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

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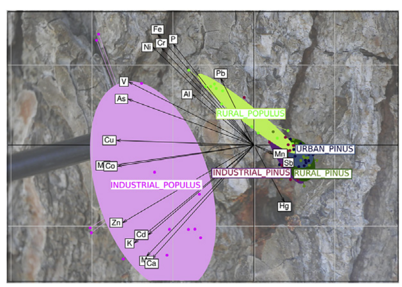
HIGHLIGHTS

- Element contents in tree rings highlight the historical variations in air pollution.
- Urban area are impacted by industrial and road emissions of the industrial harbour.
- Concentration measured in tree rings shows the increasing of industrialisation.
- Poplar is a more relevant model than pine for dendrochemical studies.

GRAPHICAL ABSTRACT



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ABSTRACT

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

To perform the study, two tree species have been selected, *Pinus halepensis* and *Populus nigra*, on a rural plot located roughly 20 km away from the industrial harbour, an urban plot located in the city of Fos-sur-Mer and an industrial plot. Our study indicated that poplar was a more relevant model for the dendrochemical studies, exhibiting a higher bioaccumulation capacity than pine except for Hg, Sb and Mn. Moreover, thanks to this work, we observed significant exposure of the trees in the urban and industrial areas to As, Cd, Co, Cu, Mo, Sb, Zn, Al, Ca, and Mg, highlighting the exposure of the territory and populations living in the vicinity of the industrial harbour. The temporal variability of the concentrations measured in the tree rings corresponds to the increasing industrialisation of the territory as well as to the evolution of the industrial processes. Thus, this project highlighted the exposure of the Gulf of Fos to atmospheric emissions (industrial, road and urban) of the industrial harbour as well as the changes over time. It also pointed out the relevance of using dendrochemistry to measure atmospheric exposure of metals and metalloids and its temporal variability.

1. Introduction

The high levels of metals and metalloids in the environment are of major concern due to their long-term persistence and their

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toxicity, even at low concentrations. The trace elements (TEs) such as As, Cd, Cr, Co, Cu, Hg, Mo, Ni, Pb, Zn pose a potential threat to ecosystems (Tremel-Schaub and Feix, 2005). These pollutants originate from human activities, notably from past and current industrial activities. Over recent decades, the improvements of industrial processes have permitted the reduction of emissions in the air, aquatic ecosystems and soils. This has been made possible, first by the combination of technological innovation and financial markets, allowing for recycling of products that, in the past, were released into the atmosphere and, secondly, by applying regulatory constraints. However, air pollution is still a cause of concern in many parts of the world and mainly in highly industrialised areas.

Due to the environmental and sanitary impacts of these industrial emissions, their atmospheric concentrations are being monitored. Studies on the levels and the spatial distribution of the pollutants are necessary to determine their origin and the associated risks. However, monitoring pollutants using active air samplers over several sites in order to measure spatial variations is currently difficult due to technical, physical and economic requirements. Indeed, their simultaneous use on several sites can cause difficulties to calibrate in a homogeneous way all the devices, which can furthermore be impacted by problems of operation leading to the stop of the continuous measurements and the loss of data. Moreover, it requires a significant economic investment relative to the cost of this type of device. The analysis of TE concentrations in lichens (Agnan et al., 2015; Ratier et al., 2018), leaves and needles (Aboal et al., 2004; Lehndorff and Schwark, 2010; Sun et al., 2010) and/or their bark (Catinon et al., 2009; Fujiwara et al., 2011; Gueguen et al., 2012) have been widely used as alternative and low-cost methods for spatial monitoring. Although sampling of tree tissues (needles, leaves or bark) or lichens can be appropriate for determining spatial distribution of TE, it only provides information on current atmospheric levels, and cannot provide temporal or historical variations of TEs, unlike dendrochemistry. Recent studies have been carried out to detect diffuse TE pollution in soils using dendrochemical methods (St Laurent et al., 2011; Cui et al., 2013; Smith et al., 2014; Maillard et al., 2016). Furthermore, the research work of Wright et al. (2014) and Odabasi et al. (2016) demonstrated that accumulation of metal/loid contaminants (As, Cr, Fe, Mo, Ni, V, Cu, Pb, Sb, Sn, and Hg) in tree rings occurred through the foliar pathway, allowing for characterization of atmospheric exposure (Wright et al., 2014; Odabasi et al., 2016). Thus dendrochemical data are of great scientific interest to determine the temporal variability of exposure to air pollutants, and to evaluate the effectiveness of investments in environmental processes to reduce industrial, urban and transport emissions, based on the hypothesis that the level of pollutants in tree rings reflect, to a certain extent, the chemical signal in the environment during ring formation (Smith et al., 2014), either through root or foliar exposure.

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

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

2. Materials and methods

2.1. Study area

This study is focused on the Gulf of Fos (South of France), which hosts the largest industrial port zone in France and Southern Europe including several heavy industry activities (refining and petrochemical industries, chemistry, coke production and steel industries, cement plant, household and industrial waste incinerators) and world-leading maritime terminals (containers, ore, oil, gas, cereals) (Fig. 1). We chose three different areas, representative of the main human environments and based on preliminary field studies and most recent results (Austruy et al., 2016; Dron et al., 2016). An industrial area located in the industrial harbour of Fos (FOS_I) and another one in the urban area of Fos-sur-Mer (FOS_U) were selected. In addition, a control rural plot (FOS_R), located in Grans more than 20 km north of Fos-sur-Mer and subjected to a north-westerly prevailing wind, limiting the influence of atmospheric emissions from the industrial harbour, was used to assess the regional background (Fig. 1).

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

2.2. Tree core and soil sampling

Two tree species, *Pinus halepensis* and *Populus nigra*, were chosen due to their high abundance in the study area as well as their use in previous dendrochemical studies (Sheppard et al., 2007; Odabasi et al., 2016). For each plot, six among the oldest healthy trees of both species were selected and sampled in March 2016, except on the urban plot (FOS-U) where no suitable poplars were found. Tree cores were collected at chest height using a 10 mm-Pressler auger. In addition, phytoscreening cores of 5 mm were collected on the most external rings of trees, as described in the Pollution Investigation using Trees (PIT) guide (Balouet and Chalot, 2015), on the different plots to sample the bark. The history of each plot was determined, and the trees were characterized and mapped. The circumferences of the trees ranged from 1.3 to 2.5 m. Ages of the sample trees were determined by counting the annual rings using a magnifying glass, they were between 26 and 70-year-old.

For each tree sample, composite soils were collected the same day using a manual auger at 0–10 cm depth. The composite soil sample was carried out from five sub-samples of equal amounts

