



# Lichens as a spatial record of metal air pollution in the industrialized city of Huelva (SW Spain)<sup>☆</sup>

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## ABSTRACT

Huelva is a highly industrialized city in SW Spain hosting, among others, a Cu smelter, a phosphate fertilizer plant, a power plant, and oil refineries. This study aims to evaluate metal concentrations in lichens as bioindicators of atmospheric pollution in the impacted urban areas. *Xanthoria parietina* species from Huelva and nearby villages, as well as reference samples from remote, non-contaminated urban areas, were analyzed for trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, Sr, As, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Er, Tm, Yb, Lu, Pb, Th, U) using Inductively Coupled Plasma-Mass Spectrometry; and for major elements (Ca, K, Mg, P, and S) by Inductively Coupled Plasma-Optical Emission Spectrometry after acid digestion.

The metal composition of *X. parietina* exhibits spatial distribution patterns with extremely elevated concentrations (Co, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, U, and S) in the surroundings of the industrial estates to <1 km distance. Mean concentrations were significantly lower in the urban areas >1 km from the pollution sources. However, air pollution persists in the urban areas up to 4 km away, as the mean concentrations of Cu, Zn, As, Cd, Sb and S remained considerably elevated in comparison to the reference samples. Though rigorous source apportionment analysis was not the aim of this study, a good positive correlation of our results with metal abundances in ambient particulate matter and in pollution sources points to the Cu smelter as the main source of pollution. Hence, the severe air pollution affecting Huelva and nearby urban areas may be considered a serious health risk to local residents.

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## 1. Introduction

The amount of aerosols —natural or anthropogenic— in the atmosphere may vary over time. Anthropogenic aerosols derive for instance from the combustion of fossil fuels and biofuels, abrasion and resuspension of natural particles by traffic, construction, and industrial or agricultural activities (Grobéty et al., 2010), and the composition of potentially toxic elements (PTEs) may vary according to the pollution source. Air pollution is recognized as a major source of contamination affecting humans and causing seven million deaths annually worldwide (WHO, 2018). Common trace elements in polluted air, such as As, Cd, Cr, Pb and Hg, are known to be toxic to humans (Tchounwou et al., 2012). The International Agency for Research on Cancer (IARC) of WHO also classifies some trace elements and their compounds —including, As, Be, Cd, Ni and Cr (VI)— as carcinogenic. Furthermore, the IARC classifies outdoor air pollution as carcinogenic to humans (Group 1) (IARC, 2013). Besides causing e.g.,

lung cancer, air pollution may have diverse impacts on respiratory, cardiovascular, nervous, urinary and digestive systems, and interfere with fetal and child development (Kampa and Castanas, 2008; Landrigan, 2017; Mabahwi et al., 2014; WHO, 2018).

A recent publication warns of short-term mortality attributed to air pollution in Spain (Ortiz et al., 2017). According to these authors, the magnitude of annual mortality related to airborne particulate matter (PM) calls for the urgent implementation of measures by public administrations to reduce PM concentrations of anthropogenic origin in towns and cities where the main source of emissions is traffic. Chronic exposure to PM may hence be the cause of various kinds of pathologies and can lead to an accumulation of metals in soft and hard tissues in the human body. Epidemiological studies have associated pediatric cancer rates to air pollution derived from chemical/energy industries in Murcia, Spain (Ortega-García et al., 2017), whereas high cancer risk in adults in the Provinces of Huelva, Seville and Cádiz has been ascribed to environmental factors, especially to air pollution from industrial and mining activities (Benach et al., 2003; López-Abente et al., 2006; Fernández-Navarro et al., 2017). Metal pollution from mining areas in Huelva has also been linked to a risk of developing pigment gallstones and the enrichment of metals in them (Parviainen et al., 2016, 2018). A study on urinary levels of As, Cd, Cr, Cu, and Ni in children in the industrialized city of Huelva showed that the mean Cd levels were higher than the levels reported

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in other European studies (Aguilera et al., 2010). Another recent study associates the cognitive behavior of children in Huelva's primary schools with high Cd concentrations in urine and hair samples (Rodríguez-Barranco et al., 2014).

Lichens are widely used as bioindicators of metal air pollution. They are capable of accumulating atmospheric metals over time, making them valid tools when evaluating air quality and determining possible sources of metal pollution (Conti and Cecchetti, 2001; Brunialti and Frati, 2014). Lichens have been successfully used in assessing metal pollution in mining areas within Canada, Ghana, Finland, Portugal, Italy, Russia and the US (Boamponsem et al., 2010; Branquinho et al., 1999; Laatikainen and Seppänen, 2017; among others), in industrial areas (Pollard et al., 2015; Salemaa et al., 2004), in the vicinity of landfills and waste incinerators (Protano et al., 2014, 2015) and in urban areas (Giordano et al., 2013; Guidotti et al., 2009; LeGalley et al., 2013; Simonetti et al., 2003).

Despite the frequent use of lichens as bioindicators of air pollution worldwide, this method is not at all commonplace in Spain. The advantage of using lichens as bioindicators of air pollution lies in the easy and low-cost sampling even in extensive spatial areas, as expensive sampling devices such as PM collectors can be avoided. Though inexpensive passive air samplers have also been developed, they are mostly used for persistent organic pollutants (Qu et al., 2018). Lichens are perennial organisms, meaning accumulated metals proportionally reflect their presence in the atmosphere. Lichens trap metals directly from the air: from mist, rainwater, gaseous adsorption or deposited and trapped aerosols. Contaminants are absorbed by the whole surface of the organism due to its lack of cuticle or stoma (Hale, 1979, 1983).

The accumulation of metals in lichens is therefore a fairly precise key when assessing chronic exposure to metal pollution in urban areas. Unlike the physicochemical meters in weather stations that offer instant measurements, lichens can record a long-term residence on the substrate.

There are numerous toxictolerant lichen species. *Xanthoria parietina* occurs frequently in anthropized environments, and has been successfully used as a bioindicator of atmospheric pollution worldwide (Scerbo et al., 2002; Brunialti and Frati, 2007; Hissler et al., 2008; Demiray et al., 2012). Dzubaj et al. (2008) found no physiological or anatomical stress symptoms in the studied lichen thalli of *X. parietina* owing to metal accumulation, concluding it is a toxictolerant species suitable for gauging the distribution of air pollution.

Several previous studies confirmed that industrial emissions affect the air quality of Huelva (Alastuey et al., 2006; Chen et al., 2016; González-Castanedo et al., 2014; Sánchez de la Campa et al., 2007, 2015; 2018; Querol et al., 2002). The varying amounts of elements and chemical compounds in airborne PM in Huelva would derive from different sources. Source apportionment analyses of PM identified a crustal source (36% of PM<sub>10</sub> and 31% of PM<sub>2.5</sub>); a traffic-related source (33% of PM<sub>10</sub> and 29% of PM<sub>2.5</sub>); an industrial source (25% of PM<sub>10</sub> and 19% of PM<sub>2.5</sub>), and a marine aerosol contribution (only in PM<sub>10</sub>, 4%) (Alastuey et al., 2006). Silica, Al, Ca, Mn, Fe, K, Sr and Mg are related to crustal sources; non-mineral C, NO<sub>3</sub><sup>-</sup> and Cr are traced to traffic emissions; trace elements (including As, Bi, Cd, Co, Cu, Ni, Pb, Ti, V and Zn), PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> are ascribed to industrial emissions; and Cl and Na to marine sources (Alastuey et al., 2006; González-Castanedo et al., 2014; Querol et al., 2002).

