. *Environ. Pollut.* 219, 72-79.  
855 (<https://doi.org/10.1016/j.envpol.2016.09.047>)

856 Vreeland, H., Weber, R., Bergin, M., Greenwald, R., Golan, R., Russell, A.G., Verma, V.,  
857 Sarnat, J.A., 2017. Oxidative potential of PM<sub>2.5</sub> during Atlanta rush hour: Measurements  
858 of in-vehicle dithiothreitol (DTT) activity. *Atmos. Environ.* 165, 169-178.  
859 (10.1016/j.atmosenv.2017.06.044)

860 Waked, A., Bourin, A., Michoud, V., Perdrix, E., Alleman, L.Y., Sauvage, S., Delaunay, T.,  
861 Vermeesch, S., Petit, J.-E., Riffault, V., 2018. Investigation of the geographical origins  
862 of PM<sub>10</sub> based on long, medium and short-range air mass back-trajectories impacting  
863 Northern France during the period 2009–2013. *Atmos. Environ.* 193, 143-152.  
864 (10.1016/j.atmosenv.2018.08.015)

865 Wang, J., Lin, X., Lu, L., Wu, Y., Zhang, H., Lv, Q., Liu, W., Zhang, Y., Zhuang, S., 2019.  
866 Temporal variation of oxidative potential of water soluble components of ambient PM<sub>2.5</sub>  
867 measured by dithiothreitol (DTT) assay. *Sci. Total Environ.* 649, 969-978.  
868 (10.1016/j.scitotenv.2018.08.375)

869 WHO, 2018. World Health Organization. Fact sheets Ambient (outdoor) air pollution.  
870 [https://www.who.int/news-room/fact-sheets/detail/ambient-\(outdoor\)-air-quality-and-](https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health)  
871 [health](https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health) accessed the 10th of June 2020.

872 Wragg, J., Klinck, B., 2007. The bioaccessibility of lead from Welsh mine waste using a  
873 respiratory uptake test. *J. Environ. Sci. Health Part A Toxic-Hazard. Subst. Environ.*  
874 *Eng.* 42, 1223-1231. (10.1080/10934520701436054)

875 Yang, A., Jedynska, A., Hellack, B., Kooter, I., Hoek, G., Brunekreef, B., Kuhlbusch, T.A.J.,  
876 Cassee, F.R., Janssen, N.A.H., 2014. Measurement of the oxidative potential of PM<sub>2.5</sub>

877 and its constituents: The effect of extraction solvent and filter type. *Atmos. Environ.* 83,  
878 35-42. (<https://doi.org/10.1016/j.atmosenv.2013.10.049>)  
879 Yu, S., Liu, W., Xu, Y., Yi, K., Zhou, M., Tao, S., Liu, W., 2019. Characteristics and  
880 oxidative potential of atmospheric PM<sub>2.5</sub> in Beijing: Source apportionment and seasonal  
881 variation. *Sci. Total Environ.* 650, 277-287. (10.1016/j.scitotenv.2018.09.021)  
882 Zielinski, H., Mudway, I.S., Bérubé, K.A., Murphy, S., Richards, R., Kelly, F.J., 1999.  
883 Modeling the interactions of particulates with epithelial lining fluid antioxidants. *Am. J.*  
884 *Physiol. Lung Cell. Mol. Physiol.* 277, L719-726. (10.1152/ajplung.1999.277.4.L719)  
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Figure 1: Principal Component Analysis related to the 57 PM<sub>2.5</sub> samples collected in Dunkerque area. Correlation coefficient between the five first axis and (a) PM<sub>2.5</sub> components considered as active variables and, (b) source contribution and oxidative potential values (OP-AAv and OP-DTTv) considered as supplementary variables ; (c) Variables factor map for axis1 – axis2 (in black: active variables ; in blue: supplementary variables).

Figure 2: Volume and mass-normalized OP-DTT (respectively OP-DTTv and OP-DTTm) and OP-AA (respectively OP-AAv and OP-AAm) roses and polar plots at Dunkerque

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Figure 4: CWT on OP-AAv, OP-DTTv, PM<sub>2.5</sub> and sources contributions estimated by the CW-NMF analysis (in  $\mu\text{g}\cdot\text{m}^{-3}$ ).

