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1 **Evaluation of historical atmospheric pollution in an industrial area by dendrochemical**  
2 **approaches**

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17

18 **Abstract**

19 We conducted a dendrochemical study in order to evaluate the exposure of territories and  
20 populations to different types of pollutants and to characterise the history of pollution in one of the  
21 most intensely industrialised areas of Europe: the industrial port zone of Fos, also heavily  
22 urbanised.

23 To perform the study, two tree species have been selected, *Pinus halepensis* and *Populus nigra*, on a  
24 rural plot located roughly 20 km away from the industrial harbor, an urban plot located in the city of  
25 Fos-sur-Mer and an industrial plot. Our study indicated that poplar was a more relevant model for

26 the dendrochemical studies exhibiting a higher bioaccumulation capacity than pine except for Hg,  
27 Sb and Mn. Moreover, thanks to this work we observed significant exposure of the trees in the  
28 urban and industrial areas to As, Cd, Co, Cu, Mo, Sb, Zn, Al, Ca, and Mg, highlighting the exposure  
29 of the territory and populations living in the vicinity of the industrial harbor. The temporal  
30 variability of the concentrations measured in the tree rings corresponds to the increasing  
31 industrialisation of the territory as well as to the evolution of the industrial processes. Thus, this  
32 project highlighted the exposure of Gulf of Fos to atmospheric emissions (industrial, road and  
33 urban) of the industrial harbor as well as the changes over time. It also point out the relevance of  
34 using dendrochemistry to measure atmospheric exposure of metals and metalloids and its temporal  
35 variability.

36

37 **Keywords:** Dendrochemistry, historical atmospheric exposure, trace metal pollution, tree rings,  
38 industrial harbor

39

## 40 **1. Introduction**

41 The high levels of metals and metalloids in the environment are of major concern due to their  
42 persistence long term and their toxicity, even at low concentrations. The trace elements (TEs) such  
43 as As, Cd, Cr, Co, Cu, Hg, Mo, Ni, Pb, Zn pose a potential threat to ecosystems (Tremel-Schaub  
44 and Feix, 2005). These pollutants originate from human activities and more precisely past and  
45 current industrial activities. Over recent decades, the improvements of industrial processes have  
46 allowed for the reduction of emissions in the air, aquatic ecosystems and in soils. This has been  
47 made possible, first by the combination of technological innovation and financial markets, allowing  
48 for recycling of products that, in the past, were released into the atmosphere and, secondly, by  
49 applying regulatory constraints. However, air pollution is still a cause of concern in many parts of  
50 the world and mainly in highly industrialised areas.

51 Due to the environmental and sanitary impacts of these industrial emissions, their atmospheric  
52 concentrations are being monitored. The levels and the spatial distribution of the pollutants is  
53 necessary to determine their origin and the associated risks. However, monitoring pollutants using  
54 active air samplers over several sites - in order to measure spatial variations - is currently difficult  
55 due to technical, physical and economic requirements. Indeed, their simultaneous use on several  
56 sites can cause difficulties to calibrate in a homogeneous way all the devices which can furthermore  
57 be impacted by problems of operation leading to the stop of the continuous measurements and the  
58 loss of data. Moreover, it requires a significant economic investment relative to the cost of this type  
59 of device. The analysis of TE concentrations in lichens (Agnan et al., 2015; Ratier et al., 2018),  
60 leaves and needles (Aboal et al., 2004; Lehndorff and Schwark, 2010; Sun et al., 2010) and / or  
61 their bark (Catinon et al., 2009; Fujiwara et al., 2011; Gueguen et al., 2012) have been widely used  
62 as alternative and low-cost methods for spatial monitoring. Although sampling of tree tissues  
63 (needles, leaves or bark) or lichens can be appropriate for determining spatial distribution of trace  
64 elements, it only provides information on current atmospheric levels, and cannot provide temporal  
65 nor historical variations of TEs, unlike dendrochemistry. Recent studies have been carried out to  
66 detect diffuse TE pollution in soils using dendrochemical methods (St Laurent et al., 2011; Cui et al.,  
67 2013; Smith et al., 2014, Maillard et al., 2016). Furthermore, the research work of Wright et al.  
68 (2014) and Odabasi et al. (2016) demonstrated that metal/loid contaminant (As, Cr, Fe, Mo, Ni, V,  
69 Cu, Pb, Sb, Sn, and Hg) accumulation in tree rings occurred through the foliar pathway, allowing  
70 for characterization of atmospheric exposure (Wright et al., 2014; Odabasi et al., 2016). Thus  
71 dendrochemical data are of great scientific interest to determine the temporal variability of exposure  
72 to air pollutants, and to evaluate the effectiveness of investments in environmental processes to  
73 reduce industrial, urban and transport emissions, based on the hypothesis that the level of pollutants  
74 in tree rings reflect, to a certain extent, the chemical signal in the environment during ring formation  
75 (Smith et al., 2014), either through root or foliar exposure.