The Cu smelter in the Punta del Sebo Estate (Huelva) has been identified as a major source of PTEs. Although the Cu smelter is estimated to make a minor contribution to the total amount of PM<sub>10</sub>, just 8% of the bulk, it is the major carrier of PTEs (Fernández-Camacho et al., 2010). Against this background, the present study evaluates air

quality and the spatial distribution of metal emissions (trace elements of interest are V, Cr, Mn, Co, Ni, Cu, Zn, Sr, As, Cd, Sb, Cs, Ba, Pb, Th, U) in the urban areas of the industrialized city of Huelva by means of lichen bioindicators.

## 2. Materials and methods

### 2.1. Description of the study site

Huelva (population 145,000), in SW Spain, is one of the oldest industrialized cities in Europe. Its immediately surrounding area harbors three large industrial parks. Punta del Sebo has a Cu smelter, an electrical power plant, and a phosphate fertilizer plant to the south, 1 km from the city (Fig. 1). The industrial estate of Nuevo Puerto, to the southeast, hosts oil refineries and a TiO<sub>2</sub> pigment plant, among others. Tartessos industrial park, roughly 3.5 km to northeast, houses a former cellulose plant that currently serves for biomass production.

The Province of Huelva is further characterized by a long history of mining activities in the Iberian Pyrite Belt, dating back to the 3rd millennium BC and peaking in the 20th century, yet leaving abandoned more than one hundred large mines and several smaller ones (Nocete et al., 2014). The mining area is located roughly 40 km from the city of Huelva. Mining activities recently reopened in Minas de Riotinto.

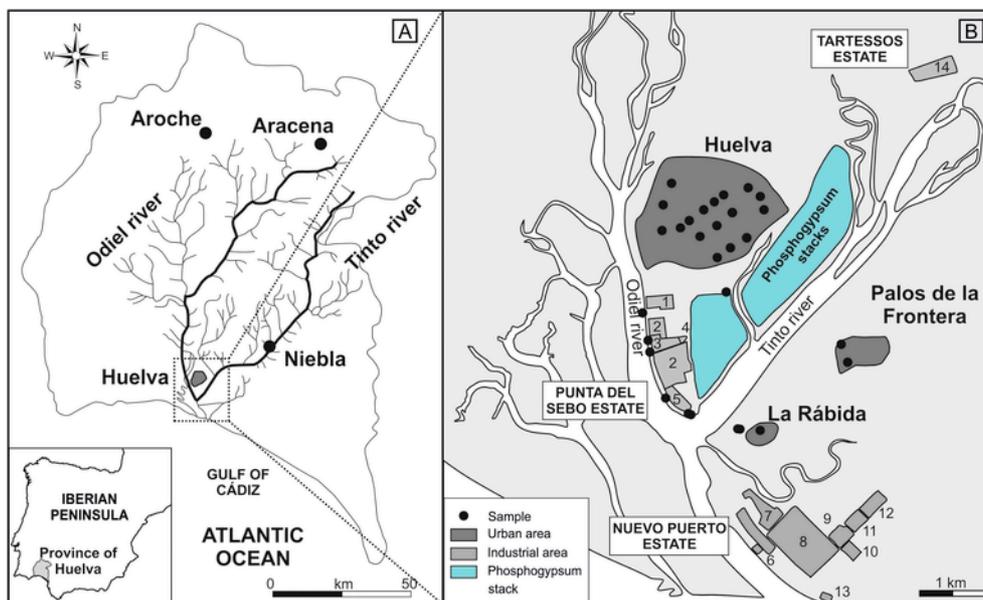
The city of Huelva lies on the coast, where the Rivers Odiel and Tinto meet, its elevation a.s.l. ranging from just a few meters up to approximately 50 m. The industrial parks of Punta del Sebo and Nuevo Puerto are nearly at sea level, while Alto Conquero is the highest neighborhood of the city.

The city has a pluviseasonal-oceanic macroclimate and pertains to a thermomediterranean bioclimatic belt, characterized by a low and dry ombroclimate (Rivas-Martínez et al., 2011). Average annual temperature is 18.2°C, and average annual precipitation is 516.8 mm (Rivas-Martínez and Rivas-Sáenz, 2018; Supplementary Fig. S1A). Precipitation is more frequent and abundant during winter. Likewise, wind directions present a seasonal trend. The winter months (from November to February) present higher dispersion, though with wind directions predominantly from the northeast; from March to October, a sea breeze from the south-southwest dominates (Supplementary Fig. S1B).

### 2.2. Sample collection and species characterization

Epiphytic lichens were collected in May 2018 from 33 locations (Figs. 1 and 2). Twenty-nine lichen samples were gathered in the city of Huelva or its surroundings, from an irregular sample grid. The locations depended on the availability of lichens in randomly distributed green areas and parks over the urban areas, which impeded application of a systematic grid. Still, care was taken to collect samples as systematically as possible, covering the whole city area and the nearby urban areas of La Rábida (500 inhabitants) just a few kilometers distance from the city, and Palos de la Frontera (10,800 inhabitants) on the other side of Tinto River.

The green area built along the river side of Odiel River near the industrial estate of Punta del Sebo was considered as part of the urban area, since many citizens use it for jogging or recreation. In addition to the urban samples, one single sample was collected in Niebla (approx. 4000 inhabitants), by the Tinto River about 25 km northeast of the city; another two samples came from Aroche (3000 inhabitants) and Aracena (8000 inhabitants), each roughly 80 km northward. The latter two samples would represent background values for a remote, semiurban and mountainous area lacking industrial activity in their



**Fig. 1.** (A) Map of the Huelva province with sample locations indicating Huelva and the three remote sampling sites at Niebla, Aracena and Aroche. (B) Map showing sample locations in the city of Huelva and its surroundings in La Rábida and Palos de la Frontera. The map also includes the industrial estates and the phosphogypsum stacks. The numbers in the industrial estates refer to (1) fertilizer plants, (2) fertilizer plants, (3) Cu smelter, (4) air gases plants and (5) power generation plants in the Punta del Sebo estate; (6) chemical plants, (7) hydrocarbons storage, (8) petrochemical plants, (9) petrochemical plants, (10) fertilizer plants, (11) chemical plants, (12) pigment (Ti oxide) plants and (13) hydrocarbons storage in the Nuevo Puerto estate; and (14) former cellulose paste plants in the Tartessos estate.

vicinity and having very light traffic. The samples from Aroche and Aracena are therefore designated as reference samples.

The toxictolerant species of *X. parietina* was chosen for this study because it proved to be the one most common and abundant in the area. Samples were carefully separated from the tree bark using a plastic knife and gloves, then placed in metal-free plastic vials. Entire thalli were collected—including the vegetative parts and the apothecia—and care was taken to collect lichen of more or less the same size. In a few cases, however, we were forced to collect smaller samples due to the scarcity of larger lichen individuals. One to six thalli were collected from a same trunk to assure enough sample material from each station. Generally, the amount gathered was close to 500 mg; when scarce sample material was available, the amount was <100 mg. Nearly all samples were picked >1.5 m above the ground to avoid the impact of soil pollution. When *X. parietina* was absent on higher parts of the trunk, we picked samples at a height of 1.0–1.5 m. The lichen substrate, *i.e.* tree species, varied due to the diversity of planted species in the green areas.

