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Trace metal and metalloid contamination levels in soils and in two native plant species of a former industrial site: Evaluation of the phytostabilization potential

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H I G H L I G H T S

- Soils and plants contamination (metals, metalloids) on a former smelting factory site.
- Identification of specific contaminated zones (slagheaps and horizontal chimney).
- Element transfer into *G. alypum* and *R. officinalis* which are metal tolerant species.
- Plant contents more dependent on soil contamination level than on plant species.
- Excluders bioconcentrate metals in roots and offer a phytostabilization potential.

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A B S T R A C T

This study aimed at identifying the extent and type of contamination of a former lead smelting site in the area of Marseille, France, dating from the industrial revolution, and to evaluate environmental hazards and opportunities for phytoremediation, a promising sustainable technology. Amongst the native plants growing in this semiarid shrub ecosystem, two perennials *Globularia alypum* L. and *Rosmarinus officinalis* L. were selected. Twenty-one soil/plant couples were collected and seventeen additional soil samples were added to better characterize the soil pollution of the area. A multi-contamination by Pb, As, Sb, Zn, Cu was demonstrated, with huge variations within the contamination levels. The soils highest concentrations were encountered along the horizontal chimney and on the slag heaps area. However, both sites differed from each other. The former was characterized by the highest Pb, As and Sb concentrations that could reach 130, 7.0 and 9.0 g kg⁻¹ respectively, the latter, by high Cu, Fe, Mn, S concentrations, even if it was also heavily contaminated by Pb and Zn. *G. alypum* and *R. officinalis* were shown to be metal-tolerant and to accumulate trace metals and As. Due to the low bioconcentration and translocation factors determined, both species may not be used for phytoextraction, but seem to be good candidates for phytostabilization.

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1. Introduction

Heavy metals are ubiquitous environmental contaminants in industrialized countries. Metal mining and smelting activities tend

to become important sources of air, soil and water pollution [1–3]. Smelting activities used to generate large volumes of slag and emit fumes with high concentrations of heavy metals (Cu, Pb, Zn) and metalloids (As, Sb), and have been causing soil degradation and ecological landscape destruction. As waste was generally left untreated after smelter activities ceased, trace metals and metalloid could be released into the environment by natural weathering processes that commonly increase their solubility and bioavailability [4,5]. Abandoned sites remain local long-term point sources of contamination. In Europe, inventories of these sites have recently been implemented. The former industrial site of l'Escalette, located in the Southeast coast of Marseille, the second urban area of France,

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is referenced in the French database BASOL [6], which is a database from the French Ministry of Ecology and Sustainable Development, on polluted sites and soils on the French territory reclaiming an action from national authorities. In 1925 the silver-lead ores smelting ceased its activities; approximately 20,000 m³ of slag were deposited on the old factory site, but slag was also scattered along the coast as road fill. Risks to the surrounding area and its inhabitants, as well as long distance transport may be aggravated by a scarce vegetation cover and occurrence of bare soils, which is common in the areas around the Mediterranean because of the scarce precipitation during summer. In April 2012, the French government promoted the National Park of Calanques, including the polluted area of l'Escalette, and in this context the supervision of this site is a first priority. Revegetation could be an effective method for site restoration, immobilizing trace elements, limiting water and wind erosions and improving landscape [7]. However, due to the extreme conditions encountered in abandoned industrial sites and to Mediterranean climatic constraints, a first step is to select appropriated plant species. In the case of l'Escalette, a double constraint drove this study: (1) to find plant species which have been previously demonstrated to grow in polluted soils and are adapted to the Mediterranean climate [8,9], and (2) that are furthermore native species to prevent any plant invasion or gene pollution in this protected area. In this context, it was important, firstly, to identify the physico-chemical properties of the site contaminated soils, including type and concentration of pollutants and, secondly, to investigate trace element transfer to some native plants and their possible application to soil phytoremediation focused on the industrial site and more specifically to soil phytostabilization in its surroundings.