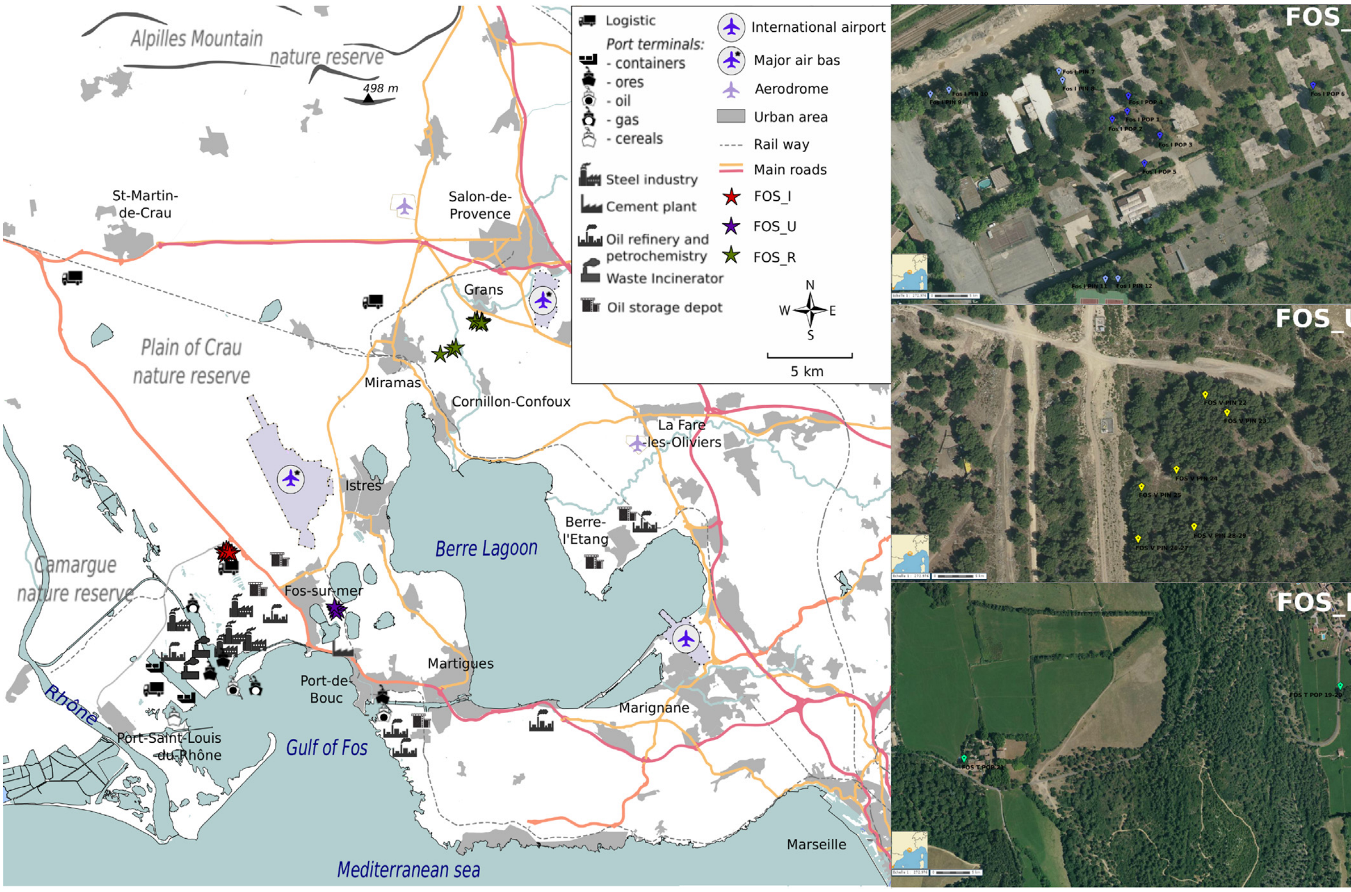

Fig. 1. Location of study plot composed of rural (FOS_R), urban (FOS_U) and industrial area (FOS_I).

(250 g) collected less than 50 cm from the tree trunk. It was produced by careful mixing and quartering of the five sub-samples to obtain the composite sample of approximately 500 g according to AFNOR standard NF ×31-100. After pH determination, the analyses of trace and major element concentrations were performed.

2.3. Sample pre-treatment and analysis

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

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

The complete mineralization of the ring and bark samples was performed according to a modified version of Barbaste's method (2004). 0.1 g of each ring or bark sample crushed to fine particles using a ball mill for 2 min 30 s at a frequency of 25 Hz (Retsch MM 400 equipped with zirconium oxide beads and capsules) were introduced into a polyethylene (LDPE) tube with 3 mL of 67% HNO_3. The tubes were placed in a heating block and heated at 80 °C for 1 h 30.1 mL of 30% H_2O_2 was added and the tubes replaced on the heating plate at 60 °C for 30 min then at 80 °C for 3 h. Each of these samples was then filtered at 0.45 μm with syringe filters in cellulose acetate. The eluate was placed in a polyethylene tube and diluted with 20 mL of ultrapure water. A certified sample, ERM CD 281 (Rye-grass), and a blank test were analysed for each series of mineralization. Pending the analysis, the samples were stored at 4 °C. The analysis of trace and major element concentrations (Al, Ca, Fe, K, Mg, Mn, P, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn) on the core and bark samples was performed by ICP-MS (Perkin-Elmer Nexion 300×). The results of the standard samples showed concentrations with an error rate of less than 20% compared to the theoretical concentrations.

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

For analysis of trace and major element pseudototal concentrations (Quevauviller, 1998), the composite samples were dried in an oven at 40 °C until a loss of mass of less than 5% in 24 h was obtained. The dry samples were then crumbled and sieved to recover the fraction less than 2 mm. A sub-sample (5 g) was crushed in an agate mortar to fine particles of less than 100 μm and used for the analysis of TEs (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn) and major elements (Al, Ca, Fe, K, Mg, Mn, P). 0.1 g of each soil sample crushed to fine particles were mineralized with 6 mL of aqua regia (1/3 HNO_3 and 2/3 HCl, AFNOR standard NF ISO 11466) in a microwave oven (March 5 CEM). After adding 4 mL of ultrapure water, the extracts were filtered with 0.45 μm cellulose acetate filters. The samples were diluted by a factor of 20 before analysis by inductively coupled mass spectroscopy (ICP-MS). For quality control, a blank test and certified standard, ERM-CC141, were included in each series of analyses. The results of the standard samples showed concentrations with an error rate of less than 20% compared to the theoretical concentrations.

2.3.3. Determination of TE bioavailable concentrations of soils

The use of DTPA to evaluate the bioavailability of TE in calcareous soils has been the subject of numerous publications (Leggett and Argyle, 1983; Chaignon, 2001) and is now recognised (AFNOR standard NF ×31-121). The extraction solution consists of 0.005 M diethylene triamine pentaacetic acid (DTPA), 0.1 M triethanolamine (TEA) and 0.01 M $CaCl_2$, the pH should be maintained at 7.3. The presence of DTPA and $CaCl_2$ in the extraction solution prevents excessive $CaCO_3$ dissolution and significant metal release (Chaignon, 2001). Thus, only the soluble and easily exchangeable fraction of TEs was extracted. 2.5 g of soil sieved to 2 mm was introduced into 5 mL of the extraction solution. The mixture was stirred for 2 h at 120 rpm at room temperature. The pH was measured in the suspension and the extracts were separated from the solid residue by centrifugation at 2300*g* for 10 min (Megafuge 40, Thermo Scientific). The supernatant was filtered on a 0.45 μm filter of cellulose acetate previously rinsed with 5 mL of ultrapure water. For each analysis series, a blank was prepared. Analysis of the bioavailable fraction of TEs was performed by ICP-MS.

2.4. Statistical analysis

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

3. Results and discussions

3.1. Pseudototal and bioavailable concentrations in soils

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

Table 1 presents the DTPA-extractable TE fraction, which represents the easily exchangeable TE fractions of the soil, complexed to the organic matter or adsorbed to the oxides of Fe, Al and Mn (Gis Sol, 2011). The soils of the area were slightly alkaline (pH = 7.66 ± 0.39, 7.48 ± 0.25 and 7.50 ± 0.23 respectively for rural, urban and industrial areas) responsible for a low mobility of most of the TEs, which did not exceed 5% of the pseudototal concentration or were very low with values close to the percent or even the thousandth for As, Cr, Co, Mn, Mo, Ni, Sb and V. On the contrary, important exchangeable fractions were measured for Cd (between 21.6 and 23.5%) and to a lesser extent for Cu, Pb and Zn, of which the DTPA-extractable fraction represented between 3 and 10% of the pseudototal fraction. This can be explained by the strong affinity of Cu and Pb for dissolved organic matter (Komarek et al., 2008; Kelepertzis et al., 2015; Safari et al., 2015). Indeed, Wu et al. (2002) found that a high pH favours the dissolution of humic acids and

Table 1
Pseudototal and bioavailable (DTPA extraction) concentrations of metal (oid)s and major elements in soil sampled on the different plots, rural (FOS_R), urban (FOS_U) and industrial area (FOS_I) (n = 6).