76 The studied territory is the industrial harbor of Fos, located in the area of Aix-Marseille-Provence  
77 Metropole (France). Since the beginning of the 19th century, this area has been adversely affected  
78 by pollution. For 50 years, the industrial and transport sectors have been growing, leading to  
79 disruptions of socio-economical, environmental and sanitary situations and leading to several  
80 protests, despite the jobs created and social and economic compensations (Daumalin, 2013; Beuret  
81 et Cadoret, 2014; Daumalin and Gramaglia, in press). Nowadays, a dense population lives in this  
82 area in proximity to almost 40 operational industrial sites. Twelve of them have been classified as  
83 SEVESO sites, making the industrial port zone of Fos one of the most industrialised ports in  
84 Europe. However, few data exist on the environmental status and health conditions in this area.  
85 Lichen biomonitoring has been carried out by the “Institut Ecocitoyen pour la Connaissance des  
86 Pollutions” (IECP) for several years on this territory, which has highlighted the current exposure of  
87 areas located at the South of the Berre lagoon, near the industrial sites (Dron et al., 2016; Ratier et  
88 al., 2018).

89 We assumed that the dendrochemical signatures would reflect the change in TE emissions in the air,  
90 aquatic ecosystems or soils, due to changes in industrial processes during past decades. This study  
91 has the following aims: (i) to study spatial variations and origin of air pollutants (TEs and major  
92 elements) by measuring concentrations in tree bark and soil samples and allowing to evaluate their  
93 use as a passive sampler; (ii) to identify the temporal variations of atmospheric exposure and thus  
94 the history of contamination in the study area by analysing the major element and TE  
95 concentrations in core tree samples. Thus, this work aims to highlight the interest of  
96 dendrochemical data in the spatial and historical variations of metal atmospheric pollution and to  
97 determine the most appropriate plant models for this approach.

98

## 99 **2. Materials and Methods**

### 100 2.1. Study area

101 This study is focused on the Gulf of Fos (South of France), which is host to the largest industrial  
102 port zone in France and Southern Europe including several heavy industry activities (refining and  
103 petrochemical industries, chemistry, coke production and steel industries, cement plant, household  
104 and industrial waste incinerators) and world-leading maritime terminals (containers, ore, oil, gas,  
105 cereals) (Figure 1). We have chosen three different areas representatives of the main human  
106 environments and based on preliminary field studies and the recent results (Austruy et al., 2016,  
107 Dron et al., 2016). An industrial area located in the industrial harbor of Fos (FOS\_I) and another  
108 one in the urban area of Fos-sur-Mer (FOS\_U) were selected. In addition, a control rural plot  
109 (FOS\_R), located in Grans more than 20 km away from Fos-sur-Mer and subject to a north-westerly  
110 prevailing wind limiting the influence of atmospheric emissions from the industrial harbor, was  
111 used to assess regional background (Figure 1).

112 Climatic conditions are provided in Figure S1 with a graph showing the mean annual temperature  
113 and rainfall variations over the period 1949-2015. The Mistral, north-westerly or westerly wind, is  
114 dominant in the area, while the south-east wind accounts for about 15 %. The temperature over this  
115 period varies from -10 to 38 °C with an average value of 15.1 °C (METEOFRANCE data, Istres  
116 station).

117

## 118 2.2. Tree core and soil sampling

119 Two tree species, *Pinus halepensis* and *Populus nigra*, were chosen due to their high abundance in  
120 the study area as well as their use in previous dendrochemical studies (Sheppard et al., 2007,  
121 Odabasi et al., 2016). For each plot, six healthy trees, among the oldest, of both species were  
122 selected and sampled in March 2016, except on the urban plot (FOS-U) where no suitable poplars  
123 were found. Tree cores were collected at chest height using a 10 mm-Pressler auger. In addition,  
124 phytoscreening cores of 5 mm were collected on the most external rings of trees, as described in the  
125 PIT guide (Balouet and Chalot, 2015), on the different plots to sample the bark. The history of each

126 plot was determined, and the trees were characterized and mapped. The circumferences of the trees  
127 ranged from 1.3 to 2.5 m. Ages of the sample trees were determined by counting the annual rings  
128 using a magnifying glass, which were between 26 and 70-years-old.

129 For each tree sample, composite soils were collected the same day using a manual auger at 0-10 cm  
130 depth. The composite soil sample was carried out from five sub-samples of equal amounts (250 g)  
131 collected less than 50 cm from the tree trunk. It was produced by careful mixing and quartering of  
132 the five sub-samples to obtain the composite sample of approximately 500 g according to AFNOR  
133 standard NF X31-100. After pH determination, the analyses of trace and major element  
134 concentrations were performed.

135

### 136 2.3. Sample pre-treatment and analysis

#### 137 2.3.1. Analysis of trace and major element concentrations in tree rings and barks

138 The tree cores and barks were dried at 40 °C until a loss of mass inferior to 5 % in 24 h and their  
139 upper surface was sanded to facilitate reading of the rings. For all sites, tree cores were cut to obtain  
140 samples formed from segments of 3 rings and each sample was processed and analysed separately.  
141 Previous to mineralization, Hg concentrations in segments were measured with an AMA-254 cold  
142 vapour atomic absorption (CV-AAS) Hg analyser (Altec Co, Czech Republic), as presented in  
143 Maillard et al. (2016). The instrument detection limit for this method is 0.006 ng of total mercury.