2. Materials and methods

2.1. Site description

The smelting factory of Escalette is located in the South of Marseille, France (Fig. 1). Its activity lasted from 1851 to 1925. During this period, around 30,000t/year of silver-galena were treated by pyrometallurgical processes. The plant, situated at the lower part of a hill, is characterized by a horizontal chimney (creeping chimney) built up hillside. Slags have been deposited directly at the vicinity of the dismissed factory and are also present on road ballasts along the nearby coast. The area is submitted to the Mediterranean climate with average minimal and maximal temperatures of 7.1 and 24.1 °C, respectively, and an annual average rainfall of 554 mm on 56 days (reference period: 1971–2000). Dominant winds are North and North-East and can reach 120 km/h. The geological underground is limestone, bare rocks dominate, covered locally by thin and stony soils. Currently a top-soil partially covers the slag heaps. Soil contamination by trace elements finds its origin in deposition of fly ashes or of volatile compounds during the ore processing and in weathering and bioalteration of slag heaps and of the damaged chimney. Naturally growing plant species were identified on the site, even on the top of the slag heaps. Depending on the inventoried zones, the number of species varies from 20 to 33 species per 100 m², and the vegetation cover from 30 to 100%. Only a few plant species occur on all zones and only for 2 woody perennials, i.e. *Globularia alypum* L. and *Rosmarinus officinalis* L., numerous individuals were available for a statistical study.

2.2. Soil and plant sampling

Five zones (Fig. 1) were selected to represent the different types of soil occupancy during the industrial activity:

- Zone 1, North of the former factory, not under the direct influence of pollutant dispersion regarding to the prevailing wind (43°13–601' N–05°21–124' E): 23 plant species per 100 m² and a vegetation cover of 70%,
- Zone 2, in a transect of 50 m on both sides of the damaged chimney (43°13–538' N–05°21–155' E and 43°13–540' N–05°21–154' E): 25 plant species per 100 m² and a vegetation cover of 30%,
- Zone 3, including the two main slag heaps (slag heap 1 43°13–501' N–05°21–091' E; slag heap 2 43°13–456' N–05°21–126' E): 27 plant species per 100 m² and a vegetation cover of 60% for slag heap 1, 33 plant species per 100 m² and a vegetation cover of 40% for slag heap 2,
- Zone 4, a small valley formed between the two slag heaps (43°13–480' N–05°21–094' E): 32 plant species per 100 m² and a vegetation cover of 100%, the high cover percentage derived from the greater occurrence of herbaceous species,
- Zone 5, South of the former factory (43°13–278' N–05°21–458' E), under the dominant wind regarding the slag heaps: 22 plant species per 100 m² and a vegetation cover of 75%.

According to the results of the phytosociological summary (not shown), it was decided to focus the study on perennials and more precisely on *G. alypum* and *R. officinalis* since both are present with numerous individuals on slag heaps in spite of the extreme growth conditions and are common in the surroundings. Indeed, some woody perennials such as *Juniperus phoenicea* L., were only represented by a few individuals.

A total of 21 plant/soil couples were taken. Roots and aerial parts of plants and soil from rooting zone were collected. For the physico-chemical characterization of soils, 17 soil samples (0–20 cm) were added. Soils were taken after removal of the litter.

2.3. Soil analyses

Soil samples were sieved on site to 2 mm mesh, air-dried at room temperature and then ground (RETSCH zm 1000 with tungsten blades) to pass through a 0.2 mm titanium sieve before analyses. pH was measured after stirring for 1 h a soil/UHQ-water mixture with a 1:5 ratio (NF ISO 10390, pH-metre Orion2 Star Thermosci-entific). Total organic carbon (TOC) quantifications were carried out with a Jena Analytic TOC-N/C2100S. Total concentrations of major elements, trace metals and metalloids were determined by X-ray Fluorescence (XRF) using a Philips Panalytical PW2400 wavelength-dispersive spectrometer (gas flow counter or scintillation counter) after grinding to 80 µm. Quality assurance-quality controls and accuracy were checked using standard soil reference materials (Fer-4) from the Canada Centre for Mineral and Energy Technology CCRMP (accuracies within 100 ± 15%).

2.4. Plant analysis

Harvested plants were divided into root and shoot parts. Plant material was carefully washed with deionized and further ultra-pure water to remove dust and soil particles, and then air-dried at room temperature. Before analysis, plant samples were ground to pass through a 0.2 mm mesh titanium sieve. About 0.5 g of dry matter was digested with the microwave digestion system Milestone start D with a HNO₃, H₂O₂ and ultra-pure H₂O mixture (volume proportion ratio 2:1:1). Extracts were analyzed for pseudo-total As, Cu, Pb and Zn contents using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY 2000 Jobin Yvon Horiba). Triplicates were performed for each sample. Standard plant reference materials (DC 73349) from China National Analysis Centre for Iron and Steel (NSC) were analyzed as a part of the quality assurance-quality control protocol (accuracies within 100 ± 10%).