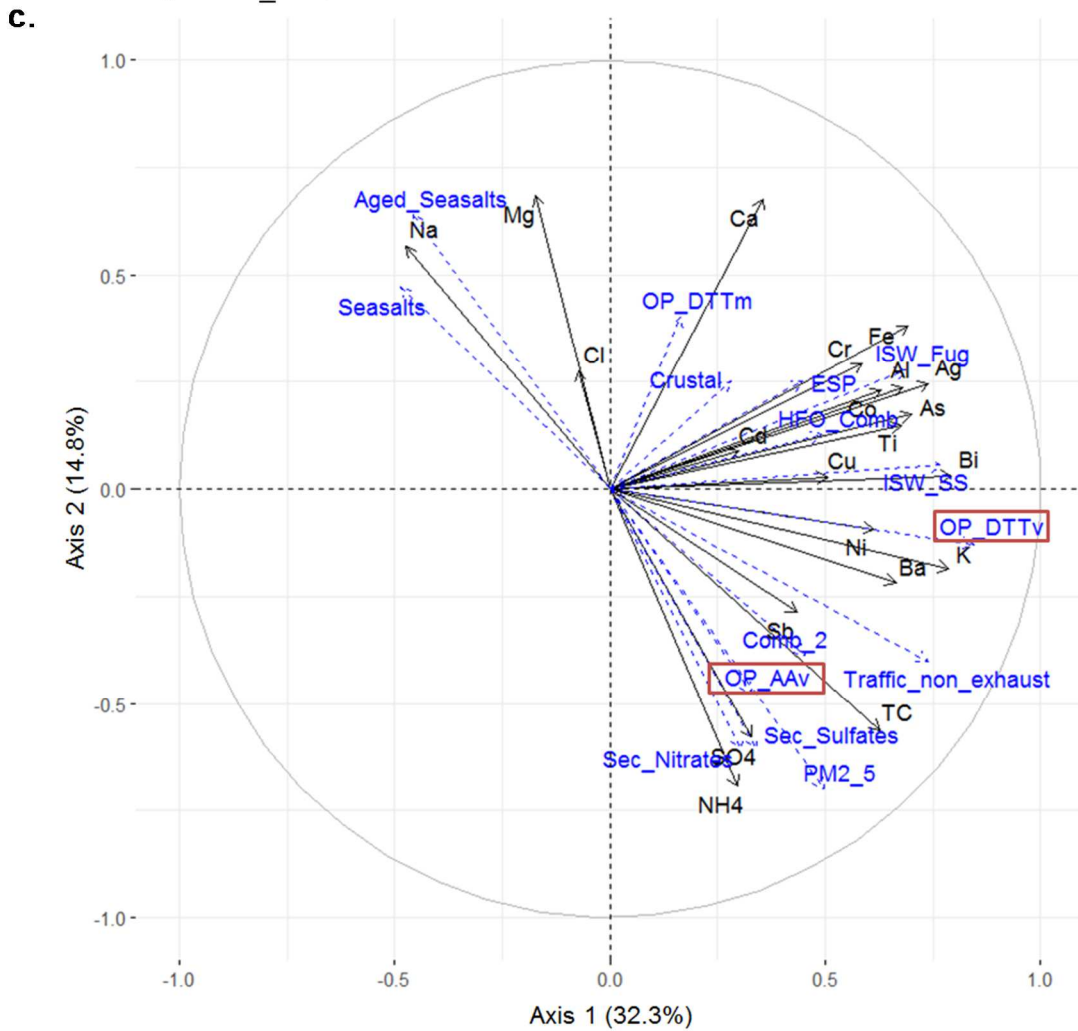
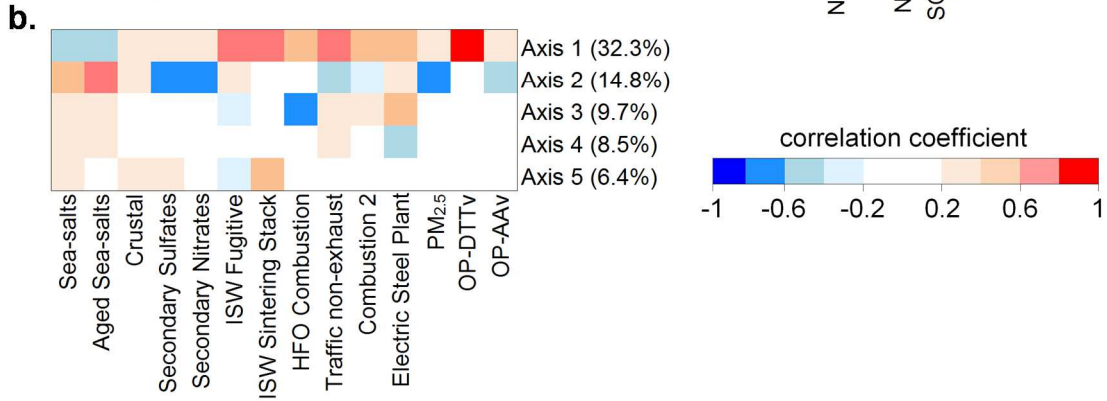
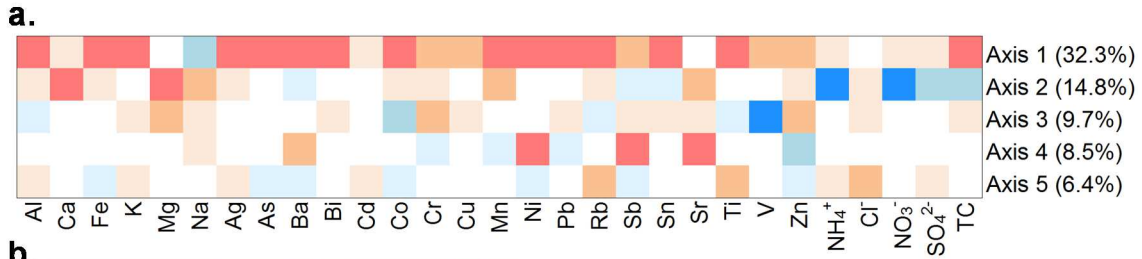
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Table 1: Average chemical composition (in  $\text{ng}\cdot\text{m}^{-3}$ ) of  $\text{PM}_{2.5}$  collected in Dunkerque and  $\text{PM}_{2.5}$  concentration (in  $\mu\text{g}\cdot\text{m}^{-3}$ )