144 The complete mineralization of the ring and bark samples was performed according to a modified  
145 version of Barbaste's method (2004). 0.1 g of each ring or bark sample crushed to fine particles  
146 using a ball mill for 2 min 30 s at a frequency of 25 Hz (Retsch MM 400 equipped with zirconium  
147 oxide beads and capsules) were introduced into a polyethylene (LDPE) tube with 3 mL of 67 %  
148 HNO<sub>3</sub>. The tubes were placed in a heating block and heated at 80 °C for 1 h 30. 1 mL of 30 % H<sub>2</sub>O<sub>2</sub>  
149 was added and the tubes replaced on the heating plate at 60 °C for 30 min then at 80 °C for 3 h.  
150 Each of these samples was then filtered at 0.45 µm with syringe filters in cellulose acetate. The

151 eluate was placed in a polyethylene tube and diluted with 20 ml of ultrapure water. A certified  
152 sample, ERM CD 281 (Rye-grass), and a blank test were analysed for each series of mineralization.  
153 Pending the analysis, the samples were stored at 4 °C. The analysis of trace and major element  
154 concentrations (Al, Ca, Fe, K, Mg, Mn, P, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn) on the  
155 core and bark samples was performed by ICP-MS (Perkin-Elmer Nexion 300X). The results of the  
156 standard samples showed concentrations with an error rate of less than 20 % compared to the  
157 theoretical concentrations.

158

### 159 2.3.2. Determination of trace and major element pseudototal concentrations in soils

160 For analysis of trace and major element pseudototal concentrations, the composite samples were  
161 dried in an oven at 40 °C until a loss of mass inferior to 5 % in 24 h was obtained. The dry samples  
162 were then crumbled and sieved to recover the fraction less than 2 mm. A sub-sample (5 g) was  
163 crushed in an agate mortar to fine particles of less than 100 µm and used for the analysis of TEs  
164 (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn) and major elements (Al, Ca, Fe, K, Mg, Mn, P).  
165 0.1 g of each soil sample crushed to fine particles were mineralized with 6 mL of aqua regia (1/3  
166 HNO<sub>3</sub> and 2/3 HCl, AFNOR standard NF ISO 11466) in a microwave oven (March 5 CEM)  
167 (Quevauviller, 1998). After adding 4 mL of ultrapure water, the extracts were filtered with 0.45 µm  
168 cellulose acetate filters. The samples were diluted by a factor of 20 before analysis by inductively  
169 coupled mass spectroscopy (ICP-MS). For quality control, a blank test and certified standard, ERM-  
170 CC141, were included in each series of analyses. The results of the standard samples showed  
171 concentrations with an error rate of less than 20 % compared to the theoretical concentrations.

172

### 173 2.3.3. Determination of TE bioavailable concentrations of soils

174 The use of DTPA to evaluate the bioavailability of TE in calcareous soils has been the subject of  
175 numerous publications (Leggett and Argyle, 1983; Chaignon, 2001) and is now recognized



176 (AFNOR standard NF X31-121). The extraction solution consists of 0.005 mol.L<sup>-1</sup> diethylene  
177 triamine pentaacetic acid (DTPA), 0.1 mol.L<sup>-1</sup> triethanolamine (TEA) and 0.01 mol.L<sup>-1</sup> CaCl<sub>2</sub>, the  
178 pH should be maintained at 7.3. The presence of DTPA and CaCl<sub>2</sub> in the extraction solution  
179 prevents excessive CaCO<sub>3</sub> dissolution and significant metal release (Chaignon, 2001). Thus, only  
180 the soluble and easily exchangeable fraction of TEs was extracted. 2.5 g of soil sieved to 2 mm was  
181 introduced into 5 ml of the extraction solution. The mixture was stirred for 2 h at 120 rpm at room  
182 temperature. The pH was measured in the suspension and the extracts were separated from the solid  
183 residue by centrifugation at 2300 g for 10 min (Megafuge 40, Thermo Scientific). The supernatant  
184 was filtered on a 0.45 µm filter of cellulose acetate previously rinsed with 5 ml of ultrapure water.  
185 For each analysis series, a blank was prepared. Analysis of the bioavailable fraction of TEs was  
186 performed by ICP-MS.

187

#### 188 2.4. Statistical analysis

189 All statistical analyses and graphical representations were performed with statistical software R (R  
190 Core Team 2015, version 3.2) and the vector graphics editor Inkscape. Compounds, which were not  
191 detected (nd) or below the limit of quantification (< l.q.) were always considered as zero. Given the  
192 sample size per station (6 replicates), Mann Whitney's nonparametric test, allowing comparison of  
193 independent samples, was used to compare the data distribution by station. Principal component  
194 analyses (standard ACP) were performed on the trace and major element contents with the  
195 representation of the individuals. It was preferred to the most constrained analyses, such as positive  
196 matrix factorisation (PMF) or non-negative matrix factorisation, in order to identify the exposure of  
197 different study plots to metallic contaminants and to distinguish the response of each two species to  
198 atmospheric exposure of TEs and major elements. In a second step, the PCA was favored to  
199 establish the variations in time and space of atmospheric exposure. Finally, in order to determine  
200 possible correlations between the different variables, the Spearman regression coefficients, a

201 nonparametric statistical dependence measure between two variables, were calculated and linear  
202 regressions were performed.