		FOS_R		FOS_U		FOS_I	
		Pseudototal	DTPA (%)	Pseudototal	DTPA (%)	Pseudototal	DTPA (%)
Al	g/kg	23.86 ± 2.61	0.0	16.79 ± 2.03	0.0	19.40 ± 1.29	0.0
Ca		75.16 ± 22.24	0.0	107.72 ± 17.85	0.0	76.13 ± 15.20	0.0
Fe		18.76 ± 3.46	0.0	10.83 ± 0.73	0.0	19.81 ± 4.19	0.0
Mg		3.72 ± 0.58	0.0	2.88 ± 0.24	0.0	4.21 ± 0.21	0.0
P		1.51 ± 0.28	0.0	1.19 ± 0.17	0.0	1.20 ± 0.23	0.0
K		5.61 ± 0.98	0.0	4.18 ± 0.28	0.0	5.09 ± 0.44	0.0
As	mg/kg	9.33 ± 1.38	0.3 ± 0.1	7.72 ± 2.18	0.4 ± 0.0	7.43 ± 2.67	0.6 ± 0.3
Cd		0.21 ± 0.06	21.6 ± 5.7	0.38 ± 0.15	23.5 ± 2.3	0.79 ± 0.19	23.1 ± 5.2
Cr		75.95 ± 4.74	0.0	60.00 ± 1.26	0.0	92.94 ± 16.38	0.0
Co		10.07 ± 1.28	0.5 ± 0.1	5.75 ± 0.49	0.6 ± 0.2	8.27 ± 0.44	1.1 ± 0.2
Cu		13.86 ± 1.58	3.4 ± 0.7	8.84 ± 3.08	4.7 ± 1.1	22.07 ± 5.12	3.1 ± 0.3
Mn		1024.00 ± 328.91	1.0 ± 0.2	531.19 ± 13.35	1.3 ± 0.3	1011.35 ± 0.16	1.5 ± 0.8
Mo		0.86 ± 0.11	1.6 ± 1.3	0.63 ± 0.25	3.2 ± 0.8	1.86 ± 0.78	1.5 ± 0.6
Ni		31.13 ± 3.56	1.0 ± 0.4	19.98 ± 1.19	1.4 ± 0.5	38.32 ± 4.19	0.9 ± 0.3
Pb		25.92 ± 7.01	4.8 ± 2.0	24.95 ± 8.07	8.2 ± 0.9	30.98 ± 8.57	4.6 ± 1.9
Sb		0.51 ± 0.12	2.2 ± 0.8	0.63 ± 0.25	2.5 ± 0.3	0.81 ± 0.28	3.1 ± 1.4
V		81.07 ± 8.45	0.0	57.17 ± 1.06	0.3 ± 0.0	80.42 ± 9.62	0.1 ± 0.1
Zn		47.50 ± 11.97	4.6 ± 3.8	53.16 ± 15.37	8.1 ± 2.7	564.87 ± 94.03	8.3 ± 4.9

increases the dissolved concentration of metals due to the formation of metal-organic complexes in solution. Similarly, Zn and Cd can adsorb on labile components and easily soluble oxy/hydroxides (Rodrigues et al., 2013). These results indicated that a large part of the TE fraction for Cd, Cu, Pb and Zn was in a potentially phytoavailable form. The same trends were observed for the different soils (FOS_R, FOS_U, FOS_I), with the largest DTPA fraction observed in soils of urban plot for all these elements. These results appeared in line with previous studies carried out on calcareous soils of the Mediterranean region (Testiati, 2012; Safari et al., 2015; Austruy et al., 2016).

3.2. Phytoscreening using tree bark samples

Fig. 2 presents the trace and major element concentrations measured in tree bark samples of *Pinus halepensis* and *Populus nigra*

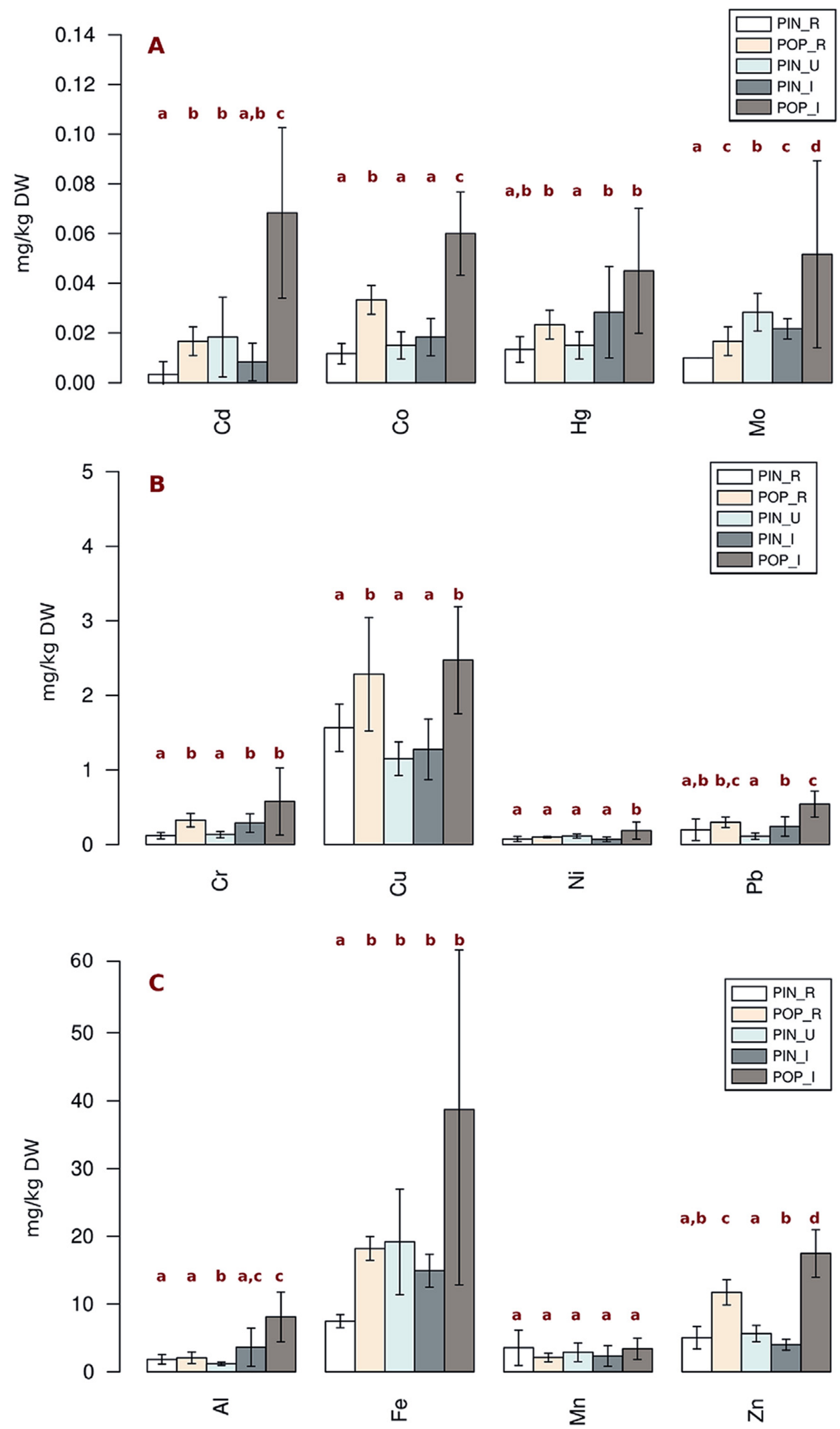

Fig. 2. Metal concentrations in the tree barks sampled on the *Pinus halepensis* (PIN) and *Populus nigra* (POP) of different study sites (Rural = R; Urban = U; and Industrial = I) (n = 6). Arsenic is inferior to detection limit.

sampled in the different plots. For the various sampled plots, the concentrations measured in the poplar bark were always higher, for a given plot, than the concentrations measured in the pine bark. In more detail, significantly higher concentrations were measured in the poplar for Cr, Cu, Zn, Cd, Co, Mo and Fe on the rural plots (FOS_R) and for Cu, Pb, Zn, Cd, Co, Mo and Ni on the polluted plots (FOS_I). These differences in accumulation capacities in various tree species have been widely documented (Migeon et al., 2009; Fantozzi et al., 2013; Baldantoni et al., 2014; Assad et al., 2016). For example, the works of Migeon et al. (2009) have showed that trees of the Salicaceae family can accumulate substantial amounts of Cd and Zn in their shoot parts, thus differing from a large range of other woody species. Most importantly, significant differences between the industrial and rural plots were observed, especially for poplars, for Zn, Cd, Co, Mo, Ni and Al. Similarly, for pines, significant differences existed for Cr, Mo and Fe between the industrial and rural plots and for Cd, Mo, Al and Fe between the urban and rural plots. At the same time, a strong heterogeneity was noticed in industrial samples while urban and rural ones were more homogeneous, showing the complexity and the diversity of industrial exposures at the local scale.

The FOS_I/FOS_R ratios ranged from 1.1 (Cu) to 3.9 (Al) for poplars and between 0.8 (Cu, Zn) and 2.0 (Al, Hg) for pines. The FOS_U/FOS_R ratios ranged from 0.6 (Al) to 3.1 (Cd) for pines (no poplar in the urban area). Indeed, the highest concentrations for TEs and major elements were measured in the urban and industrial plots and the lowest concentrations in the rural area except for Fe and Mn. Thus, these results highlighted the impact of atmospheric emissions from the industrial harbour of Fos on the chemical composition of tree barks collected in the industrial zone or in the nearby urban periphery. This is confirmed by previous research carried out in the area, which highlighted the impact of industrial harbour emissions on the environment (Austruy et al., 2016; Dron et al., 2016; Ratier et al., 2018) notably for the contents of Cr, Cd, Fe, Pb, Zn and Co. For these metals, the major sources of emissions in the area are the steel industry and road traffic emissions (Sylvestre et al., 2017). These results proved that TE concentrations measured in tree bark are suitable bioindicators of the metal content of soil and a relevant passive monitor of atmospheric pollution (Barbes et al., 2014; Zhai et al., 2016). Indeed, tree bark can provide reliable results for estimating long-term air pollution because its structure retains metals and metalloids for a long time (Berlizov et al., 2007), whereas leaves fall periodically.