### 2.3. Sample treatment and analysis

The lichens were treated in the ISO-10000 cleanroom of the Instituto Andaluz de Ciencias de la Tierra (IACT, CSIC-University of Granada, Spain) and analyzed at IACT and at the Centro de Instrumentación Científica (CIC) of the University of Granada. Samples were not washed so as to avoid potential leaching of soluble particles (Bargagli, 1998). First, the samples were dried at 40 °C for 24 h, then they were cleaned of foreign objects such as tree bark and ground, in an agate mortar with pestle. Subsequently, samples were frozen at –28 °C and ground again to obtain fine and homogenized powder. Before analysis, they were lyophilized overnight by means of Telstar LyoQuest at the Laboratory for Crystallographic Studies (IACT), and 50 mg of sample was weighed in PTFE vials. Acid digestion was performed by adding 2 mL of purified HNO<sub>3</sub> (65%) and 0.25 mL of HF

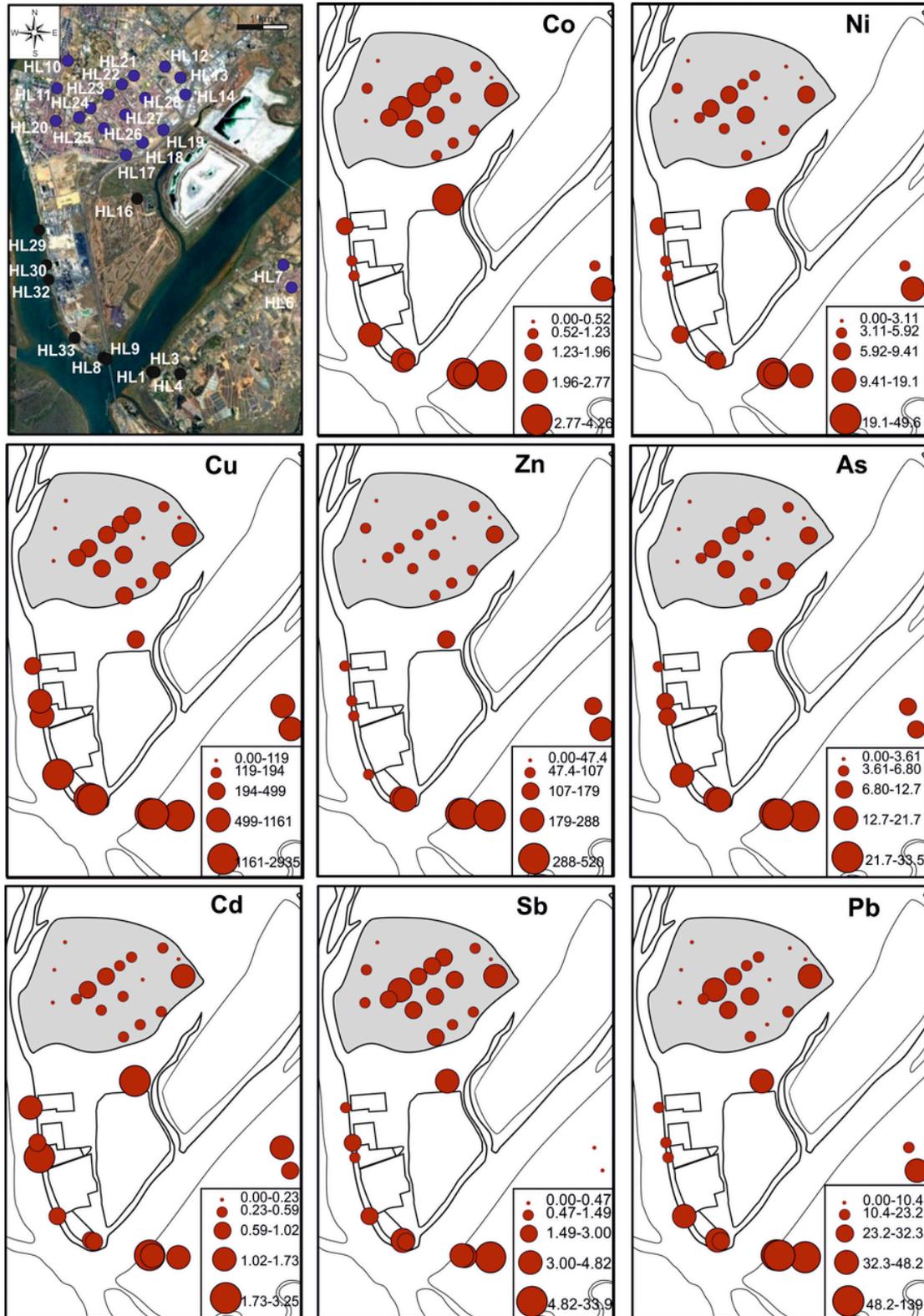
under a metal-free ISO-100 vertical laminar flow hood in the clean-room laboratory. The mixture was placed in Parr pressure reactors and heated at 150 °C during 12 h. The solution was then evaporated to complete dryness on a hot plate at 55 °C, again brought into solution by adding 1 mL purified HNO<sub>3</sub> (65%), and diluted for analysis.

Two matrix-matched lichen certified reference materials were tested to control the quality of analyses, including IAEA-336 provided by the International Atomic Energy Agency and BCR-482 by the European Commission (Supplementary Table S1). Procedural blanks were also run to counter possible contributions from the digestion procedure.

Twenty-five trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, Sr, As, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Er, Tm, Yb, Lu, Pb, Th, U) were analyzed using an Agilent 8800 TripleQuad Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at IACT, and the major elements (Ca, K, Mg, P, and S) by means of Perkin Elmer Optima 8300 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) at CIC.

### 2.4. Statistical analysis

IBM SPSS Statistics 24 software was used for statistical analysis of the results. The lichen dataset exhibited a non-normal distribution pattern. Basic descriptive statistics, Spearman's correlation, and Mann Whitney *U* test for the estimation of the significance of the differences between study and reference areas were calculated. The Mann Whitney *U* test also served to evaluate differences between defined zones within the study area. The significance level was set at  $\alpha=0.05$ . Principal Component Analysis (PCA) was also performed for lichens. For the PCA of the elements of interest, Varimax rotation was used. Finally, Pearson's correlation was applied to compare our data with previously published results regarding the chemical composition of PM in Huelva.



**Fig. 2.** Concentrations (mg/kg) of PTEs, P and S in lichens from the city of Huelva and its surroundings. The map in the upper left corner indicates the Zone 1 with samples marked with black circles and Zone 2 with blue circles. The concentrations of Co, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, U and S are significantly higher in the Zone 1 in comparison to the Zone 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