203

### 204 **3. Results and discussions**

#### 205 3.1. Pseudototal and bioavailable concentrations in soils

206 Pseudototal and bioavailable trace and major element concentrations measured in the three areas are  
207 provided in Table 1. The pseudototal TE concentrations in soils were substantially higher in the  
208 industrial area as compared with the rural and urban areas except for As, Co and V and significantly  
209 higher for Cd, Cr, Mo and Zn. The soil acted as a final sink for the elements deposited from the air  
210 (Pacyna and Pacyna, 2001, Mico et al., 2006) or transferred by falling needles or leaves (Batjes,  
211 2000; Rauch and Pacyna, 2009). Therefore, the TE enrichment measured in the soils of the  
212 industrial area reflected the diffuse atmospheric pollution caused by the industrial port zone of Fos-  
213 sur-Mer. Beyond the diffuse pollution, the pseudototal soil concentrations were also the  
214 consequence of a higher natural biogeochemical background in Grans as compared with Fos-sur-  
215 Mer because of the geological substratum nature characterized by calcirudites in Grans (Austruy et  
216 al., 2016). This is notably the case for As, Co, Ni, Pb, V and Fe.

217 Table 1 presents the DTPA-extractable TE fraction, which represents the easily exchangeable ET  
218 fractions of the soil, complexed to the organic matter or adsorbed to the oxides of Fe, Al and Mn  
219 (Gis Sol, 2011). The soils of the area were slightly alkaline ( $\text{pH} = 7.66 \pm 0.39$ ,  $7.48 \pm 0.25$  and  $7.50$   
220  $\pm 0.23$  respectively for rural, urban and industrial areas) responsible for a low mobility of most of  
221 the TEs, which did not exceed 5 % of the pseudototal concentration or were very low with values  
222 close to the percent or even the thousandth for As, Cr, Co, Mn, Mo, Ni, Sb and V. On the contrary,  
223 important exchangeable fractions were measured for Cd (between 21.6 and 23.5 %) and to a lesser  
224 extent for Cu, Pb and Zn, of which the DTPA-extractable fraction represented between 3 and 10 %  
225 of the pseudototal fraction. This can be explained by the strong affinity of Cu and Pb for dissolved

226 organic matter (Komarek et al., 2008, Kelepertzis et al., 2015, Safari et al., 2015). Indeed, Wu et al.  
227 (2002) found that a high pH favours the dissolution of humic acids and increases the dissolved  
228 concentration of metals due to the formation of metal-organic complexes in solution. Similarly, Zn  
229 and Cd are able to complex with labile components and easily soluble oxy/hydroxides (Rodrigues et  
230 al., 2013). These results indicated that a large part of the TE fraction for Cd, Cu, Pb and Zn was in a  
231 potentially phytoavailable form. The same trends were observed for the different soils (FOS\_R,  
232 FOS\_U, FOS\_I), with the largest DTPA fraction observed in soils of urban plot for all these  
233 elements. These results appeared in line with previous studies carried out on calcareous soils of the  
234 Mediterranean region (Testiati, 2012; Safari et al., 2015; Austruy et al., 2016).

235

### 236 3.2. Phytoscreening using tree bark samples

237 Figure 2 presents the trace and major element concentrations measured in tree bark samples of  
238 *Pinus halepensis* and *Populus nigra* sampled in the different plots. For the various sampled plots,  
239 the concentrations measured in the poplar bark were always higher, for a given plot, than the  
240 concentrations measured in the pine bark. Differences in accumulation capacities in various tree  
241 species has been widely documented. For example, the works of Migeon et al. (2009) have showed  
242 that trees of the Salicaceae family can accumulate substantial amounts of Cd and Zn in their shoot  
243 parts, thus differing from a large range of other woody species. In more detail, significantly higher  
244 concentrations were measured in the poplar for Cr, Cu, Zn, Cd, Co, Mo and Fe on the rural plots  
245 (FOS\_R) and for Cu, Pb, Zn, Cd, Co, Mo and Ni on the polluted plots (FOS\_I). Most importantly,  
246 significant differences between the industrial and rural plots were observed, especially for poplar,  
247 for Zn, Cd, Co, Mo, Ni and Al. Similarly, for pines, significant differences existed for Cr, Mo and  
248 Fe between the industrial and rural plots and for Cd, Mo, Al and Fe between the urban and rural  
249 plots. At the same time, a strong heterogeneity was noticed in industrial samples while urban and

250 rural ones were more homogeneous, showing the complexity and the diversity of industrial  
251 exposures at the local scale.