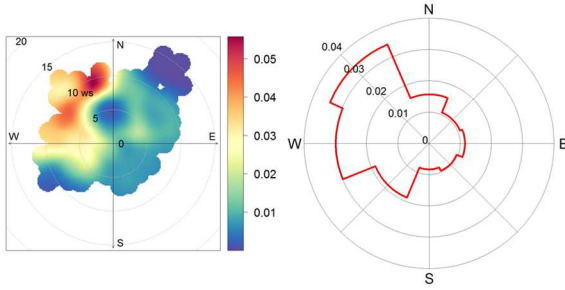
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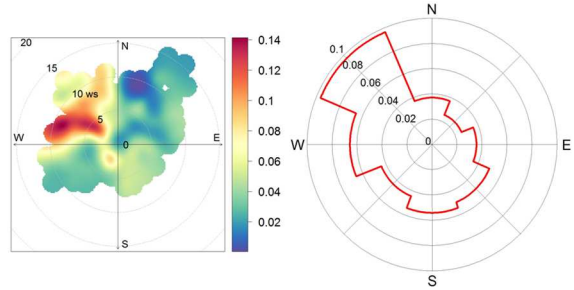
Table 4: Spearman correlation coefficient ( $r$ ) between Oxidative Potential derived from AA and DTT depletion measurements (OP-AA<sub>v</sub> and OP-DDT<sub>v</sub> respectively) and  $\text{PM}_{2.5}$  constituents,  $\text{PM}_{2.5}$  concentrations and sources contributions – only correlation coefficients for which  $p < 0.05$  are reported (\* $p < 0.001$  ; bold:  $r > 0.6$  ; italic:  $r < 0.4$ )