3.3. Accumulation of TEs and major elements in tree rings

For all the elements considered in this study, the method used proved to be efficient in obtaining sufficient quantities of wood for the mineralisation and ICP-analysis. The data set included 4640 concentrations of elements measured over 232 3-year segments of tree rings.

Table 2 presents the average concentrations in tree rings and the statistical significance (p-value, Kruskal test) of data for each site and each tree species. On average, the most abundant TEs were Fe, Al, Zn and Mn. The lowest average concentrations were Hg, As, Sb, V and Cd. Large variations in concentrations were measured between trees of a same plot mainly in the industrial area for Al, Mg, Cd, Hg or Pb in pines and Al, Ca, Fe, Mg and K for poplars. Emissions in the industrial harbour are multiples, fixed and often channelled through chimneys up to 120 m high. Thus, the smoke plumes can affect two trees that are in geographical proximity in very different ways. The variability of TE contents in industrial zones can be explained by the micro-meteorological conditions, as well as the environment close to the stations (vegetation cover, buildings, nature of emissions, …) (Sylvestre et al., 2017; Ratier et al., 2018).

Table 2
Average metal (loid) and major element concentrations (mg/kg DW) in the tree rings of *Pinus halepensis* and *Populus nigra* of different study sites between 1975 and 2015. The statistical significance (n = 14, kruskal test) of plot for each tree species are also shown, in red p-value < 0.01.

	Average geometrric mean					P-value	
	PIN_R	PIN_U	PIN_I	POP_R	POP_I	PIN	POP
As	0.008	0.007	0.010	0.010	0.020	0.030	0.001
Cd	0.027	0.038	0.051	0.051	0.222	0.003	0.000
Cr	0.400	0.454	0.678	1.115	0.917	0.232	0.215
Co	0.022	0.016	0.018	0.053	0.096	0.042	0.003
Cu	0.751	0.728	0.680	1.099	2.167	0.408	0.000
Hg	0.007	0.006	0.007	0.005	0.006	0.889	0.036
Mn	3.253	7.845	3.662	2.653	3.566	0.006	0.154
Mo	0.109	0.152	0.113	0.444	0.915	0.030	0.000
Ni	0.124	0.169	0.252	0.419	0.460	0.030	0.491
Pb	0.134	0.118	0.154	1.257	0.392	0.056	0.000
Sb	0.013	0.009	0.016	0.006	0.008	0.001	0.006
V	0.025	0.021	0.026	0.067	0.073	0.178	0.662
Zn	5.618	4.809	5.566	6.523	27.53	0.073	0.000
Al	10.87	8.522	23.53	5.586	19.91	0.000	0.004
Ca	1713	1499	1543	1327	4421	0.763	0.000
Fe	20.01	28.23	20.63	93.23	63.75	0.009	0.048
Mg	147.7	129.6	202.5	143.1	424.7	0.018	0.000
P	51.22	43.96	39.29	73.24	77.90	0.162	0.748
K	672.0	630.2	688.5	740.9	4421	0.131	0.000

Furthermore, this variability, observed in different dendrochemical studies (Kirchner et al., 2008; Odabasi et al., 2016), may be the consequence of the physiological mechanisms related to element sequestration and allocation. Various analytical methods have been used to identify internal physiological and anatomical processes in wood (biomineralization, development of cracks or checks, heartwood/sapwood differentiation, …) that can affect cation concentrations, notably for major elements (Ca, K, Fe) (Smith and Shortle, 1996; Smith et al., 2014). On another more, intra-tree variations between the different rings were measured, with variations up to 200% in particular for Zn, Hg, Co or Cu, illustrating the variability in the exposure of individuals over time.

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

Fig. 3 shows a principal component analysis (PCA) performed on the average concentrations of major elements and TEs measured in poplar and pine rings sampled from the various plots. The first two axes of this PCA explained 62% of the variance. The first axis (40% of the variance) distinguished Mn, Sb and Hg from other chemical elements notably Cu, Co and Mo. The positive values of this axis were related to the Mn, Sb and Hg contents. The major elements were mainly distributed over the second axis (22% of the variance), the positive values of this axis being related to Mg, K and Ca. This analysis shows a distribution of data, in particular for poplars, as a function of the two axes. Indeed, the positioning of poplars on the industrial plot (on average, axis 1 = –4.47 and axis 2 = 1.41) compared to those of the rural plot (on average, axis 1 = –0.50 and axis 2 = –1.82) highlights the influence of many TEs on poplars in the industrial zone such as Zn, Cd, Mo, Co, Cu, As, V but also Ni, Fe and Cr for the most recent data (2014, 2011 and 2008). On the contrary, the pines of the different plots showed a widely homogeneous distribution (axis 1 = 1.9, 1.8, 1.7 and axis 2 = 0.3, –0.1, 0.2 respectively for PIN_R, PIN_U and PIN_I).

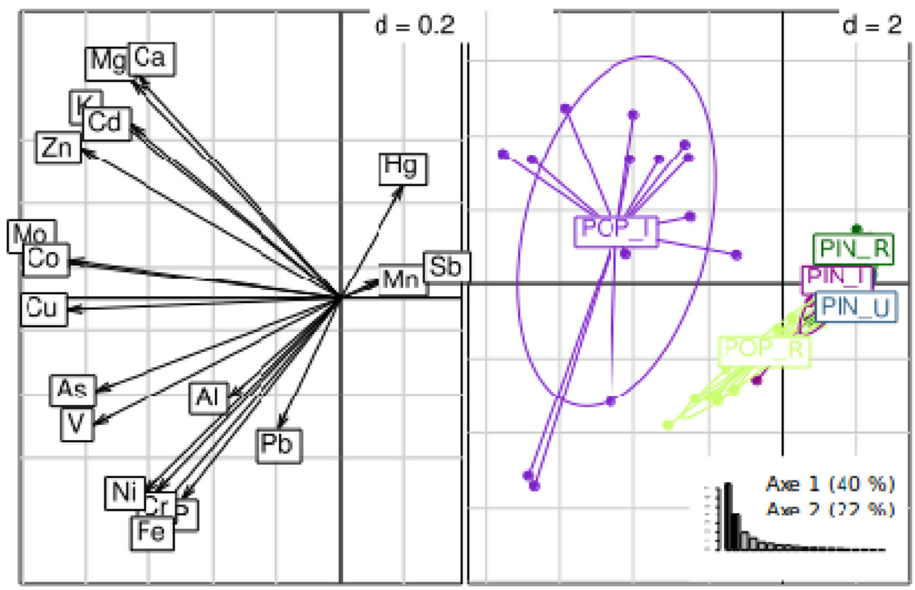

Fig. 3. Principal component analysis (PCA) on average trace and major element concentrations measured in each 3-year segments of *Populus nigra* (POP_I in purple, POP_R in light green) and *Pinus halepensis* (PIN_I in magenta, PIN_U in blue, PIN_R in dark green) (n = 67). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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

These results were confirmed by the average concentrations of TE and major elements measured over the period 1975–2015 in pines and poplars presented in Table 2. On the industrial plot, we found significantly higher levels of TE and major elements in poplars for Mg, K, Ca, Fe, Mo, Pb, V, Co, Cu, Zn, As and Cd. On the contrary, the pines had higher contents for Hg, Sb and Mn. A recent study (Arnold et al., 2018) had demonstrated the ability of pines to take up Hg by the stomata pathway and translocate it into tree rings via the phloem, in contrast to poplars for which the non-stomatal pathway appears to be predominant for Hg uptake. The higher bioaccumulation of TE in poplar rings may be the consequence of the surface morphology of poplar leaves and especially the density of trichomes, which could increase its potential to trap atmospheric pollutants and to take them up via the stomata of the epidermis. Several reports have shown that as leaf surfaces become rougher, the accumulation of TEs increase due to their greater ability to trap particles (Sawidis et al., 2011). In addition, poplars having lower leaf area may have higher rates of gas exchange per unit leaf area (Kloeppel et al., 2000).