252 The FOS\_I/FOS\_R ratios ranged from 1.1 (Cu) to 3.9 (Al) for poplar trees and between 0.8 (Cu,  
253 Zn) and 3.5 (Sr) for pines. The FOS\_U/FOS\_R ratios ranged from 0.6 (Al) to 3.1 (Cd) for pines (no  
254 poplar in the urban area). Indeed, the highest concentrations for TEs and major elements were  
255 measured in the urban and industrial plots and the lowest concentrations in the rural area except for  
256 Fe and Mn. Thus, these results highlighted the impact of atmospheric emissions from the industrial  
257 harbor of Fos on the chemical composition of tree barks collected in the industrial zone or in the  
258 nearby urban periphery. This is confirmed by previous research works carried out in the area, which  
259 highlighted the impact of the industrial harbor emissions on the environment (Austruy et al., 2016,  
260 Dron et al., 2016, Ratier et al., 2018) notably for the contents of Cr, Cd, Fe, Pb, Zn and Co. For  
261 these metals, the major sources of emissions in the area are the steel industry and road traffic  
262 emissions (Sylvestre et al., 2017). These results proved that TE concentrations measured in tree  
263 bark are suitable bioindicators of the metal content of soil and a relevant passive monitor of  
264 atmospheric pollution (Barbes et al., 2014; Zhai et al., 2016). Indeed, tree bark can provide reliable  
265 results for estimating long-term air pollution because its structure retains metals and metalloids for a  
266 long time (Berlizov et al., 2007), whereas leaves fall periodically.

267

### 268 3.3. Accumulation of TEs and major elements in tree rings

269 For all the elements considered in this study, the method used proved to be efficient in obtaining  
270 sufficient quantities of wood for the mineralisation and ICP-analysis. The data set included 4,640  
271 concentrations of elements measured over 232 3-year segments.

272 Table 2 presents the average concentrations in tree rings and the statistical significance (p-value,  
273 kruskal test) of data for each site and each tree species. On average, the most abundant TEs were  
274 Fe, Al, Zn and Mn. The lowest average concentrations were Hg, As, Sb, V and Cd. Large variations

275 in concentrations were measured between trees of a same plot mainly in the industrial area for Al,  
276 Mg, Cd, Hg or Pb in pines and Al, Ca, Fe, Mg and K for poplars. Emissions in the industrial harbor  
277 are multiples, fixed and often channelled through chimneys up to 120 m high. Thus, the smoke  
278 plumes can affect two trees that are in geographical proximity in very different ways. The  
279 variability of TE contents in industrial zones can be explained by the micro-meteorological  
280 conditions, as well as the environment close to the stations (vegetation cover, buildings, nature of  
281 emissions, ...) (Sylvestre et al., 2017; Ratier et al., 2018). Furthermore, this variability, observed in  
282 different dendrochemical studies (Kirchner et al., 2008; Odabasi et al., 2016), may be the  
283 consequence of the physiological mechanisms related to element sequestration and allocation.  
284 Previous studies have emphasized the trends of cation distribution in the stemwood of living trees  
285 as a result of the interaction between tree physiology and abiotic factors. Various analytical methods  
286 have been used to identify internal physiological and pathological processes in wood that affect  
287 cation concentration (Smith and Shortle, 1996; Smith et al, 2014). Otherwise, intra-tree variations  
288 between the different rings were measured, with variations up to 200 % in particular for Zn, Hg, Co  
289 or Cu, illustrating the variability in the exposure of individuals over time.

290 Most importantly, significant differences were observed for many elements between the rural, urban  
291 and industrial plots. Indeed, poplar cores showed significantly higher concentrations in the  
292 industrial zone for Cd, Cu, Hg, Mo, Zn, Al, Ca, Mg and K (Mann-Whitney test). Similarly, for  
293 pines, significant differences were measured for Cd, Ni and Al between industrial and rural plots  
294 and for Mo, Ni and Fe between urban and rural plots. These results reflect the major pollutants  
295 emitted by the industrial harbor of Fos, namely Zn, Pb, Cu and to a lesser extent Cr and Cd (IREP,  
296 2016, Dron et al., 2016).

297 Figure 3 shows a principal component analysis (PCA) performed on the average concentrations of  
298 major elements and TEs measured in poplar and pine rings sampled from the various plots. The first  
299 two axes of this PCA explained 61.6 % of the variance. The first axis (40 % of the variance)

300 distinguished Mn, Sb and Hg from other chemical elements notably Cu, Co and Mo. The positive  
301 values of this axis were related to the Mn, Sb and Hg contents. The major elements were mainly  
302 distributed over the second axis (22 % of the variance), the positive values of this axis being related  
303 to Mg, K and Ca. This analysis shows a distribution of data, in particular for poplars, as a function  
304 of two axes. Indeed, the positioning of poplars on the industrial plot (on average, axis 1 = -4.47 and  
305 axis 2 = 1.41) compared to those of the rural plot (on average, axis 1 = -0.50 and axis 2 = -1.82)  
306 highlights the influence of many TEs on poplars in the industrial zone such as Zn, Cd, Mo, Co, Cu,  
307 As, V but also Ni, Fe and Cr for the most recent data (2014, 2011 and 2008). On the contrary, the  
308 pines of the different plots showed a widely homogeneous distribution (axis 1 = 1.9, 1.8, 1.7 and  
309 axis 2 = 0.3, -0.1, 0.2 respectively for PIN\_R, PIN\_U and PIN\_I).