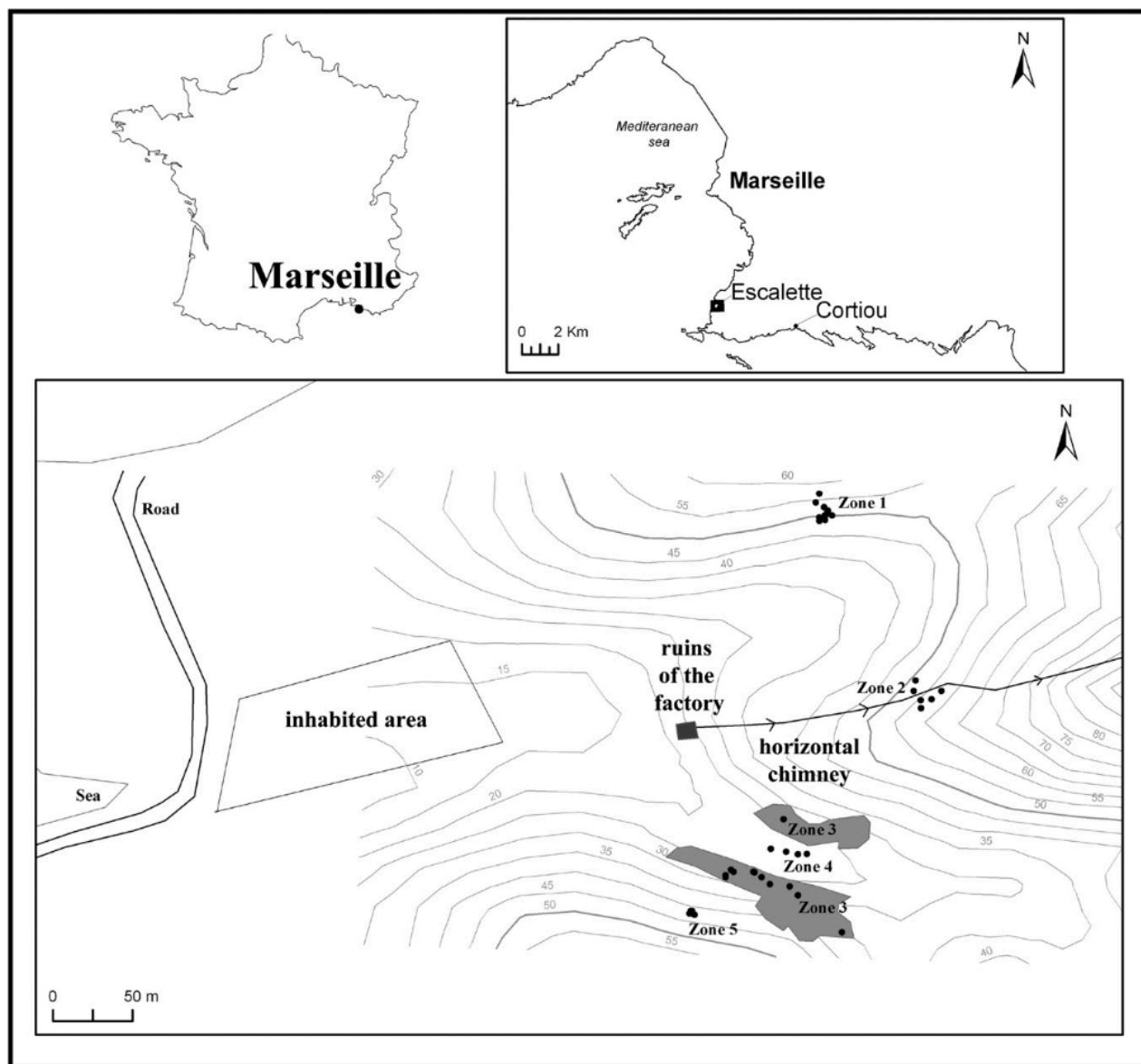


Fig. 1. Location of l'Escalette former industrial site (Marseille, France) and of the sampling points.

Bioaccumulation factors (BCF) and translocation factors (TF) were computed according to the following formula [10]:

$$BCF = \frac{C_2}{C_1}$$

$$TF = \frac{C_3}{C_2}$$

where C_1 , C_2 , C_3 are average concentrations of trace element in soil, roots and shoots, respectively.

2.5. Statistical analysis

All statistical processing of the collected data was performed using the statistical programme package version 17 of SPSS® (Statistic Programme for Social Science). Principal component analysis (PCA) was applied to normalized data, such that the covariance matrix coincides with the correlation matrix. Suitability of data sets

for factor analysis was ensured using Kaiser-Meyer-Olkin (KMO) and Barlett's tests.