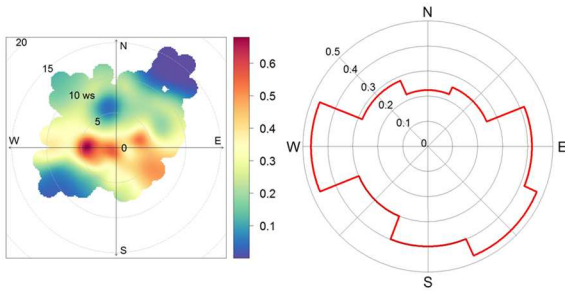
**OP-DTTm**



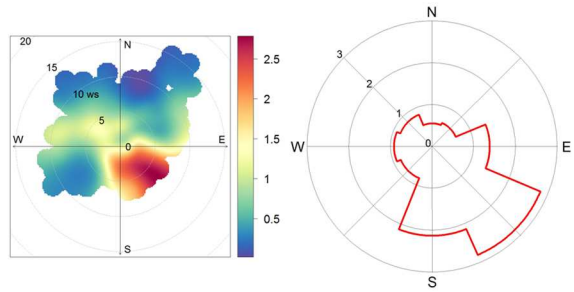
**OP-AAm**

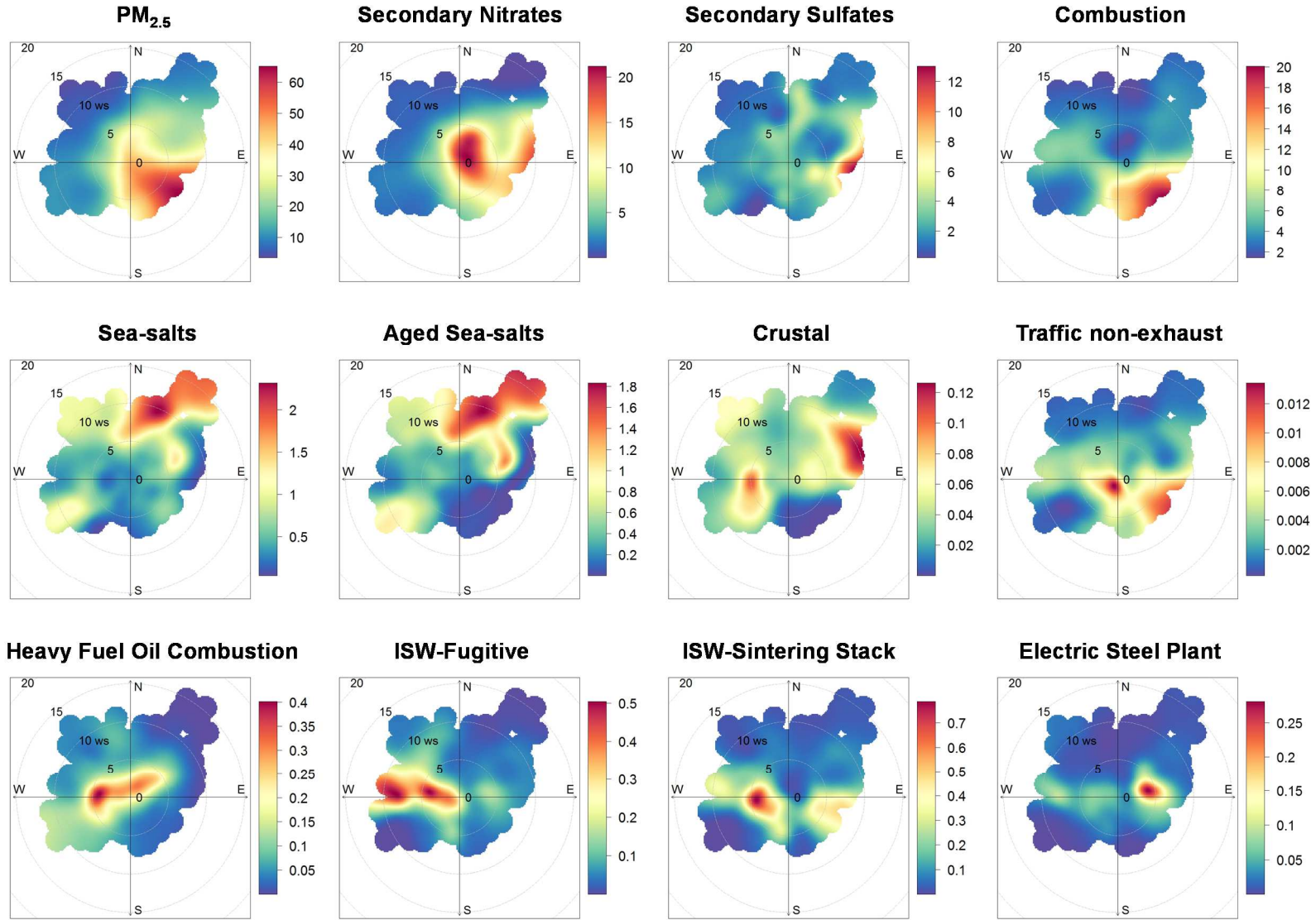


**OP-DTTv**

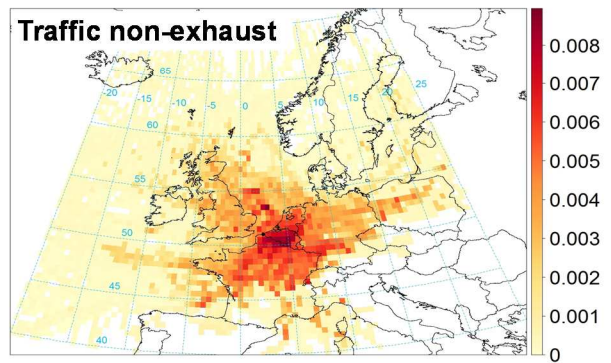
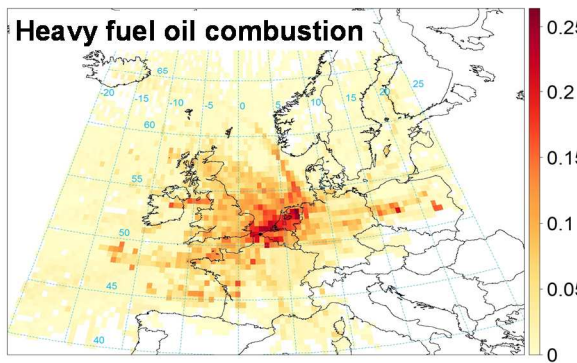