310 These TEs, impacting the poplars of the industrial plot, were emitted by various industrial activities  
311 represented on the industrial harbor of Fos, such as the steel industry (As, Cd, Cr, Co, Cu, Hg, Ni,  
312 Pb, V, Zn and Fe), refineries (Cd, Cu, Ni, Zn and V), chemical plants (Co, Hg, Ni, V and Zn),  
313 cement plants (Pb, V and Al) or road traffic (Cu, Sb) (Sylvestre, 2016, IREP, 2016). These  
314 pollutants bioaccumulated in tree rings appeared to reflect atmospheric exposure. The absence of  
315 correlations between the contents measured in the soil and those measured in the rings, whatever the  
316 metal or species of tree considered ( $R_{\text{pearson}} < 0.5 - p\text{-value} > 0.05$ ), confirmed the impact of the  
317 atmospheric exposure.

318 These results were confirmed by the average concentrations of TE and major elements measured  
319 over the period 1975-2015 in pines and poplars presented in Table 2. On the industrial plot, we  
320 found significantly higher levels of TE and major elements in poplars for Mg, K, Ca, Fe, Mo, Pb, V,  
321 Co, Cu, Zn, As and Cd. On the contrary, the pines had higher contents for Hg, Sb and Mn. A recent  
322 study (Arnold et al., 2018) had demonstrated the ability of pines to take up Hg by the stomata  
323 pathway and translocate it into tree rings via the phloem, in contrast to poplars for which the non-  
324 stomatal pathway appears to be predominant for Hg uptake. The higher bioaccumulation of TE in

325 poplar rings may be the consequence of the surface morphology of poplar leaves and especially the  
326 density of trichomes, which could increase its potential to trap atmospheric pollutants and to take  
327 them up via the stomata of the epidermis. Several reports have shown that as leaf surfaces become  
328 rougher, the accumulation of TEs increase due to their greater ability to trap particles (Sawidis et  
329 al., 2011). In addition, poplars having lower leaf area, can have higher rates of gas exchange per  
330 unit leaf area (Kloeppe et al., 2000).

331 Our dataset highlighted the potential of higher plants as bioindicators or biosensors of atmospheric  
332 pollutants due to a high surface area and hydrophobic nature of plant surfaces (Frescholtz et al.,  
333 2003, Burken et al., 2011; Xiong et al., 2016). Indeed, airborne contaminants are taken up either by  
334 the stomatal pathway or attracted to the waxy cuticle and the surfaces of the stem or bark and  
335 further taken up to the non-stomatal pathway. This work specified the relevance of poplar for use in  
336 dendrochemical studies because of its high bioaccumulation capacity (Sheppard et al., 2007a,  
337 2012b, Migeon et al., 2009, Barbes et al., 2014). According to these findings highlighting a  
338 significant response of the poplar to the historical environmental changes of TE and major element  
339 concentrations in the atmosphere, we further concentrated our study on poplar.

340

#### 341 3.4. Influence of socio-historical evolution of Gulf of Fos on the TE and major element 342 concentrations in tree rings

343 The basic hypothesis of dendrochemistry is that the contaminants recorded in tree rings are not  
344 mobile and may reflect the historical changes of environmental levels (Watmough, 1999;  
345 Lebourgeois, 2010; Maillard et al., 2016; Odabasi et al., 2016). However, once taken up, elements  
346 can bind to the xylem, phloem, or ray cells, or can continue to be mobile, being radially or vertically  
347 translocated in the stem (Hagemeyer, 1993). Compartmentalization of elements between heartwood  
348 and sapwood may also affect their distribution within the stem. The same is true of the seasonal and  
349 spatial variability in the tree micro-environment that may influence the distribution of elements

350 within the stem (Kirchner et al., 2008). Consequently, it is necessary to identify the most  
351 appropriate TEs to reflect historical variations in environmental contents. A number of elements  
352 have been included in previous studies (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn,  
353 Mo, Ni, Sr, Pb, V and Zn) while As, Cd, Cu, Hg, Pb and Zn are the most commonly analysed  
354 (Kirchner et al., 2008; Rauch et al., 2009; St. Laurent et al., 2011; MacDonald et al., 2011; Smith et  
355 al., 2014; Wright et al., 2014; Mihaljevič et al., 2015; Maillard et al., 2016; Odabasi et al., 2016). In  
356 this study, 19 elements were analysed on tree rings (Al, Ca, Fe, K, Mg, Mn, P, As, Cd, Co, Cr, Cu,  
357 Hg, Mo, Ni, Pb, Sb, V, Zn), and they were among the most commonly encountered and were  
358 considered suitable for dendrochemical studies (Odabasi et al., 2016). Furthermore, they constitute  
359 the main metallic pollutants emitted by the industrial port zone of Fos (IREP, 2016).