3. Result and discussion

3.1. Soil characteristics and contamination levels

Soils were stony; their thicknesses varied from place to place but were generally less than 50 cm. Raw results on soil characteristics are summarized in Table 1. Soils were alkaline with pH belonging to the typical pH range, 7.5–8.5, of soils from calcareous areas. pH of soils collected near the chimney or on slag heaps, could locally reach values higher than 8.5, certainly in relation with deposits of anthropogenic alkaline materials. TOC varied from 0.9% to 7.6%, the highest concentration being observed in zone 5 located at the South of the former factory. Concentrations of Ca, Si, Fe, S were found in large ranges of concentrations, from 58 to 313 g kg⁻¹ for Ca, from 47 to 237 g kg⁻¹ for Si, from 7.1 to 104 g kg⁻¹ for Fe and from 0.7 to 17 g kg⁻¹ for S. Observed concentrations of major elements

Table 1
Physico-chemical characteristics of soils from l'Escalette, mean $\pm$ SD ($n=3$).

Zone	Sampling points	pH	TOC (g kg ⁻¹)	Major elements (g kg ⁻¹)								CI			
				Mg	Ca	Fe	Mn	S	P	K	Al	Si			
1	1.1	8.2 $\pm$ 0.1	32.0 $\pm$ 1.2	11.0 $\pm$ 0.8	69.1 $\pm$ 5.2	19.7 $\pm$ 1.2	0.68 $\pm$ 0.06	0.90 $\pm$ 0.06	0.23 $\pm$ 0.01	9.62 $\pm$ 0.8	34.2 $\pm$ 2.1	237 $\pm$ 19	0.80 $\pm$ 0.07		
	1.2	8.3 $\pm$ 0.3	40.7 $\pm$ 1.3	13.7 $\pm$ 0.9	57.8 $\pm$ 4.6	19.3 $\pm$ 1.0	0.83 $\pm$ 0.07	1.5 $\pm$ 0.4	0.28 $\pm$ 0.01	10.2 $\pm$ 0.9	33.8 $\pm$ 2.5	226 $\pm$ 17	1.9 $\pm$ 0.8		
	1.3	8.5 $\pm$ 0.3	49.5 $\pm$ 2.5	10.9 $\pm$ 0.7	133 $\pm$ 10	15.4 $\pm$ 0.8	0.38 $\pm$ 0.01	1.4 $\pm$ 0.3	0.36 $\pm$ 0.02	7.3 $\pm$ 0.8	26.0 $\pm$ 1.8	127 $\pm$ 9	0.8 $\pm$ 0.06		
	1.4	8.2 $\pm$ 0.2	40.0 $\pm$ 3.1	7.14 $\pm$ 0.5	313 $\pm$ 12	7.01 $\pm$ 0.2	0.23 $\pm$ 0.0	1.7 $\pm$ 0.6	0.23 $\pm$ 0.01	2.3 $\pm$ 0.1	7.2 $\pm$ 0.9	47.2 $\pm$ 3	0.5 $\pm$ 0.02		
	1.5	8.1 $\pm$ 0.1	40.0 $\pm$ 2.8	7.92 $\pm$ 0.6	278 $\pm$ 17	11.5 $\pm$ 0.6	0.30 $\pm$ 0.0	1.2 $\pm$ 0.1	0.34 $\pm$ 0.02	3.4 $\pm$ 0.2	11.6 $\pm$ 1.1	70.4 $\pm$ 6	0.4 $\pm$ 0.01		
	1.6	8.0 $\pm$ 0.1	40.0 $\pm$ 2.9	8.2 $\pm$ 0.6	273 $\pm$ 12	10.7 $\pm$ 0.8	0.30 $\pm$ 0.01	1.3 $\pm$ 0.1	0.32 $\pm$ 0.01	3.6 $\pm$ 0.2	12.0 $\pm$ 0.9	69.9 $\pm$ 5	0.4 $\pm$ 0.02		