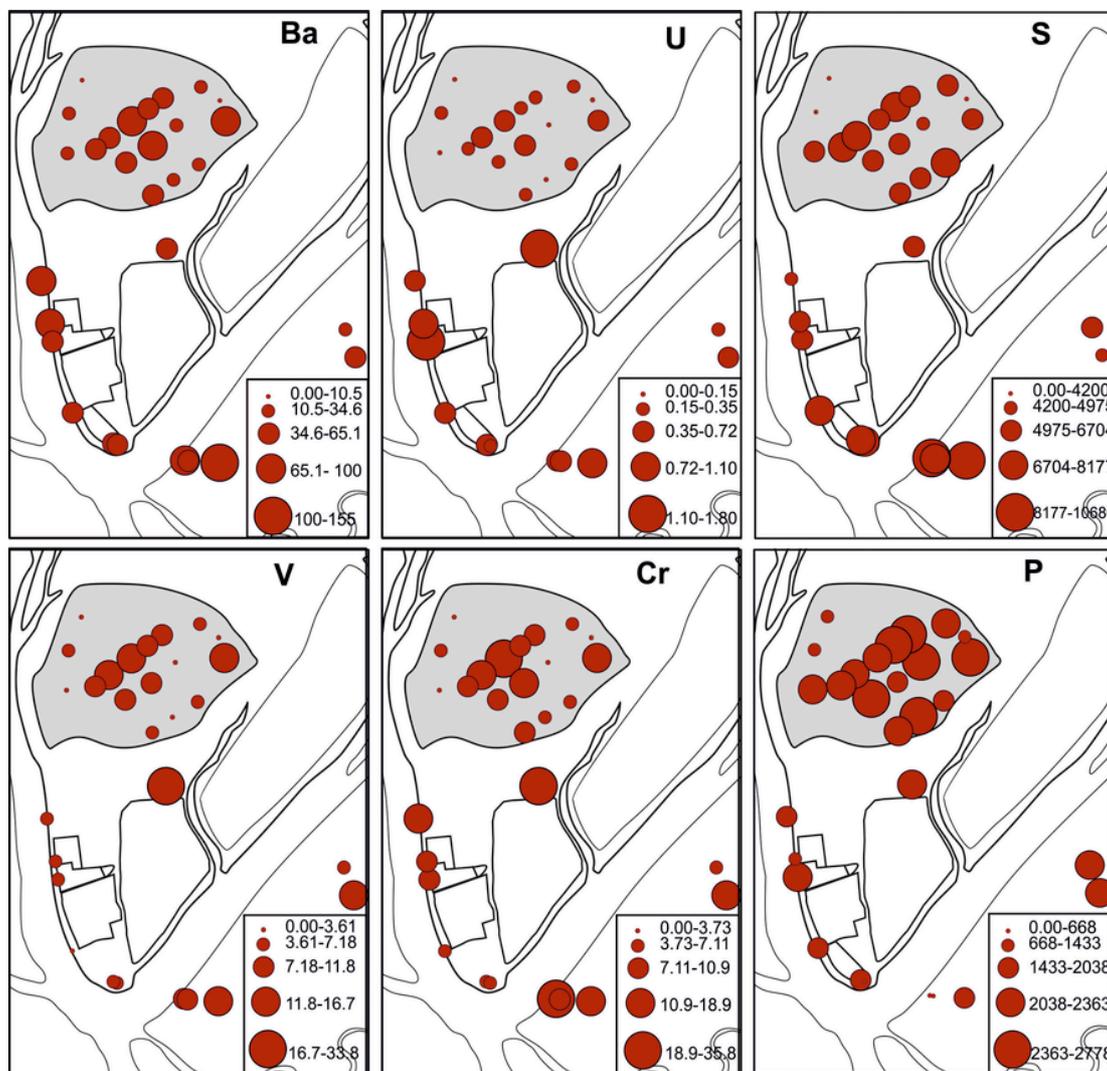


Fig. 2. (Continued)

### 3. Results

#### 3.1. City of Huelva

Lichens from the city of Huelva and the surrounding urban areas (the study area) gave elevated concentrations of PTEs. A full description of their chemical composition is offered in Supplementary Table S2, while a summary of the basic statistics is given in Table 1A. Copper (mean 769 mg/kg), Zn (138 mg/kg), Mn (57 mg/kg), Ba (54 mg/kg), Pb (31 mg/kg), Sr (14 mg/kg), As (11 mg/kg) and Cr (11 mg/kg) were the PTEs showing the highest concentrations. Vanadium, Ni and Sb exhibited maximum values > 30 mg/kg, though the mean values were < 10 mg/kg; in turn, Co, Cd, Cs, Rare Earth Elements (REE), Th and U exhibited much lower values (Table 1A).

The PTEs plotted in Fig. 2 showed a spatial distribution with higher concentrations close to the industrial estates of Punta del Sebo and Nuevo Puerto. Based on this observation, the samples were divided into two zones in Fig. 2: samples marked with black circles (less than 1 km from the industrial estates) are denominated as Zone 1, whereas the rest of the samples, marked with blue circles, are denominated as Zone 2. Generally speaking, all PTEs showed maxi-

imum concentrations in Zone 1. Concentrations decreased farther away from the pollution sources, *i.e.* in Zone 2 (Table 1B). Fig. 2 highlights metal abundances in the green area constructed alongside the Punta del Sebo estate (Samples HL8, 9, 29, 30, 32 and 33) and La Rábida (HL1, 3, 4). Here, besides the recreational area, there are monuments, a museum, and the premises of the University campus of La Rábida.

For instance, Cu exhibited up to 2935 mg/kg and Zn up to 520 mg/kg in samples collected next to the Cu smelter. Some PTEs (Cu, Zn, Cd and Pb) exhibited elevated concentrations in the urban area of Palos de la Frontera, some 4 km from the industrial estates (Fig. 2). Within the city, samples HL21-24 from a highly trafficked avenue generally exhibited the highest concentrations of PTEs, whereas lower metal concentrations tended to appear in the samples from Alto Conquero district (HL10 and 11) and near the University campus of El Carmen (HL12, 13 and 28). Sulfur (mean 6284 mg/kg) presented a distribution pattern similar to PTEs, with higher concentrations in Zone 1, though S concentration remained elevated in Zone 2 as well. Phosphorous concentrations (1924 mg/kg), on the contrary, were higher in Zone 2 than in Zone 1. Vanadium and Cr showed higher concentrations in the city and nearby urban areas than in the green area next to the Punta del Sebo Estate.

**Table 1**

Min., Max., mean, median values (mg/kg) and standard deviation (SD) for elemental concentrations in lichens (A) in Huelva and references areas (Aroche and Aracena) and (B) in Zone 1 and Zone 2 in Huelva. N=sample number.