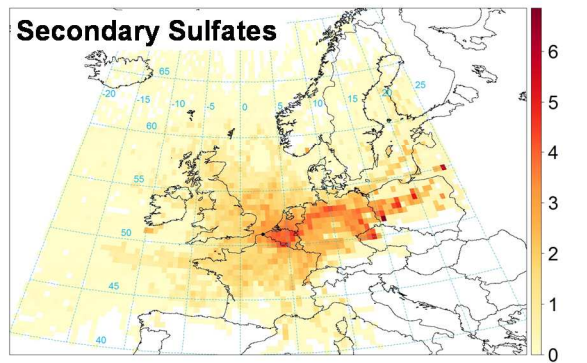
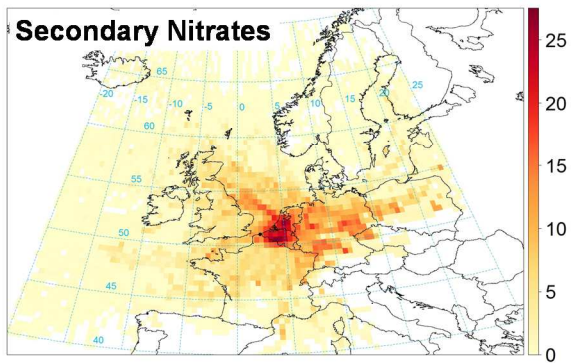
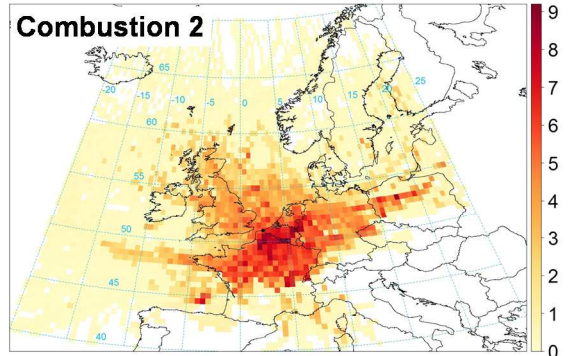
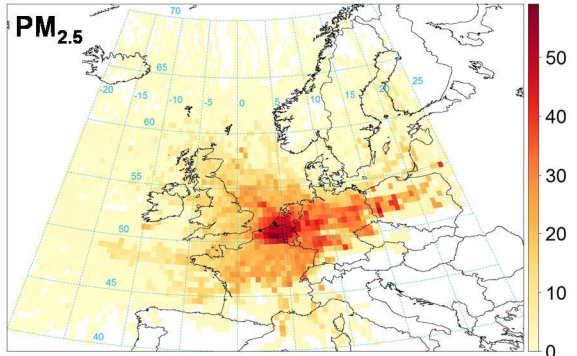
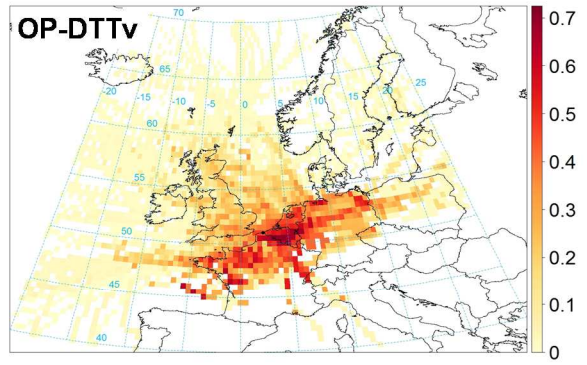
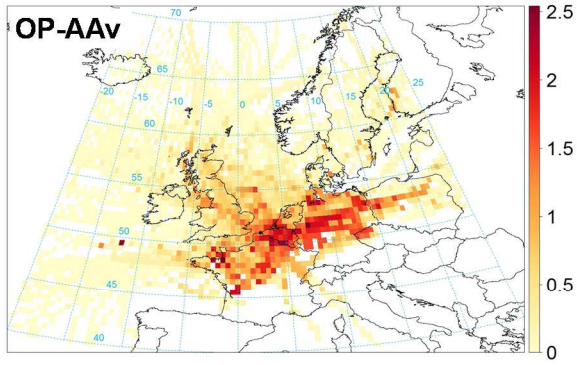