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

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

The basic hypothesis of dendrochemistry is that the contaminants recorded in tree rings are not mobile and may reflect the historical changes of environmental levels (Watmough, 1999; Lebourgeois, 2010; Maillard et al., 2016; Odabasi et al., 2016). However, once absorbed, elements can bind to the xylem, phloem, or ray cells, or can continue to be mobile, being radially or vertically translocated in the stem (Hagemeyer, 1993). Compartmentalization of elements between heartwood and sapwood may also affect their distribution within the stem (Smith and Shortle, 1996). The same is true of the seasonal and spatial variability in the tree microenvironment that may influence the distribution of elements within the stem (Kirchner et al., 2008). Consequently, it is necessary to identify the most appropriate TEs to reflect historical variations in environmental contents. A number of elements have been included in previous studies (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Sr, Pb, V and Zn) while As, Cd, Cu, Hg, Pb and Zn are the most commonly analysed (Kirchner et al., 2008; Rauch and Pacyna, 2009; St. Laurent et al., 2011; MacDonald et al., 2011; Smith et al., 2014; Wright et al., 2014; Mihaljevič et al., 2015; Maillard et al., 2016; Odabasi et al., 2016). In this study, 19 elements were analysed on tree rings (Al, Ca, Fe, K, Mg, Mn, P, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn), and they were among the most commonly encountered and were considered suitable for dendrochemical studies (Odabasi et al., 2016). Furthermore, they constitute the main metallic pollutants emitted by the industrial port zone of Fos (IREP, 2016).

In order to show the relevance of the data and the historical variations measured, Fig. 4 and S2 provide the contents of elements

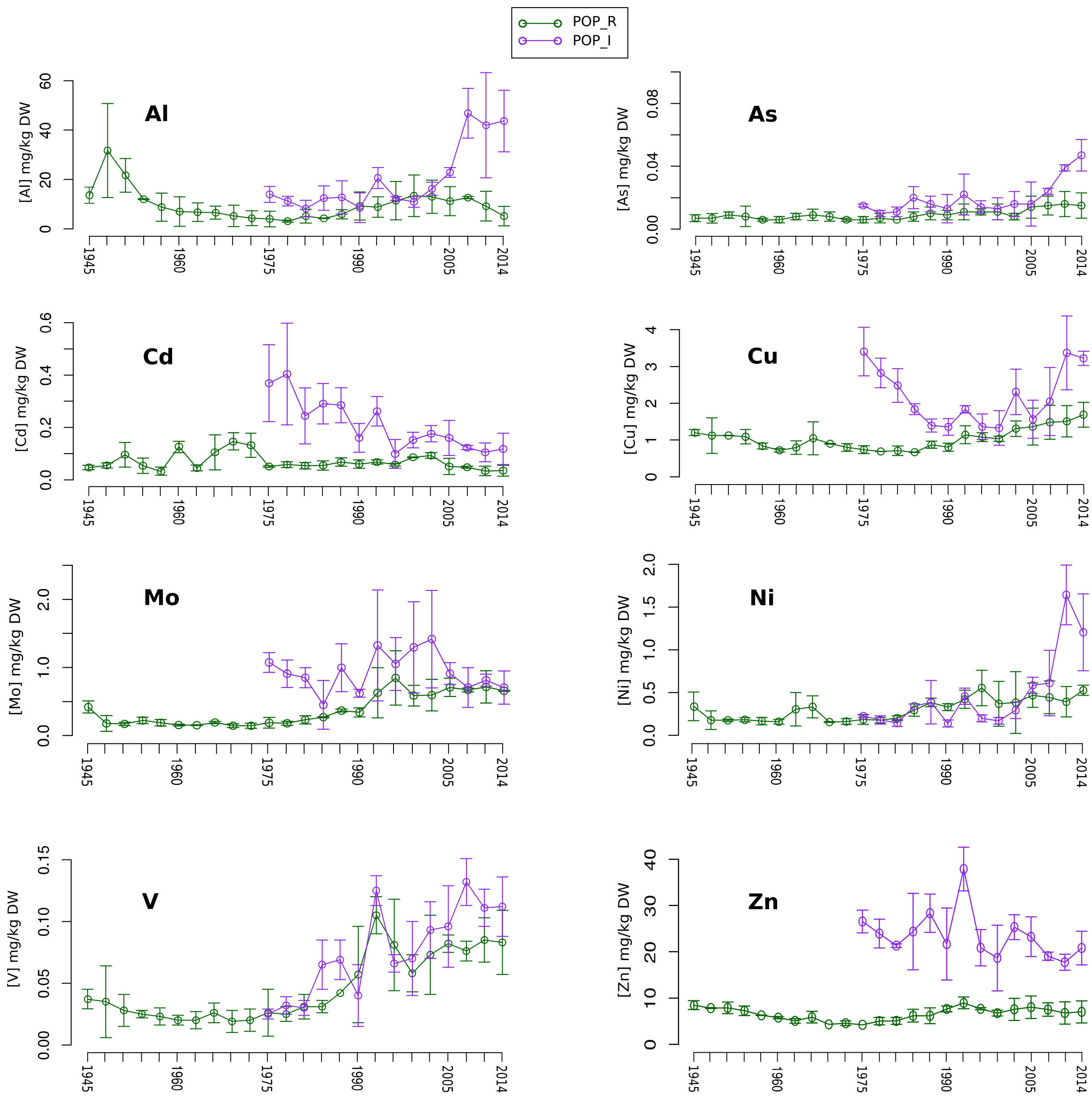

Fig. 4. Historical variations of Al, As, Cd, Cu, Mo, Ni, V et Zn measured in poplars. Green and purple markers-lines indicate background (POP_R) and industrial sites (POP_I), respectively (n = 6). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

measured over time in poplar rings sampled from the industrial plot in comparison with variations observed at the background site (rural plot) for all the elements considered in this study. For As, Cd, Co, Cu, Mo, Sb, Zn, Al, Ca, Mg and K concentrations were significantly higher in the poplar sampled on the industrial plot compared to the rural plot. In addition, while low variations were observed in the rural plot, significant temporal variations were observed on the industrial plot for many TEs. An increasing trend between 1975 and 2015 was observed for Cr, Ni, Pb, As, V, Al and Fe. Conversely, a decrease of Cd, Hg and Zn concentrations was measured over the same period. Indeed, on the industrial plot, the concentrations increased by 213 and 121% respectively for Al and As between 1975 and 2015 and decreased by 25 and 17% respectively for Cd and Zn over the same period. Similar analyses were performed for pines (Figure S3), and confirmed the lower TE contents of pines as compared with poplars. The high standard deviation did not allow us to conclude but trends are similar to those observed for poplars.

Thus, the increase of the TE bioaccumulation in poplar tree rings matched the intensification and diversification of the industrial activities in Fos-sur-Mer, characterized by an increase of the site number in the area between 1975 and 2015. While the creation of the autonomous port of Marseille officially began in 1966, the main industrial sites were set up between 1965 and 1990, including petrochemical, chemical and the steel industries (Figure S4). The industrialisation of the area has been accompanied by a significant increase of maritime and road traffic and has promoted the urbanisation of the territory, thus multiplying the atmospheric emission sources of metals and metalloids (Sylvestre, 2016). On the contrary, a reduction in industrial emissions of Cd, Hg and Zn has been observed at European levels since the 1990s, in connection with the technical progress made in the industrial processes (Queguiner et al., 2009; Harmens et al., 2007), which was confirmed as well for the Fos area by the observed decrease in TE concentrations in tree rings. Similarly, the temporal variability of saw-tooth zinc was consistent with the French pollutant emissions register (IREP, 2016). Futhermore, strong correlations were observed between the reported emissions in French pollutant emission register (IREP, 2016) and the bioaccumulation of TE in the poplar rings collected on the industrial plot for 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-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-value < 0.05). The high concentrations and their variations measured at the industrial site in relation to the background site, matching the industrialisation of the area, highlight the relevance of the dendrochemistry to study the historical variations of TEs in industrialised regions such as the Fos industrial area.