A	Huelva (N=29)					Reference area (N=2)					B Zone 1 (N=10)					Zone 2 (N=19)				
	Min	Max	Mean	Med.	SD	Min	Max	Mean	Med.	SD	Min	Max	Mean	Med.	SD	Min	Max	Mean	Med.	SD
V	1.9	34	8.5	6.2	6.5	11	17	14	14	4.0	3.1	34	9.7	5.5	9.3	1.9	17	7.9	7.2	4.7
Cr	2.8	36	11	8.8	7.4	11	14	12	12	2.3	5.0	36	13	8.8	9.7	2.8	23	9.4	9.0	5.7
Mn	19	153	57	48	31	127	133	130	130	3.9	22	153	57	41	40	19	106	57	51	26
Co	0.29	4.3	1.7	1.5	1.1	1.5	2.5	2.0	2.0	0.7	1.1	4.3	2.6	2.4	1.2	0.29	2.5	1.3	1.2	0.7
Ni	1.0	50	7.9	5.6	9.0	5.1	6.2	5.6	5.6	0.7	4.4	50	13	9.3	13	1.0	12	4.9	4.1	2.9
Cu	60	2935	769	349	853	19	24	22	22	4.1	314	2935	1611	1843	963	60	1161	325	310	255
Zn	37	520	138	91	116	55	63	59	59	5.6	66	520	218	186	157	37	288	96	86	56
Sr	4.3	33	14	13	6.1	15	21	18	18	4.5	9.4	33	17	16	7.0	4.3	20	12	11	4.9
As	2.3	34	11	9.8	8.1	2.9	3.5	3.2	3.2	0.4	4.7	34	19	19	9.3	2.3	13	7.5	8.2	3.5
Cd	0.11	3.3	0.90	0.70	0.74	0.15	0.29	0.22	0.22	0.10	0.73	3.3	1.6	1.4	0.8	0.11	1.3	0.53	0.47	0.32
Sb	0.29	34	3.6	1.8	6.1	0.71	1.2	0.94	0.94	0.34	0.90	34	5.9	3.1	9.9	0.29	8.3	2.3	1.7	2.0
Cs	0.093	1.3	0.42	0.35	0.30	0.58	0.74	0.66	0.66	0.12	0.13	1.3	0.52	0.37	0.45	0.093	0.64	0.37	0.35	0.18
Ba	9.5	155	54	52	30	51	57	54	54	3.9	52	155	76	64	31	9.5	80	42	43	22
La	0.71	10	1.9	1.3	1.7	1.3	2.7	2.0	2.0	1.0	1.0	10	2.4	1.2	2.8	0.71	3.3	1.6	1.4	0.75
Ce	1.3	17	3.8	2.9	3.1	2.7	6.1	4.4	4.4	2.4	1.3	17	4.5	2.3	4.8	1.4	6.8	3.5	3.0	1.6
Pr	0.14	1.8	0.42	0.30	0.33	0.34	0.73	0.54	0.54	0.27	0.20	1.8	0.49	0.28	0.50	0.14	0.84	0.39	0.31	0.20
Nd	0.58	6.5	1.6	1.2	1.2	1.3	2.8	2.1	2.1	1.0	0.79	6.5	1.9	1.1	1.8	0.6	3.39	1.5	1.2	0.79
Sm	0.11	1.4	0.32	0.23	0.26	0.31	0.63	0.47	0.47	0.22	0.15	1.4	0.36	0.20	0.38	0.11	0.70	0.30	0.24	0.16
Er	0.042	0.40	0.15	0.13	0.083	0.16	0.32	0.24	0.24	0.12	0.072	0.40	0.16	0.15	0.094	0.042	0.33	0.14	0.12	0.078
Tm	0.0063	0.058	0.022	0.020	0.012	0.024	0.046	0.035	0.035	0.016	0.0091	0.058	0.024	0.021	0.01	0.0063	0.047	0.021	0.02	0.011
Yb	0.041	0.33	0.1	0.13	0.075	0.15	0.31	0.23	0.23	0.11	0.068	0.33	0.16	0.15	0.077	0.041	0.32	0.14	0.12	0.076
Lu	BDL	0.056	0.022	0.020	0.012	0.024	0.047	0.035	0.035	0.016	0.011	0.056	0.024	0.022	0.013	BDL	0.051	0.021	0.018	0.012
Pb	3.5	139	31	22	29	14	15	15	15	1.2	20	139	53	44	37	3.5	48	20	16	14
Th	0.20	2.9	0.57	0.45	0.50	0.48	0.83	0.66	0.66	0.25	0.27	2.9	0.71	0.41	0.81	0.20	1.2	0.50	0.47	0.22
U	0.080	1.8	0.50	0.35	0.43	0.33	0.39	0.36	0.36	0.044	0.35	1.8	0.88	0.70	0.51	0.080	0.71	0.30	0.25	0.18
Al	810	5212	2537	2242	1290	1806	5325	3566	3566	2488	1078	5212	2609	1943	1544	810	5199	2500	2350	1180
Ca	1118	5059	2456	2037	1065	2720	6283	4502	4502	2520	1540	5059	2691	2449	1170	1118	4792	2332	1864	1016
Fe	800	13283	4201	3520	2978	4088	4833	4461	4461	527	1568	13283	5774	4558	4110	800	6846	3373	3223	1804
Mg	142	3313	1343	1354	715	568	1285	926	926	507	182	3313	1607	1790	896	142	2099	1204	1293	578
P	176	2778	1924	2151	636	1779	1920	1849	1849	100	176	2221	1460	1755	741	1292	2778	2169	2239	415
S	2964	10681	6284	5935	1666	2698	2973	2836	2836	195	4570	10681	7373	7685	1914	2964	8048	5711	5795	1216

### 3.2. Remote urban reference areas

We took three samples from remote urban areas (Niebla, Aroche and Aracena). Yet here we focus on the samples from the villages of Aroche and Aracena as reference samples, representing remote urban areas with no industrial activity or related impact. The Niebla sampling site was discarded as a reference because some elements of interest were elevated (Supplementary Table S2; Cu 136 mg/kg, Zn 75 mg/kg, As 62 mg/kg and Pb 148 mg/kg). This sample most likely evidenced dusting from a cement plant located in Niebla village.

The elemental compositions of the samples from Aroche and Aracena were alike (Supplementary Table S2; Table 1A). Manganese (mean 130 mg/kg), Zn (59 mg/kg), Ba (54 mg/kg), Cu (mean 22 mg/kg), Sr (18 mg/kg), Pb (15 mg/kg), V (14 mg/kg) and Cr (12 mg/kg) were among the most abundant PTEs in the reference area. The mean concentrations of Ni (5.6 mg/kg), Ce (4.4 mg/kg), As (3.2 mg/kg), Co (2.0 mg/kg), Nd (2.1 mg/kg), Sb (0.94 mg/kg), Cs (0.66 mg/kg), Th (0.66 mg/kg), U (0.36 mg/kg), and Cd (0.22 mg/kg) exhibited lower values (Table 1A). The mean values for S and P were respectively 2836 mg/kg and 1849 mg/kg.

## 4. Discussion

### 4.1. Comparison of PTE concentrations in lichens

Division of the study area into Zone 1 and 2 highlighted the extreme PTE concentrations in the immediate surroundings (<1 km) of the industrial estates. The Mann Whitney *U* test indicated that mean concentrations of Co, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, U and S were significantly higher in Zone 1 when compared to Zone 2. Phosphorous concentrations, on the other hand, were significantly higher in Zone 2.

Mean values of Ni, Cu, Zn, As, Cd, Sb, Pb and S were much higher in the study area than in the reference area (Table 1A). However, according to the Mann Whitney *U* test, only Cu and S exhibited significantly higher values in the study area. When samples from Zone 1 were compared with samples from the reference area, the former were significantly enriched in Cu, Zn, As, Cd, Pb and S, implying significant air pollution in the surroundings of the industrial estates. Spearman correlations of these elements signaled a strong positive correlation (Table S3).

The mean concentrations of V, Cr, Mn, Co, Sr, Cs, Ce, Nd, Al and Ca were slightly higher in the reference area samples than in those collected from the study area (Table 1A). Nonetheless, according to the Mann Whitney *U* test, Mn was the only element presenting significantly higher concentrations in the reference area. The other elements presented just slight differences in terms of mean values. In all cases, trace element concentrations varied much more, their maximum values substantially elevated in the study area (with respect to the reference area; Table 1A). Barium, the remainder of the REE, Th and U exhibited similar mean values for the study area and the reference area, though again the maximum values were considerably higher in the study area. Spearman correlations showed a strong positive correlation of Mn with V and Cr.