360 In order to show the relevance of the data and the historical variations measured, Figures 4 and S2  
361 provide the contents of elements measured over time in poplar rings sampled from the industrial  
362 plot in comparison with variations observed at a background site (rural plot) for all the elements  
363 considered in this study. For As, Cd, Co, Cu, Mo, Sb, Zn, Al, Ca, Mg and K concentrations were  
364 significantly higher in the poplar sampled on the industrial plot compared to the rural plot. In  
365 addition, while low variations were observed in the rural plot, significant temporal variations were  
366 observed on the industrial plot for many TEs. An increasing trend between 1975 and 2015 was  
367 observed for Cr, Ni, Pb, As, V, Al and Fe. Conversely, a decrease of Cd, Hg and Zn concentrations  
368 was measured over the same period. Indeed, on the industrial plot, the concentrations increased by  
369 213 % and 121 % respectively for Al and As between 1975 and 2015 and decreased by 25 and 17 %  
370 respectively for Cd and Zn over the same period. Thus, the increase of the TE bioaccumulation in  
371 tree rings matched the intensification and diversification of the industrial activities in Fos-sur-Mer,  
372 characterized by an increase of the site number in the area between 1975 and 2015. While the  
373 creation of the autonomous port of Marseille officially began in 1966, the main industrial sites were  
374 set up between 1965 and 1990, including petrochemical, chemical and the steel industries (Figure



375 S4). The industrialisation of the area has been accompanied by a significant increase of maritime  
376 and road traffic and has promoted the urbanisation of the territory, thus multiplying the atmospheric  
377 emission sources of metals and metalloids (Sylvestre, 2016). On the contrary, a reduction in  
378 industrial emissions of Cd, Hg and Zn has been observed at European levels since the 1990s, in  
379 connection with the technical progresses made in the industrial processes (Queguiner et al., 2009 ;  
380 Harmens et al., 2007), which was confirmed as well for the Fos area by the present observed  
381 decrease in TE concentrations in tree rings. Similarly, the temporal variability of saw-tooth zinc was  
382 consistent with the French pollutant emissions register (IREP, 2016). Furthermore, strong  
383 correlations were observed between the reported emissions in French pollutant emission register  
384 (IREP, 2016) and the bioaccumulation of TE in the poplar rings collected on the industrial plot for  
385 the period 2003-2015; this is notably the case for V ( $R^2 = 0.85$ , p-value < 0.05), Cd ( $R^2 = 0.92$ , p-  
386 value < 0.01), Sb ( $R^2 = 0.81$ , p-value < 0.05), As ( $R^2 = 0.90$ , p-value < 0.05 ) or Hg ( $R^2 = 0.77$ , p-  
387 value < 0,05). Therefore, the high concentrations and their variations measured at the industrial site  
388 in relation to the background site, matching the industrialisation of the area, highlights the relevance  
389 of the dendrochemistry to study the historical variations of TEs in industrialised regions such as the  
390 Fos industrial area.

391 A more detailed observation of the temporal variability of the measured concentrations in the poplar  
392 rings sampled from the industrial field revealed common trends between the different elements  
393 studied. During the period 1986-1988, concentrations increased for all elements except for Cu and  
394 As. Three other significant peaks for many TEs occurred, one for the period 1977-1979 for Cd, Cr,  
395 Mo, Pb and V, the second between 1992 and 1994 for all elements except Hg and the last one  
396 between 2007 and 2009 with significant increases measured for Cu, Cr Ni, Mo and As. These peaks  
397 may correspond to high industrial production leading to larger emissions or industrial accidents  
398 (ARIA, 2017). For example, between 1986 and 1988, the bioaccumulation of many TEs such as Mo  
399 or Hg may have increased as the consequence of the establishment and commissioning of the

400 chemical plants starting in 1986. Similarly, between 2007 and 2009, an increase in Cu, Cr, Ni, Mo  
401 and As concentrations was observed that may have been caused by an increased in industrial  
402 accidents leading to atmospheric emissions of TEs with nearly 40 industrial accidents recorded  
403 during this period for the industrial harbor of Fos against only 9 industrial accidents on average  
404 recorded over a period of 3 years since 1975 (ARIA, 2017). Thus, the bioaccumulation of TEs in  
405 tree rings reflected the major impact of emissions from the industrial activities of Fos (Sylvestre et  
406 al., 2017).