A more detailed observation of the temporal variability of the measured concentrations in the poplar rings sampled from the industrial field revealed common trends between the different elements studied. During the period 1986–1988, concentrations increased for all elements except for Cu and As. Three other significant peaks for many TEs occurred, one for the period 1977–1979 for Cd, Cr, Mo, Pb and V, the second between 1992 and 1994 for all elements except Hg and the last one between 2007 and 2009 with significant increases measured for Cu, Cr Ni, Mo and As. These peaks may correspond to high industrial production leading to larger emissions or industrial accidents (ARIA, 2017). For example, between 1986 and 1988, the bioaccumulation of many TEs such as Mo or Hg may have increased as the consequence of the establishment and commissioning of the chemical plants starting in 1986. Similarly, between 2007 and 2009, an increase in Cu, Cr, Ni, Mo and As concentrations was observed that may have been caused by an increase in industrial accidents leading to atmospheric emissions of TEs with nearly 40 industrial accidents recorded during this period for the industrial harbour of Fos against only 9 industrial accidents on average recorded over a period of 3 years since 1975 (ARIA, 2017). Thus, the bioaccumulation of TEs in tree rings reflects the major impact of emissions from the industrial activities of Fos (Sylvestre et al., 2017).

Fig. 5 provides a principal component analysis (PCA) carried out on concentrations measured in poplars on the rural and industrial plots and ranked by decade. The first two axes of this PCA explained 52% of the variance. The first axis, representing 27% of data variability, allowed for distinguishing Hg and Pb from other TEs with a strong influence of As, Mo, Al and V. The positive values of this axis were related to the Pb and Hg contents. Axis 2, which represents 25% of data variability, differentiated two groups with, amongst others, Cd, Zn, Hg, Mg, Ca or K anti-correlated to Fe, Cr, Ni, Pb or P. The distribution of the concentrations observed in tree rings and grouped by decade highlighted the influence of the two axes. Firstly, axis 1 allowed a differentiation in space (PC1 = 0.88 and −0.40 for POP_R and POP_I respectively), industrial plots being mainly correlated to As, Mo, Al, V, Ni, Cr, or Fe. This reveals the important exposure of these plots over time as compared to the rural plots. Secondly, the concentrations measured in poplars followed a distribution over time along axis 2. Indeed, the results showed a similar succession along the axis of the decades whichever plot considered, rural or industrial. However, the positioning of the decades of the industrial plot showed greater variations than on the rural plot on the PCA plot. Thus, until the end of the 1990s, the main TEs impacting this area were Zn, Cd, Hg and to a lesser extent Cu and Sb. After the 2000's, the trees have preferentially bioaccumulated Fe, Cr, Ni, V, As and Al targeting the iron and steel industry, one of the main emitting activities currently on the Gulf of Fos (IREP, 2016). These results confirmed the temporal variability of TE concentrations observed in Fig. 4 and S2 and at the European level these previous decades (Pacyna and Pacyna, 2001; Harmens et al., 2007; EU, 2014).

Linear regressions were applied to TEs (Figure S5), aiming at specifying the TEs having a similar behaviour in the industrial area (Reimann et al., 2008). These linear regressions illustrate the association of Fe, Al, Cr, V, Ni and Pb variables ($R^2 > 0.5$, p-

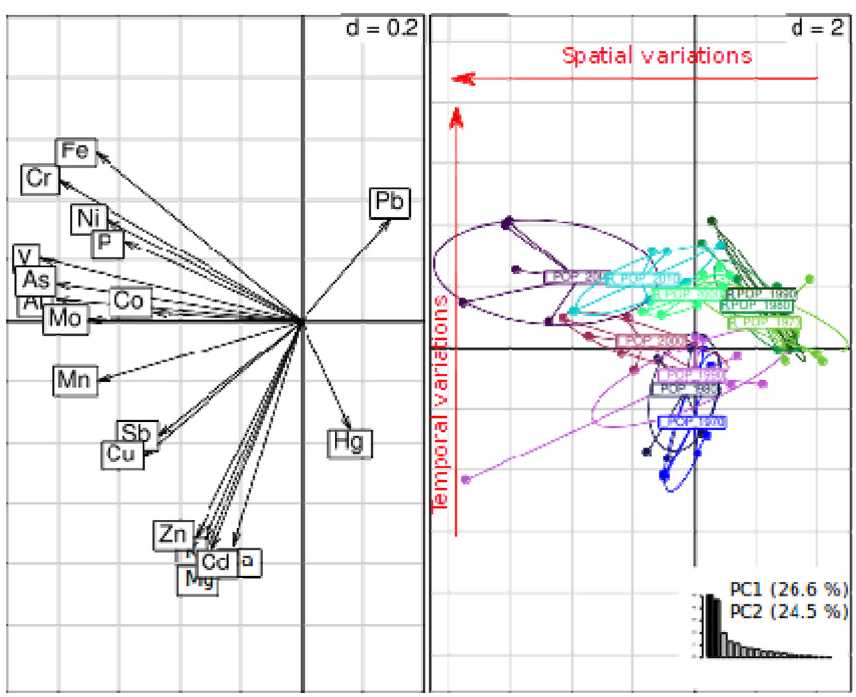

Fig. 5. Principal component analysis (PCA) on the metal and major element concentrations averaged by decades and measured in Populus nigra sampled in rural (POP_R) or industrial plots (POP_I) (n = 28). The left graph presents the distribution of the different variables (ETs and major elements) in the factorial design (PC 1 and 2). The right graph represents the observations in the same factorial design.

value < 0.001) which may be related to the iron and steel industry. Indeed, although the importance of Fe and Al is often attributed to soil dust inputs (Agnan et al., 2015; Liu et al., 2013), high levels measured in poplar rings sampled in the industrial plot and the large variations observed (Fig. 4 and S2) clearly highlighted the steel activities and possibly ore terminals as predominant contributors. According to the PCA analysis (Fig. 5), Al appeared to be influenced by other important sources that could be the aluminate cement plant which could contribute to the bioaccumulation of Al. Moreover, Cd and Zn were significantly correlated ($R^2 = 0.24$, p-value < 0.005) confirming the results of the PCA; these are mainly emitted by petroleum refineries (Sylvestre et al., 2017). Finally, a strong correlation was observed between Sb, Cu and Pb (Sb-Pb and Sb-Cu $R^2 = 0.46$ and 0.44 respectively, p-value < 0.005) whose emissions are partly linked to past and current emissions from road traffic (Sylvestre et al., 2017; Hjortenkrans, 2008).

4. Conclusions

The main objective of this study was to evaluate the extent of exposure of the territory to atmospheric emissions of the industrial harbour of Fos through dendrochemical approaches. These methods have been used for several years to measure the root and/or foliar exposure to TEs over time (Smith et al., 2014; Maillard et al., 2016; Odabasi et al., 2016). Indeed, the dendrochemical signature allows for monitoring of historical changes in exposure levels to TEs, although there is no current consensus on the tree species that are the most suitable for dendrochemical studies. This dendrochemical study carried out on two tree species, *Pinus halepensis* and *Populus nigra*, firstly highlighted the relevance of using poplar in dendrochemical studies for the measurement of the atmospheric pollutant exposure because it efficiently discriminated between the industrial and the rural areas. This result points to a foliar transfer that has also been observed in many research studies (Al-Khasman et al., 2011; Liu et al., 2013; Xiong et al., 2014; Shahid et al., 2017) for ultrafine particles emitted by industrial activity.

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.12.072.

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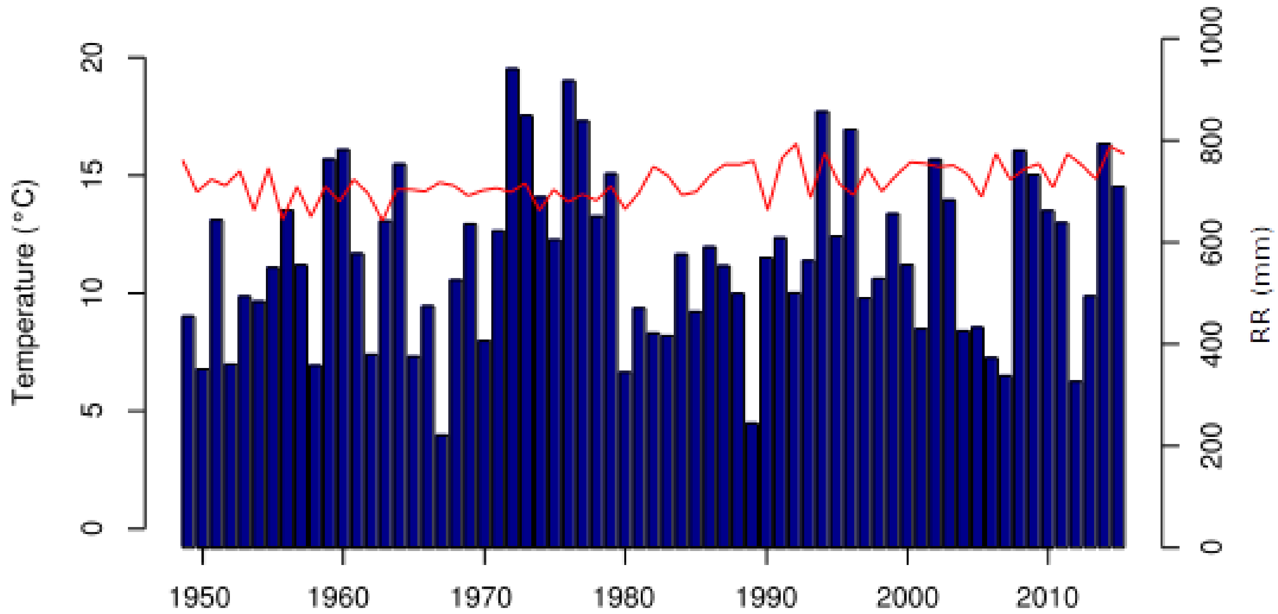

Figure S1: Average data of temperature (°C) and rainfall (mm) measured during the period 1949-2015 on the weather station of Istres (13) (METEOFRANCE data).