**OP-AAv**









<b>Species</b>	<b>Mean</b>	<b>Median</b>	<b>Min</b>	<b>Max</b>	<b>SD</b>	<b>1st Qu</b>	<b>3rd Qu</b>
Al	26.5	22.5	2.52	112.2	18.7	14.8	30.7
Ca	76.2	62.7	19.4	286	48.2	43.7	88.4
Fe	155	84.0	9.1	1542	231	37.1	195
K	122.7	91.1	29.2	358	83.0	62.0	156
Mg	61.9	39.3	4.35	305	64.1	16.6	72.1
Na	372	225	21.1	2225	419	105	404
Ag	0.07	0.04	0.00	0.42	0.08	0.01	0.09
As	1.09	0.78	0.00	9.45	1.38	0.31	1.45
Ba	0.88	0.74	0.19	5.01	0.67	0.56	1.08
Bi	0.15	0.11	0.00	0.62	0.14	0.04	0.26
Cd	0.46	0.23	0.01	7.98	1.08	0.08	0.44
Co	0.18	0.12	0.02	0.9	0.17	0.07	0.25
Cr	1.36	0.79	0.07	9.88	1.55	0.52	1.61
Cu	3.13	1.63	0.17	31.0	4.46	0.81	4.25
Mn	13.7	4.84	0.12	92.4	20.7	1.59	14.3
Ni	5.36	3.23	0.73	41.55	6.35	1.91	6.29
Pb	14.8	8.26	0.75	118	18.4	3.95	18.8
Rb	0.57	0.43	0.05	4.86	0.73	0.19	0.57
Sb	1.05	0.63	0.00	15.0	2.05	0.37	1.10
Sn	1.03	0.80	0.08	5.43	0.98	0.28	1.33
Sr	0.49	0.40	0.16	1.87	0.32	0.30	0.59
Ti	2.00	1.10	0.00	15.2	2.66	0.29	2.47
V	5.16	3.13	0.49	23.1	5.31	1.84	5.84
Zn	67.6	26.4	1.96	625	113	8.38	88.5
NH <sub>4</sub> <sup>+</sup>	2010	1380	172	4817	1301	1043	3128
Cl <sup>-</sup>	692	576	39.35	1752	409	418	841
NO <sub>3</sub> <sup>-</sup>	8678	3619	331	49066	10683	1837	11545
SO <sub>4</sub> <sup>2-</sup>	2754	2008	127	9642	2022	1399	3453
TC	5151	3612	805	17547	4246	2008	6881
PM <sub>2.5</sub> (µg/m <sup>3</sup> )	29.2	18.8	3.1	90.8	24.4	11.30	44.30

Source	Markers (by order of abundance)	Contribution (ng·m <sup>-3</sup> )	
		Average ± SD	(min - max)
Sea-salts	Cl <sup>-</sup> , Na, Mg	699 ± 605	(0 - 3000)
Aged Sea-salts	SO <sub>4</sub> <sup>2-</sup> , Na, NO <sub>3</sub> <sup>-</sup> , Mg, Cl <sup>-</sup>	566 ± 595	(0 - 2166)
Crustal	Ca, Al, Fe, Mg, K	56 ± 55	(0 - 257)
Secondary Sulfates	SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup>	2645 ± 2313	(0 - 10985)
Secondary Nitrates	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	10294 ± 13601	(0 - 60318)
Heavy Fuel Oil Combustion	TC, V, Ni	145 ± 163	(0 - 620)
Combustion 2	TC, NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , K	5444 ± 4312	(0 - 19352)
Traffic non-exhaust	Zn, Fe, Sb, Sn, Cr, Al, Pb, Mn, Cu	4.7 ± 4.3	(0 - 25)
ISW-Fugitive	Fe, Ca, Zn, Al, Mn, Pb, As	150 ± 204	(0 - 1296)
ISW-Sintering Stack	Cl <sup>-</sup> , K, NH <sub>4</sub> <sup>+</sup> , Fe, Pb, Rb, Cd	209 ± 271	(0 - 1382)
Electric Steel Plant	Zn, Fe, Pb, Mg, Pb, Cr, Ca, Mn, Cu	77 ± 142	(0 - 746)