407 Figure 5 provides a principal component analysis (PCA) carried out on concentrations measured in  
408 poplars on the rural and industrial plots and ranked by decade. The first two axes of this PCA  
409 explained 52 % of the variance. The first axis, representing 27 % of data variability, allowed for  
410 distinguishing Hg and Pb from other TEs with a strong influence of As, Mo, Al and V. The positive  
411 values of this axis were related to the Pb and Hg contents. Axis 2, which represents 25 % of data  
412 variability, differentiated two groups with, amongst others, Cd, Zn, Hg, Mg, Ca or K anti-correlated  
413 to Fe, Cr, Ni, Pb or P. The distribution of the concentrations observed in tree rings and grouped by  
414 decade highlighted the influence of the two axes. Firstly, axis 1 allowed a differentiation in space  
415 ( $PC1 = 0.88$  and  $-0.40$  for POP\_R and POP\_I respectively), industrial plots being mainly correlated  
416 to As, Mo, Al, V, Ni, Cr, or Fe. This reveals the important exposure of these plots over time as  
417 compared to the rural plots. Secondly, the concentrations measured in poplars followed a  
418 distribution over time along axis 2. Indeed, the results showed a similar succession along the axis of  
419 the decades whichever plot considered, rural or industrial. However, the positioning of decades of  
420 the industrial plot showed greater variations than on the rural plot on the PCA plot. Thus, until the  
421 end of the 1990s, the main TEs impacting this area were Zn, Cd, Hg and to a lesser extent Cu and  
422 Sb. After the 2000's, the trees have preferentially bioaccumulated Fe, Cr, Ni, V, As and Al targeting  
423 the iron and steel industry, one of the main emitting activities currently on the Gulf of Fos (IREP,  
424 2016). These results confirmed the temporal variability of TE concentrations observed in Figure 4

425 and S2 and at the European level these previous decades (Pacyna et Pacyna, 2001; Harmens et al.,  
426 2007; EU, 2014).

427 Linear regressions were applied to TEs (Figure S3), aiming at specifying the TEs having a similar  
428 behaviour in the industrial area (Reimann et al., 2008). These linear regressions illustrate the  
429 association of Fe, Al, Cr, V, Ni and Pb variables ( $R^2 > 0.5$ , p-value  $< 0.001$ ) which may be related to  
430 the iron and steel industry. Indeed, although the importance of Fe and Al is often attributed to soil  
431 dust inputs (Agnan et al., 2015, Liu et al., 2016), high levels measured in poplar rings sampled in  
432 the industrial plot and the large variations observed (Figure 4 and S2) clearly highlighted the steel  
433 activities and possibly ore terminals as predominant contributors. According to the PCA analysis  
434 (Figure 5), Al appeared to be influenced by other important sources that could be the aluminate  
435 cement plant which could contribute to the bioaccumulation of Al. Moreover, Cd and Zn were  
436 significantly correlated ( $R^2 = 0.24$ , p-value  $< 0.005$ ) confirming the results of the PCA; these are  
437 mainly issued by petroleum refineries (Sylvestre et al., 2017). Finally, a strong correlation was  
438 observed between Sb, Cu and Pb (Sb-Pb and Sb-Cu  $R^2 = 0.46$  and  $0.44$  respectively, p-value  $<$   
439  $0.005$ ) whose emissions are partly linked to past and current emissions from road traffic (Sylvestre  
440 et al., 2017, Hjortenkrans 2008).

441

#### 442 **4. Conclusion**

443 The main objective of this study was to evaluate the extent of exposure of the territory to  
444 atmospheric emissions of the industrial harbor of Fos through a dendrochemical approach. This  
445 method has been used for several years to measure the root and/or foliar exposure to TEs over time  
446 (Smith et al., 2014, Maillard et al., 2016; Odabasi et al., 2016). Indeed, the dendrochemical  
447 signature allows for monitoring of historical changes in exposure levels to TEs, although there is no  
448 current consensus on the tree species that are the most suitable for dendrochemical studies. This  
449 dendrochemical study carried out on two tree species, *Pinus halepensis* and *Populus nigra*, firstly

450 highlighted the relevance of using poplar in dendrochemical studies for the measurement of the  
451 atmospheric pollutant exposure because it efficiently discriminated between the industrial, urban  
452 and the rural areas. This result points to a foliar transfer that has also been observed in many  
453 research studies (Al-Khasman et al., 2011, Liu et al., 2013, Xiong et al., 2016, Shahid et al., 2017)  
454 for ultrafine particles emitted by industrial activity.

455 The comparison of three sites, a rural plot (Grans, FOS\_R) located more than 20 km from known  
456 sources of industrial emissions, a plot located in urban area (Fos-sur-Mer, FOS\_U) and finally an  
457 industrial plot located in the industrial harbor of Fos (FOS\_I), clearly highlights the exposure of the  
458 residential areas situated on the periphery of the industrial-port zone, especially for the main TEs  
459 emitted by the industries of the area (Cd, Co, Cu, Mo, Sb, Zn, Al) (IREP, 2016). The temporal  
460 variability of TE concentrations measured in tree rings did not allow for identifying and dating the  
461 contamination events with certainty, although trends emerged with similar variations of some TEs  
462 over short periods of time that may indicate a change in exposure sources with an exposure mainly  
463 marked by Zn, Cd, Hg (petroleum refineries) between 1975 and 1990 and by Al, As, Cr, Ni, V, Fe  
464 (steel and metallurgical activities) after the 2000s. As a consequence, it also highlighted  
465 the evolution of industrial processes over time with a reduction of the most toxic TE concentration  
466 (Cd, Hg, Pb) at the atmospheric level. This study helped to provide information on the evolution of  
467 industrial, road and even urban emissions of this territory, which is home to one of the largest  
468 industrial harbors in France and Southern Europe. Thus, this work has endeavoured to highlight the  
469 relevance of dendrochemical methods for evaluating the exposure to air pollution over time.

470

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475

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