It is interesting to observe the division of PCA into two components: on the one hand Co, Ni, Cu, Zn, Sr, As, Cd, Sb, Ba, Pb, Th, U and S, and on the other, V, Cr, Mn and P (Fig. 3). The first component represents elements from anthropogenic sources in the urban areas of Huelva, whereas the second component attests to elements that exhibited higher mean concentrations from natural terrestrial source. The origin of Cr in the reference samples cannot be clearly attributed, as it

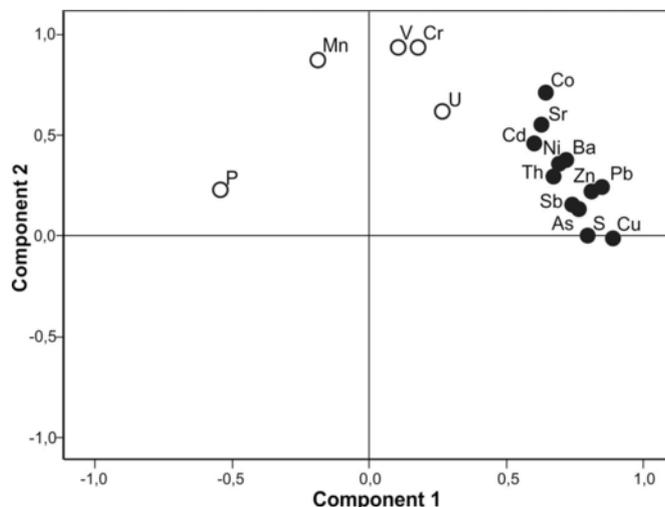


Fig. 3. Principal component analysis of chemical composition of lichens.

may have to do with traffic emissions. Phosphorous did not correlate well with either component, but fitted best with the reference samples. The poor correlation of P was corroborated by means of Spearman's essay (Table S3). It may be due to its predilective character with respect to this nutrient.

### 4.2. Pollution sources and correlation with lichen chemistry

Vast mining and metallurgic activities severely affect the air quality of the Province of Huelva. In the mining district of Riotinto in the Iberian Pyrite Belt, the PM in wind-blown dust from local mines and contaminated soils guards the signature of mining wastes with high concentrations of sulfide-related metals (As, Bi, Cd, Cu, Pb, Sb, Zn), and is a persistent source of air pollution in the nearby villages (Castillo et al., 2013; Fernández-Caliani et al., 2013). Yet given the distance (30–40 km) of the Iberian Pyrite Belt mining activities from the actual city of Huelva and our reference areas, their influence upon the sampled lichens is assumed to be negligible.

In contrast, the city of Huelva and its surrounding urban areas are severely affected by industrial activities (Alastuey et al., 2006; Chen et al., 2016; González-Castanedo et al., 2014; Sánchez de la Campa et al., 2007, 2015; 2018; Querol et al., 2002). Moreover, according to Sánchez de la Campa et al. (2015), pyrometallic activities bear a greater impact on the air quality of Huelva Province overall than mining activities. This is due to the ultrafine particles enriched in PTEs that can be transported over long distances.

The prevailing inland sea breeze, plus the location of the main industrial estates between the coast and the city, drives industrial emissions toward the urban areas. Many studies also indicate that Odiel and Tinto Rivers channel winds towards the estuary in NW and NE directions (Fernández-Camacho et al., 2010; Querol et al., 2002). The location of Huelva city at the confluence of these rivers therefore favors emission transport to the urban areas.

The Cu smelter has been signaled as the major source of inhalable fine airborne particles carrying toxic and carcinogenic elements, thereby representing a potential health risk to local residents (Fernández-Camacho et al., 2010; González-Castanedo et al., 2014). The latter authors (González-Castanedo et al., 2014) researched in detail the composition of emissions from Huelva's Cu smelter, distinguishing between: refining furnace, flash smelting furnace, sulfuric plant, converter unit and crushing plant. Total metal abundances decreased in the following relative order: Cu, Pb, Zn, As, Ni, Cd, Cr, Ba

—though it must be said that emissions varied considerably among the studied units (Table 2).

The chemical composition of lichens points to air pollution characteristic of industrial emissions. We compared (Pearson's correlation) the elemental concentrations (elements of interest in Table 2) in lichens with the total amounts of elements from the Cu smelter, and separately the concentrations from the different units. The relative elemental abundances showed a good positive correlation for total concentrations from the smelter ( $r=0.86$ ), while comparison with the different units revealed that the refining furnace ( $r=0.91$ ) and crushing plant ( $r=0.99$ ) exhibited very positive correlations. The other units did not correlate with the chemical composition of lichens ( $r=0.12-0.33$ ).

The impact of emissions from industrial estates has been previously recorded in monitoring stations within the city of Huelva, and generally speaking, the main trace element abundances in the airborne PM in the city decrease in the following relative order: Cu, Ti, Zn, Pb, Ba, Mn, V, Sr, As, Mo, Cd (Table 2; Querol et al., 2002; Sánchez de la Campa et al., 2007, 2015). In the past, Cu, Ti, Zn, and As exhibited values exceeding the target values set by the European Commission, whereas Pb, Ni, and Cd surpassed these limits only occasionally (Querol et al., 2002). Comparison of the chemical composition of lichens with data from the observation stations in the city also showed a good correlation ( $r=0.83-0.90$ ; Table 2).

Elevated concentrations of phosphate in PM measured in the monitoring stations (Querol et al., 2002) can be ascribed to the phosphoric acid fertilizer plant. *X. parietina* is a phosphate predilective species, meaning that the presence of this natural nutrient favors its growth, so that its P concentrations are naturally elevated. This explains why the mean P concentrations in the reference samples from Aroche and Aracena are similar to the mean values for lichens in Huelva. In fact, lichen P concentrations are especially high in Zone 2, suggesting that the phosphate emissions affect the city more than the immediate vicinity of the fertilizer plant.

Some of the previously cited authors further divide industrial emissions in Huelva into two sources: petrochemical and TiO<sub>2</sub> production (Ni, Co, V, Ti, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>) or a mixed metallurgical and phosphate source (Bi, Cd, Cu, Pb, PO<sub>4</sub><sup>3-</sup>, As, and Zn). Although our

study does not aim to identify sources in detail, the Cu smelter in the Punta del Sebo Estate is recognized as a major pollutant source. In particular, the elevated concentrations of Cu, Zn, Pb and As in lichens are ascribed to smelter emissions.

Traffic emissions are also assumed to have an impact on the chemistry of lichens in the city center. Previous studies (Querol et al., 2002; Alastuey et al., 2006; González-Castanedo et al., 2014) report that Cr in PM is associated with traffic emissions. In our study, the Cr concentrations peaked in the urban areas, especially along high-traffic avenues in Huelva and in La Rábida (Fig. 2; Table S2), suggesting the influence of exhaust fumes.

The impact of the TiO<sub>2</sub> pigment plant cannot be evaluated, as Ti was not analyzed in lichens nor in view of the petrochemical plants. Further investigation of stable and radiogenic isotopes would help identify the pollution source of some metals. For instance, the isotopic signature of Pb could point to its origin, distinguishing the Cu smelter from remnant Pb recycling in the ambient.

The resuspension of fine particles from superficial soil during the dry season may also have an impact on air quality, hence on lichen chemistry. Industrial activity in Huelva reportedly affects metal concentrations in soils as well (Guillen et al., 2012, 2011; Zuluaga et al., 2017). The urban soils in Huelva, especially in the Punta del Sebo Industrial Estate, contain high concentrations of As (up to 2121 mg/kg), Cd (25.7 mg/kg), Co (124 mg/kg), Cr (170 mg/kg), Cu (10,000 mg/kg), Hg (20,117 µg/kg), Ni 52 (mg/kg), Pb (5271 mg/kg) and Zn (4707 mg/kg) (Zuluaga et al., 2017). The sediments of the river banks alongside the city also have elevated metal concentrations, showing Pb isotope signatures similar to those of the sulfides in the Iberian Pyrite Belt (Zuluaga et al., 2017). This finding is attributed to the deposition of suspended material carried in the river water from upstream. Additionally, phosphogypsum, which is a waste by-product of the fertilizer industry deposited on the salt marshes of the Tinto River (Fig. 1), is a potential source of metal air pollution, containing high concentrations of Pb, Sb, Mn, V, Cu, Co, Ni and Cr (Macías et al., 2017). Therefore, the dusting of soils affected by industrial activities and unremediated phosphogypsum may contribute to the metal air pollution in Huelva.