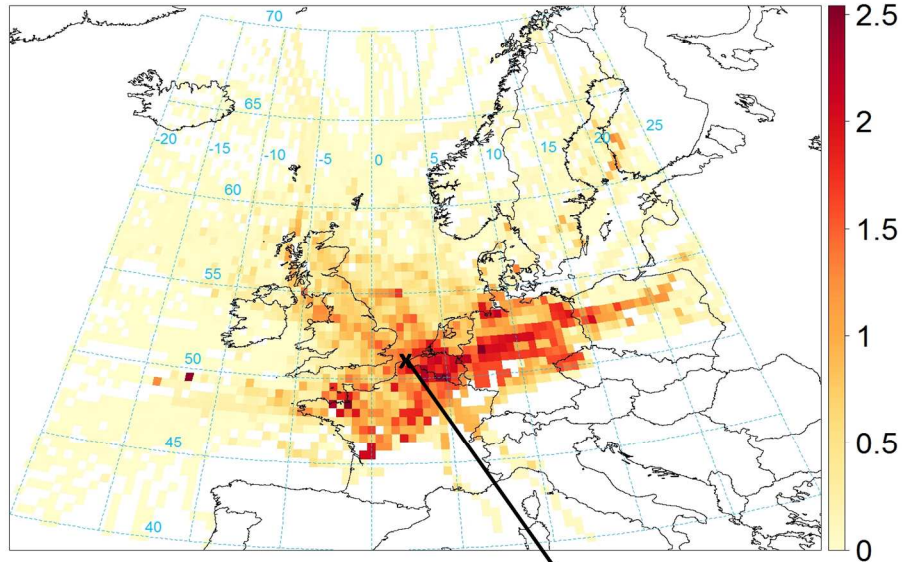
Site	Type	Leaching agent	OP-DDTv (nmol·min <sup>-1</sup> ·m <sup>-3</sup> )	OP-DTTm (pmol·min <sup>-1</sup> ·µg <sup>-1</sup> )	OP-AAv (nmol·min <sup>-1</sup> ·m <sup>-3</sup> )	OP-AAm (pmol·min <sup>-1</sup> ·µg <sup>-1</sup> )	PM <sub>2.5</sub> (µg·m <sup>-3</sup> )	PM <sub>10</sub> (µg·m <sup>-3</sup> )	Reference
Dunkerque (FR)	urban industrial	G + Shk (24 h)	0.36	17.7	1.12	55	29.2		This study
Paris (FR)	urban	E + US (1 h)	0.23						(Jedynska et al., 2017)
Atlanta (USA)	urban	H <sub>2</sub> O + US (30 min)	0.22	24					(Gao et al., 2020)
Hangzhou city (PRC)	urban	H <sub>2</sub> O + US (30 min)	0.62	6.39			63.1		(Wang et al., 2019)
Beijing (PRC)	urban	H <sub>2</sub> O + US (30 min)	12.6	130			113.8		(Yu et al., 2019)
Bologna (IT)	urban	PBS + US (15 min)	0.3-1.7		0.2-0.6				(Visentin et al., 2016)
Birmingham (USA)	urban	H <sub>2</sub> O + US (30 min)			0.75				(Fang et al., 2016)
Grenoble (FR)	urban	G + Shk (2 h)	1.00-4.12		0.17-2.46			7.4-22.3	(Calas et al., 2019)
Nice (FR)	background urban	G + Shk (2 h)	1.81-3.00		0.31-1.91			13.1- 21.4	(Calas et al., 2019)
Talence (FR)	background urban	G + Shk (2 h)	1.08-2.97		0.21-1.59			8.7-26.2	(Calas et al., 2019)
Passy (FR)	background urban	G + Shk (2 h)	1.91-10.0		0.30-7.20			8.6-59.2	(Calas et al., 2019)
Sarno (IT)	background urban	H <sub>2</sub> O + US (30 min)	0.19	11.67			16.3		(Cesari et al., 2019)
Lecce (IT)	background urban	H <sub>2</sub> O + US (30 min)	0.29	18.4			16.8		(Chirizzi et al., 2017)
Trento (IT)	background urban	PBS + US (15 min)	0.58	50	0.7	50		19	(Pietrogrande et al., 2018)
Site in Netherlands	background urban	PBS + No Filt	1.4				17.3		(Janssen et al., 2014)
Athens (GR)	background urban	H <sub>2</sub> O + US (30 min)	0.33	27.98					(Paraskevopoulou et al., 2019)
Salento (IT)	suburban	PBS + US (15 min)	0.19-0.29	10-11	0.09-0.21	5-8	20-26		(Perrone et al., 2019)
Patalia (IN)	semi-urban	M+H <sub>2</sub> O + US (30 min)	3.8	27			150		(Patel and Rastogi, 2018)
Atlanta (USA)	side street	H <sub>2</sub> O + US (30 min)	0.78	50			15.6		(Vreeland et al., 2017)
Belgrade (BU)	tunnel traffic	H <sub>2</sub> O + Shk (90 min)	0.37	9.43					(Jovanovic et al., 2019)
Atlanta (USA)	highway	H <sub>2</sub> O + US (30 min)	1.08	70			18.3		(Vreeland et al., 2017)
Ala (IT)	industrial (Zn)	PBS + US (15 min)	0.61	120	1.4	60		20.3	(Pietrogrande et al., 2018)