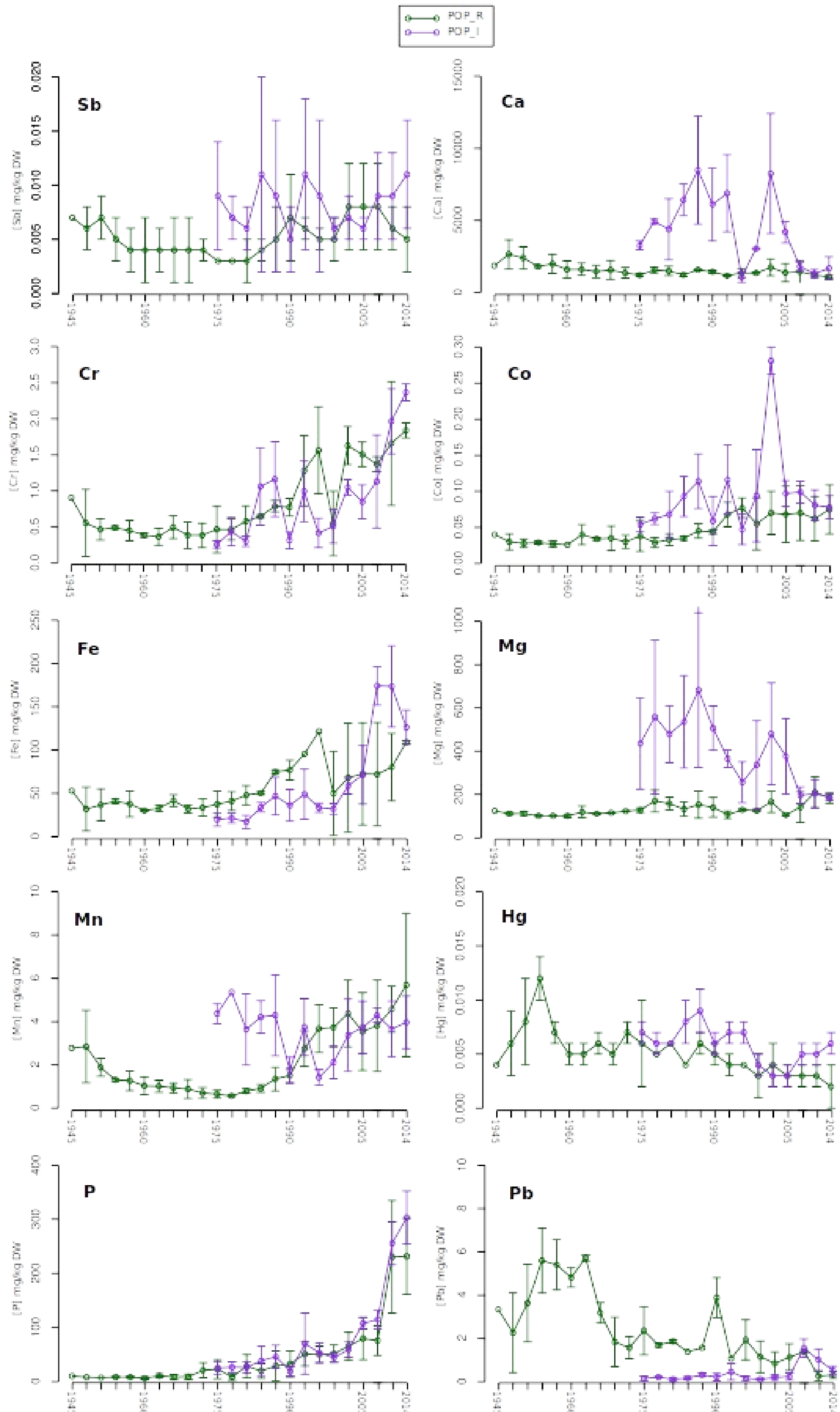

Figure S2: Historical variations of Sb, Ca, Co, Cr, Fe, Mg, Mn, Hg, P, Pb and Si measured in poplars. Green and purple markers-lines indicate background(FOS_R) and industrial sites (FOS_I), respectively (n=6). Histogramms represent the industrial site number.

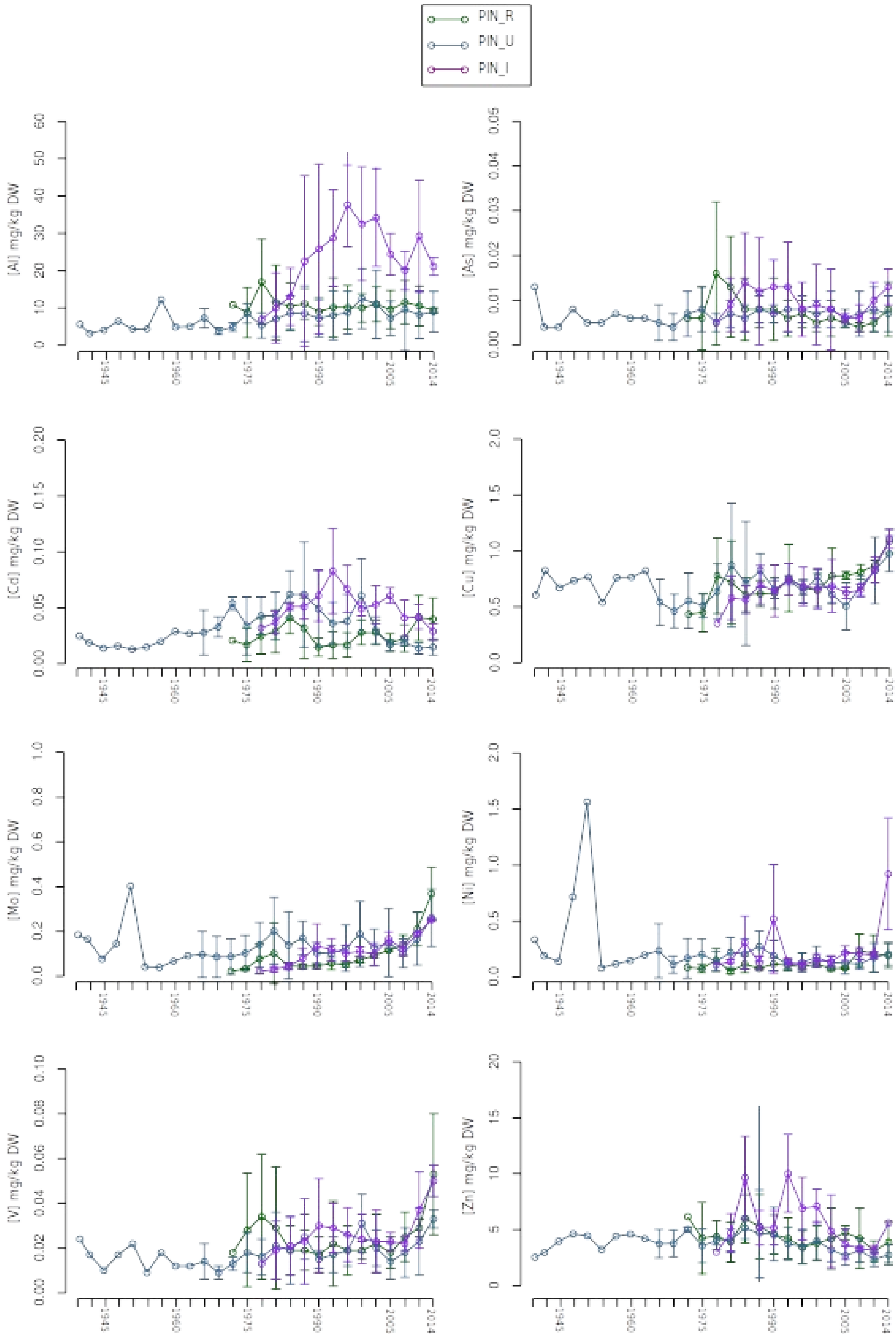

Figure S3: Historical variations of Al, As, Cd, Cu, Mo, Ni, V et Zn measured in pines. Green and purple markers-lines indicate background (POP_R) and industrial sites (POP_I), respectively (n=6).