**Table 2**

PTE concentrations in Lichens and in PM in pollution sources and in observation stations in the city of Huelva and the Pearson's correlation  $r$ -values for PTEs (bold font) that are pointed out as major pollutants from the Cu smelter and that have significantly higher mean values in lichens in Zone 1 in comparison to reference area (<sup>a</sup>González-Castanedo et al., 2014; <sup>b</sup>Sánchez de la Campa et al., 2007; <sup>c</sup>Querol et al., 2002; <sup>d</sup>Sánchez de la Campa et al., 2015).

$r$ -value	Lichens (Huelva)	Cu smelter (Total) <sup>a</sup>	Flash furnace <sup>a</sup>	Refining furnace <sup>a</sup>	Crushing plant <sup>a</sup>	Converter <sup>a</sup>	Sulfuric plant <sup>a</sup>	City (Manuel Lois) <sup>b</sup>	City (Manuel Lois) <sup>c</sup>	City (Campus El Carmen) <sup>d</sup>
		0.86	0.16	0.91	0.99	0.33	0.12	0.88	0.90	0.83
Unit	mg/kg Mean	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	ng/m <sup>3</sup> Mean	ng/m <sup>3</sup> Mean	ng/m <sup>3</sup> Mean
V	8.5	5.0	1.2	0.64	0.12	0.82	2.2	7	15	4.2
Cr	11	65	4.5	13	5.8	18	24	3	6	2.3
Mn	57							12	30	5.5
Co	1.7	3.2	0.37	0.34	0.55	0.99	0.95	0.4	1	0.21
Ni	7.9	179	7.6	17	15	80	60	4	5	2.65
<b>Cu</b>	769	1212	303	415	420	25	50	50	210	62
<b>Zn</b>	138	671	191	256	22	44	158	30	112	47
Sr	14	2.93	0.92	0.63	0.33	0.42	0.64	4	11	2.85
<b>As</b>	11	319	260	54	1.9	0.73	2.8	3.2	9	5.4
<b>Cd</b>	0.90	150	109	0.98	0.28	0.47	40	0.6	1	0.64
Sb	3.6	9	7.1	0.87	0.44	0.07	0.52	2	4	0.83
Cs	0.42	0.02	0.02	<0.01	<0.01	<0.01	<0.01	0.1	0.2	0.05
Ba	54	53	9.4	12	10.1	8.7	13	23	35	13
La	1.9	0.79	0.09	0.09	0.05	0.37	0.18			0.3
<b>Pb</b>	31	730	586	116	15	5.0	6.7	20	83	12
Th	0.57	0.38	0.08	0.08	0.06	0.06	0.1	0.3	0.6	0.06
U	0.50	0.82	0.18	0.18	0.13	0.12	0.2	0.4	0.6	0.06

#### 4.3. Suitability of *X. parietina* and study limitations

Lichens characteristically accumulate and retain metals exceeding their physiological requirements, then tolerate these high concentrations by sequestering metals extracellularly (Bačkor and Loppi, 2009). Mycobiont hyphae (fungi), especially those forming the upper cortex of lichen thalli, accumulate most of the PTEs from the environment. Selecting *X. parietina* for this study proved to be a good choice, providing for a high level of surface contact with atmospheric pollutants, potentially enabling the accumulation of large amounts of trace metals in polluted areas (Rola and Osyczka, 2019). Additionally, Dzubaj et al. (2008) reported no stress responses in *X. parietina* under atmospheric pollution, corroborating this species' suitability for such studies. The elemental composition in thalli of *X. parietina* has furthermore been reported to reliably reflect the chemical composition of PM in the air (Scerbo et al., 1999, 2002; Cuny et al., 2004; Rola and Osyczka, 2019). In our study, the chemical composition of the lichens from the city of Huelva correlated well with the composition of PM of the pollution sources (Cu smelter) and PM analyzed in the city area.

Notwithstanding, some discussion surrounds the use of *X. parietina* when biomonitoring air pollution. The different parts of lichen thalli may accumulate metals at varying rates, and the age and size of the *X. parietina* thalli can influence metal concentrations (Suetina, 2001). For instance, during short-term accumulation in transplanted lichens, higher concentrations of Cd, Cr, Ni, and Pb may be found in the peripheral vegetative parts of *X. parietina* in comparison to apothecia; whereas Zn reportedly exhibits a higher concentration in the apothecia (Rola and Osyczka, 2019). Still, an analysis of *in-situ* *X. parietina* for biomonitoring purposes confirmed that there is an age-dependent metal distribution —*i.e.* the older, central parts of the thalli contain higher concentrations than the younger, peripheral parts (Nimis et al., 2001).

Any sampling of lichens in urban areas is limited to green areas, and the amount and size of lichens may be small. Therefore, representative and uniform sampling, as well as sample homogenization, were priorities in this study. The whole lichen thalli were sampled in order to bypass discussion about such potential differences in the metallic accumulation characteristics of vegetative parts versus apothecia. At any rate, it is worth noting that some samples collected in the proximities of the industrial estates (HL1, 3, 6, 32, and 33) were smaller (<1 cm Ø) in size than the other samples; and despite the smaller size of *X. parietina* at these sampling points, they proved to be among the most metal-enriched samples. This comes to show that the organism's small size does not determine its metal accumulation under exposure, as opposed to larger *X. parietina*.

There may be competition between metal ions (Cu, Zn, Cd, Pb) for binding sites in *X. parietina*, which could have implications for biomonitoring. Paoli et al. (2018) studied metal binding in lichens using wet adsorption studies, though in nature lichens might also trap metals from aerosols. According to these authors, the proportion between extracellular and total contents varied among those essential micronutrients (Cu, Zn) that also accumulated intracellularly, while it hardly changed for the elements (Cd, Pb) that mainly accumulated in the cell wall ligands. Further, metal uptake was proportionally lower for richer multi-metal solutions in comparison to single metal solutions. In our case, such a competition between metal ions cannot be ignored, but it did not seem to distort the results; there was good, positive correlation between the pollution sources. Hence, we infer that the metal abundances in *X. parietina* in Huelva reliably reflect the prevailing air quality conditions.

#### 4.4. Comparison to other industrial areas

The distribution of PTEs in lichens (*X. parietina*) has also been studied in Dunkirk (Northern France), where a large industrial area houses petrochemistry, chemistry, and metallurgy activities as well as a power plant (Cuny et al., 2004). The industrial setting of Dunkirk is similar to our study site, and the proximity of residential areas raises concern, as elevated PTE concentrations were gauged in urban areas proximal to industrial activities. The mean values of the target element of their study are comparable to those of our study (As  $3 \pm 1.9$  mg/kg, Cd  $0.9 \pm 0.5$  mg/kg, Hg  $0.2 \pm 0.09$  mg/kg, Ni  $13 \pm 10$  mg/kg, Pb  $41 \pm 36$  mg/kg, V  $15 \pm 16$  mg/kg, Zn  $186 \pm 128$  mg/kg).