	OP-DTTv	OP-AAv		OP-DTTv	OP-AAv
<i>Species</i>			<i>Species</i>		
Al	<b>0.63*</b>		V	0.47*	
Ca			Zn	<b>0.74*</b>	0.49*
Fe	<b>0.77*</b>	0.51*	NH <sub>4</sub> <sup>+</sup>	0.50*	0.31
K	0.67*	0.55*	Cl <sup>-</sup>		
Mg	-0.31	-0.54*	NO <sub>3</sub> <sup>-</sup>	<b>0.68*</b>	0.39
Na	-0.53*	<b>-0.62*</b>	SO <sub>4</sub> <sup>2-</sup>	0.56*	0.28
Ag	<b>0.73*</b>	0.52*	TC	<b>0.72*</b>	<b>0.68*</b>
As	<b>0.75*</b>	<b>0.61*</b>			
Ba	<b>0.79*</b>	<b>0.69*</b>	<i>Source contribution</i>		
Bi	<b>0.79*</b>	0.39	Sea-salts	-0.40	-0.39
Cd	<b>0.82*</b>	0.47*	Aged Sea-salts	-0.55*	<b>-0.67*</b>
Co	<b>0.66*</b>		Crustal		
Cr	<b>0.70*</b>	0.56*	Secondary Sulfates	0.58*	0.38
Cu	<b>0.85*</b>	<b>0.64*</b>	Secondary Nitrates	<b>0.67*</b>	0.34
Mn	<b>0.72*</b>	0.33	HFO Combustion	0.45*	
Ni	<b>0.63*</b>	0.28	Combustion 2	0.37	0.54*
Pb	<b>0.79*</b>	<b>0.63*</b>	Traffic non-exhaust	<b>0.80*</b>	<b>0.66*</b>
Rb	<b>0.75*</b>	0.54*	ISW-Fugitive	<b>0.67*</b>	0.46*
Sb	<b>0.70*</b>	<b>0.60*</b>	ISW-Sintering Stack	<b>0.60*</b>	0.53*
Sn	<b>0.82*</b>	<b>0.61*</b>	Electric Steel Plant	<b>0.64*</b>	0.43*
Sr		-0.45*			
Ti	<b>0.67*</b>	0.32	<i>Oxidative potential</i>		
			OP-DTTv		0.46*
PM <sub>2.5</sub>	<b>0.67*</b>	0.45*	OP-AAv	0.46*	

# PM<sub>2.5</sub> Oxidative Potential

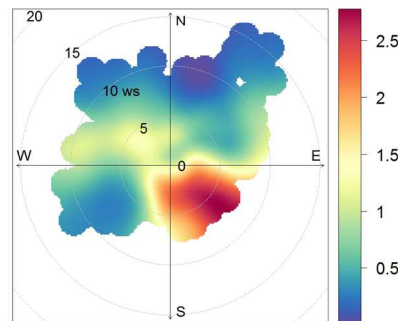
## Ascorbid Acid assay



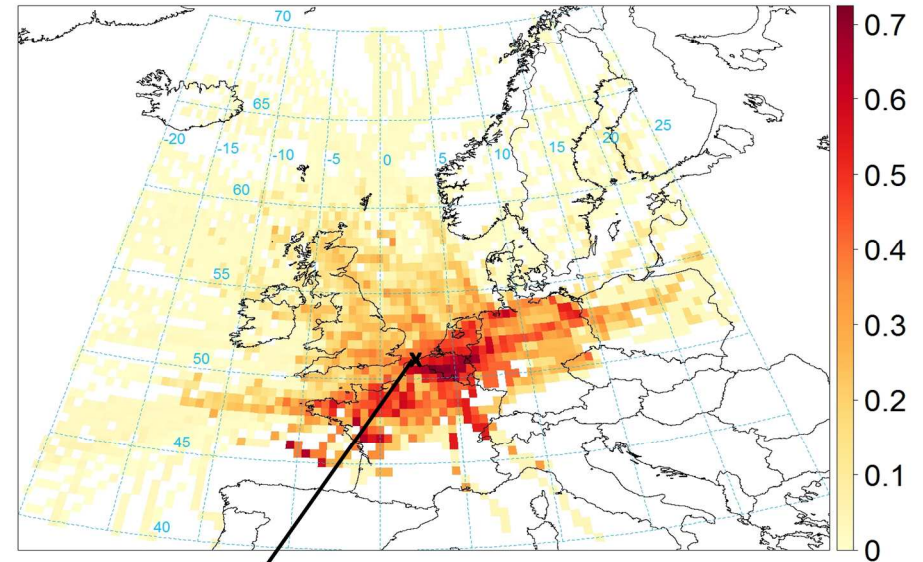
**Related to:**

Local and distant sources:  
- Road traffic and biomass combustion

PM<sub>2.5</sub> concentration levels



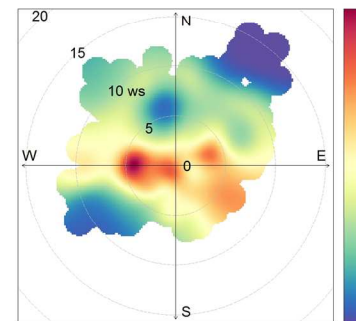
## Dithiothreitol assay



**Related to:**

Local industrial sources :  
- Integrated steelworks  
- Electric Steel Plant

Local and distant sources:  
- Heavy fuel oil combustion  
- Traffic non-exhaust  
- Combustion possibly



No contribution of sea-salts, aged sea-salts, crustal sources, secondary sulfates and secondary nitrates to OP values