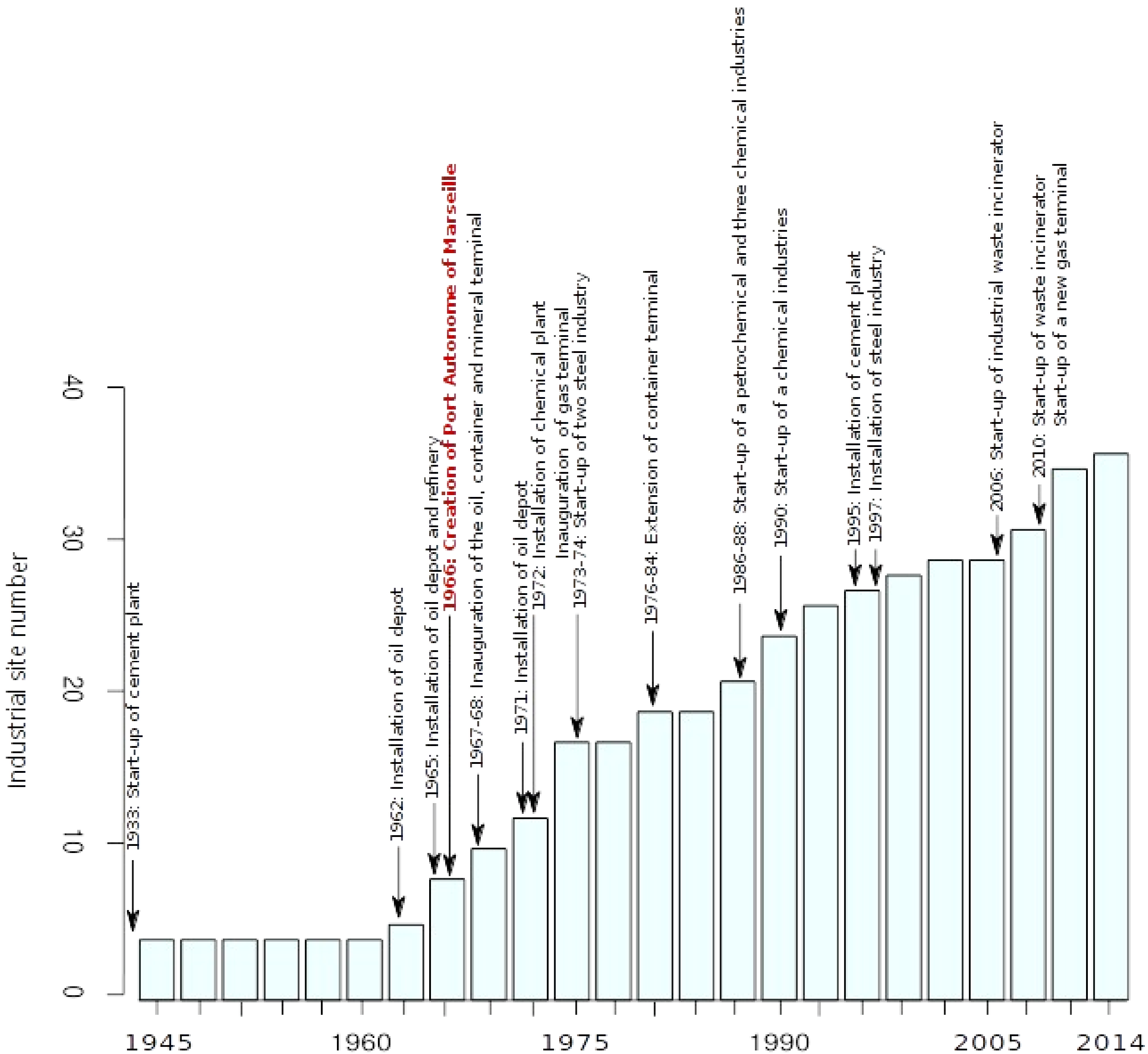

Figure S4: Chronology of establishment and commissioning of the main industrial sites and port terminals in the industrial port zone of Fos.

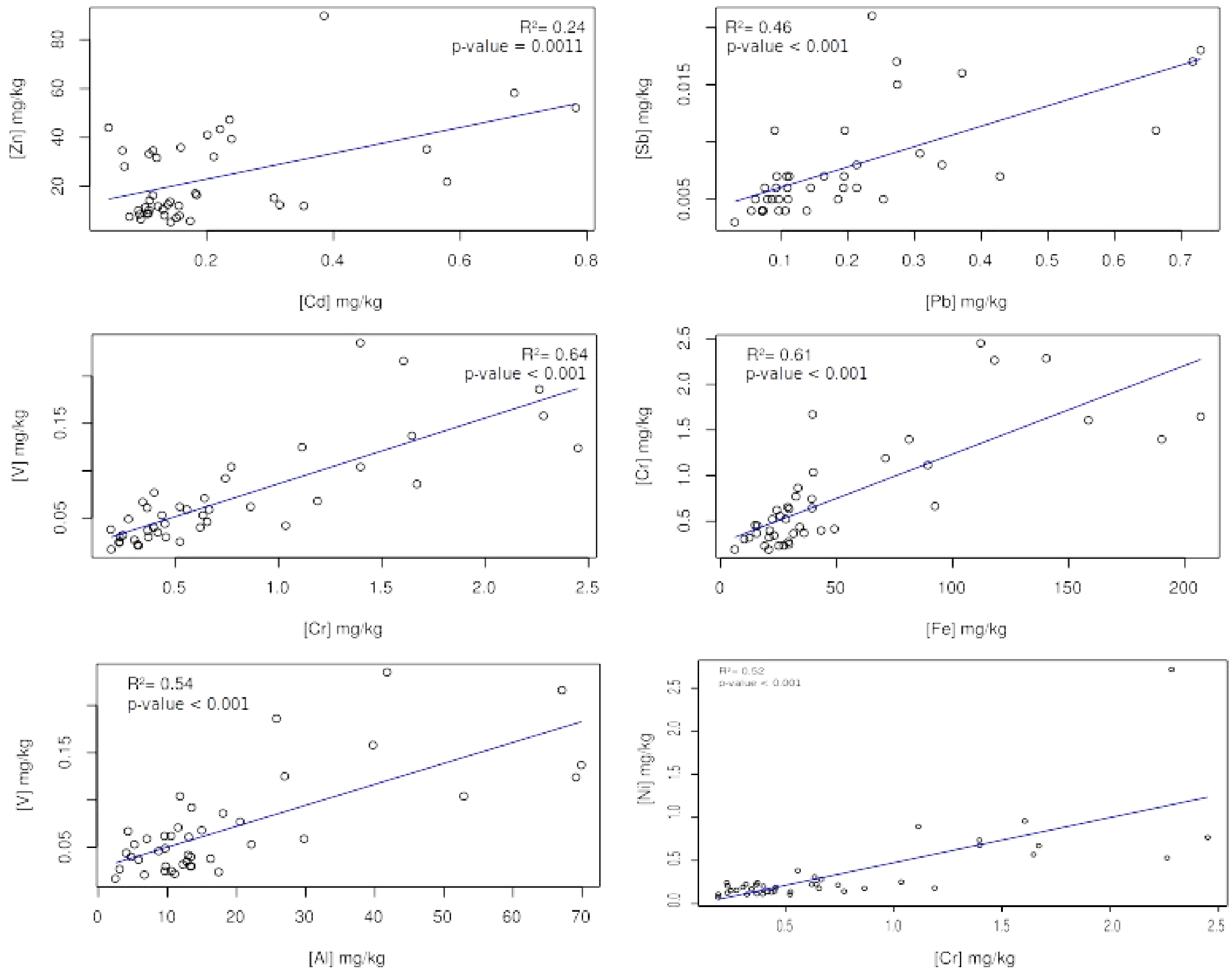

Figure S5: Linear regressions on metal concentrations measured in tree rings of poplars sampled in the industrial plot (n = 42).