In Russia, a Cu smelter by the city of Karabash was identified as a major source of atmospheric pollution, though resuspension of dust from polluted soil in the historic mining area cannot be ruled out as a pollution source (Spiro et al., 2004; Williamson et al., 2008; Pollard et al., 2015). The *in-situ* lichens (*Hypogymnia physodes*) of the Karabash area contained elevated mean concentrations of As ( $11 \pm 6.5$  mg/kg), Cu ( $128 \pm 108$  mg/kg), and Pb ( $309 \pm 204$  mg/kg), and transplanted lichens in the immediate vicinity of the smelter accumulated up to 105 mg/kg of As, 909 mg/kg of Cu, and 841 mg/kg of Pb (Pollard et al., 2015). Moreover, a blast furnace in Karabash, producing relatively high Cu and Fe emissions, was found to affect proximal (mainly <10 km) areas to the smelter, while emissions from their converter with Pb–Zn-rich particles showed a greater impact on distal deposition (Williamson et al., 2008).

In SW Finland, the Harjavalta Cu-Ni smelter has been identified as a major source of metal pollution (Salemaa et al., 2004; Salo et al., 2012). Although they did not grow close to the smelter (<0.5 km), *Cladina* species and *Cetraria islandica* collected at distances of 2–4 km from the smelter exhibited elevated mean concentrations of metals (Cd  $0.7 \pm 0.4$  mg/kg, Cu  $359 \pm 228$  mg/kg, Mn  $48 \pm 43$ , Ni  $69 \pm 54$  mg/kg, Zn  $72 \pm 27$  mg/kg, Pb  $30 \pm 20$  mg/kg; Salemaa et al., 2004). The levels for Cu, Cd, Mn, Zn, and Pb were similar to our concentrations in Zone 2 of Huelva, presenting slight variations in the cases of Zn and Pb. Nickel was considerably more elevated in the Harjavalta area than in Huelva, which is ascribed to the Ni smelting activities in Harjavalta.

A steel factory and traffic emissions were identified as sources of atmospheric pollution in Košice (Slovak Republic; Dzubaj et al., 2008), their mean values in *X. parietina* (peripheral parts) being comparable to our study for Pb (34 mg/kg) and Zn (146 mg/kg), whereas Cd (1.9 mg/kg), Mn (211 mg/kg) and Sb (51 mg/kg) exhibited higher concentrations and Cu (30 mg/kg) and Fe (3033 mg/kg) lower contents than in Huelva. The highest metal concentrations overall were found close to the steel plant, highlighting it as the major pollution source (Dzubaj et al., 2008). Studies in Italy likewise reported higher metal concentrations in *X. parietina* (peripheral parts) that grew in the vicinity of industrial areas and close to high-traffic roads (Scerbo et al., 1999, 2002), yet the mean values from Livorno and Pisa Provinces were below our results (As  $1.3 \pm 2.2$  and  $0.2 \pm 0.2$  mg/kg, respectively; Cd  $0.2 \pm 0.1$  and  $0.3 \pm 0.1$  mg/kg; Cr  $7.5 \pm 13$  and  $2.8 \pm 2.2$ ; Hg  $0.1 \pm 0.1$  and  $0.1 \pm 0.02$  mg/kg; Ni  $6.3 \pm 10.0$  and  $1.8 \pm 1.8$  mg/kg; Pb  $12 \pm 13$  and  $5.2 \pm 5.4$  mg/kg; V  $3.7 \pm 4.7$  and  $1.5 \pm 1.0$  mg/kg; Zn  $46 \pm 53$  and  $32 \pm 17$  mg/kg).

The maximum values of Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, U, and S in Huelva Zone 1 come to demonstrate that urban areas in the proximity (<1 km) of industrial estates suffer the most from metal emissions. Health risks may affect the employees in the industrial estates and nearby residents or employees, for instance in La Rábida, as well

as people occasionally using the recreational areas or visiting other attractions within the impacted area. In Huelva, the elevated concentrations of numerous metals are in line with those of other industrial areas having similar characteristics (Cuny et al., 2004). The fact that the mean concentrations of PTEs were significantly lower in the city-side area (Zone 2) does not mean that the air quality there improves considerably. In the zone 2, Cu exhibits 15 times higher mean concentrations and Zn, As, Cd, Sb, and S exhibit twice as high mean concentrations as in the references areas (Aroche and Aracena). Indeed, many studies show that the main pollutant levels in PM of Huelva are substantially higher than in other urban areas in Spain (Querol et al., 2002; Sánchez de la Campa et al., 2007, 2015).

Unfortunately, a comparison of lichen chemistry in other parts of Spain—with or without the impact of industrial activities—is not feasible, since we lack published data; but European studies afford an important reference for this purpose. As mentioned earlier, the metal concentrations in the lichens of Zone 2 in Huelva resemble those of other areas suffering from severe air pollution at a similar distance from industrial activity (Cuny et al., 2004; Salemaa et al., 2004). In Turku (SW Finland), a city which is more or less the same size as Huelva (186,700 inhabitants), traffic emissions are indicated as major source of metals in lichens (*Hypogymnia physodes*) (Salo et al., 2012). Moreover, in Turku, Cr ( $20 \pm 22$  mg/kg) and Mn ( $88 \pm 22$  mg/kg), respectively associated with traffic and crustal sources, along with V ( $11 \pm 6.3$  mg/kg), exhibited slightly higher mean values than in Zone 2 of Huelva (Table 1B), whereas Cd ( $0.7 \pm 0.2$  mg/kg), Co ( $1.4 \pm 0.7$  mg/kg), Ni ( $4.5 \pm 2.2$  mg/kg), and Zn ( $113 \pm 40$  mg/kg) were similar in the two cities. Contrariwise, the mean values of As, Cu, Fe and Pb were considerably higher in the urban areas of Huelva (Table 1) than in Turku ( $<3$  mg/kg,  $11 \pm 6.0$  mg/kg,  $2400 \pm 1380$  mg/kg and  $12 \pm 4.0$  mg/kg, respectively; Salo et al., 2012).

## 5. Conclusions

This investigation reveals the spatial distribution of the chemical composition of lichens (*X. parietina*) in the highly industrialized city of Huelva, SW Spain, as compared with reference samples from an area without the influence of industrial activities, 80 km from the city. The use of epiphytic lichens as bioindicators of atmospheric metal pollution is not a common practice in Spain, and this paper is novel in demonstrating their utility for identifying spatial pollution patterns in an urban area. The results can be extrapolated and interpreted as a spatial distribution of PTEs in the atmosphere. The chemistry of lichens is well correlated with published data on PM composition in the city, and also with the emissions from the Cu smelter in the Punta del Sebo industrial estate, corroborating that the lichens reliably reflect the quality of the air. The air quality of urban areas around Huelva can thereby be evaluated in more detail with multiple observation points.

The impact of metal emissions from industrial activities, especially from the Cu smelter, correlates with extremely high concentrations of PTEs in lichens in the immediate surroundings of the industrial estates, thus implying potential health risks to humans. However, a mixed pollution source is most likely in an urban environment. The mean concentrations of Co, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb, U, and S were significantly higher in Zone 1 of study ( $<1$  km from the source) than in Zone 2 ( $>1$  km); yet the mean concentrations for instance of Cu, Zn, As, Cd, Sb, and S in Zone 2 remained considerably elevated with respect to the reference area. Only Cu and S exhibited statistically significant differences. These findings establish that metal pollution reaches urban areas located  $>4$  km from the major pollution sources, *i.e.*, industrial activities. In addition to the city of Huelva, the

nearby villages La Rábida and Palos de la Frontera are affected by the impact of industrial emissions.

## Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.07.086>.

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**E T O C B L U R B**

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Extreme concentrations of potentially toxic elements in lichens in urban areas surrounding industrial estates imply severe air pollution and a potential health risk to residents.