	1.7	8.0 $\pm$ 0.1	40.0 $\pm$ 2.7	8.6 $\pm$ 0.7	247 $\pm$ 10	14.2 $\pm$ 0.9	0.23 $\pm$ 0.01	1.4 $\pm$ 0.1	0.34 $\pm$ 0.01	4.0 $\pm$ 0.2	13.7 $\pm$ 0.9	84.1 $\pm$ 7	0.1 $\pm$ 0.0		
2	1.8	8.0 $\pm$ 0.2	35.8 $\pm$ 1.8	9.0 $\pm$ 0.45	245 $\pm$ 9	9.9 $\pm$ 0.4	0.17 $\pm$ 0.008	0.9 $\pm$ 0.04	0.30 $\pm$ 0.01	4.8 $\pm$ 0.2	15.3 $\pm$ 0.7	74.7 $\pm$ 6	0.2 $\pm$ 0.01		
	1.9	8.0 $\pm$ 0.1	37.9 $\pm$ 1.9	8.4 $\pm$ 0.42	243 $\pm$ 9	11.6 $\pm$ 0.6	0.18 $\pm$ 0.008	1.4 $\pm$ 0.07	0.26 $\pm$ 0.01	4.4 $\pm$ 0.2	14.0 $\pm$ 0.6	78.0 $\pm$ 6	0.2 $\pm$ 0.01		
	1.10	7.9 $\pm$ 0.2	43.4 $\pm$ 2.1	10.5 $\pm$ 0.52	89.3 $\pm$ 5	19.2 $\pm$ 0.1	0.76 $\pm$ 0.004	1.4 $\pm$ 0.06	0.36 $\pm$ 0.01	9.5 $\pm$ 0.4	29.6 $\pm$ 1.4	217 $\pm$ 11	0.5 $\pm$ 0.02		
	2.1	8.9 $\pm$ 0.6	21.6 $\pm$ 2.1	6.0 $\pm$ 0.4	212 $\pm$ 12	8.1 $\pm$ 0.7	0.30 $\pm$ 0.01	2.8 $\pm$ 0.01	0.21 $\pm$ 0.01	2.1 $\pm$ 0.1	7.3 $\pm$ 0.8	76.7 $\pm$ 6	2.0 $\pm$ 0.6		
	2.2	8.8 $\pm$ 0.6	38.0 $\pm$ 2.5	10.6 $\pm$ 1.0	135 $\pm$ 9	14.6 $\pm$ 1.0	0.83 $\pm$ 0.04	1.8 $\pm$ 0.05	0.51 $\pm$ 0.03	5.1 $\pm$ 0.4	21.1 $\pm$ 1.9	134 $\pm$ 9	0.5 $\pm$ 0.04		
	2.3	8.7 $\pm$ 0.6	24.0 $\pm$ 1.9	7.92 $\pm$ 0.6	209 $\pm$ 9	10.4 $\pm$ 0.7	0.60 $\pm$ 0.04	1.6 $\pm$ 0.04	0.36 $\pm$ 0.01	3.5 $\pm$ 0.3	13.3 $\pm$ 0.8	96.1 $\pm$ 7	1.2 $\pm$ 0.7		
	2.4	8.6 $\pm$ 0.6	34.8 $\pm$ 2.1	8.2 $\pm$ 0.7	179 $\pm$ 11	13.0 $\pm$ 1.0	0.60 $\pm$ 0.05	1.9 $\pm$ 0.03	0.43 $\pm$ 0.02	3.8 $\pm$ 0.3	14.4 $\pm$ 0.9	137 $\pm$ 9	1.6 $\pm$ 0.7		
3	2.5	8.3 $\pm$ 0.4	30.0 $\pm$ 2.0	8.5 $\pm$ 0.6	172 $\pm$ 12	12.3 $\pm$ 0.9	0.50 $\pm$ 0.02	2.0 $\pm$ 0.03	0.34 $\pm$ 0.01	4.4 $\pm$ 0.3	16.5 $\pm$ 1.2	152 $\pm$ 12	1.4 $\pm$ 0.6		
	2.6	8.1 $\pm$ 0.2	30.0 $\pm$ 1.2	14.7 $\pm$ 1.1	74.0 $\pm$ 6.5	22.6 $\pm$ 0.8	0.80 $\pm$ 0.06	0.7 $\pm$ 0.06	0.25 $\pm$ 0.01	8.7 $\pm$ 1.1	37.2 $\pm$ 2.8	217 $\pm$ 16	0.2 $\pm$ 0.01		
	3.1	8.5 $\pm$ 0.2	31.0 $\pm$ 1.4	10.4 $\pm$ 0.9	215 $\pm$ 12	23.7 $\pm$ 0.8	0.60 $\pm$ 0.03	2.2 $\pm$ 0.1	0.53 $\pm$ 0.02	4.7 $\pm$ 0.4	19.2 $\pm$ 1.4	133 $\pm$ 11	0.3 $\pm$ 0.01		
	3.2	8.8 $\pm$ 0.8	26.2 $\pm$ 1.6	10.9 $\pm$ 0.9	183 $\pm$ 12	40.4 $\pm$ 3	0.70 $\pm$ 0.04	6.6 $\pm$ 0.1	0.83 $\pm$ 0.05	3.0 $\pm$ 0.3	13.2 $\pm$ 1.1	116 $\pm$ 9	1.8 $\pm$ 0.7		
	3.3	8.8 $\pm$ 0.6	19.0 $\pm$ 1.1	8.16 $\pm$ 0.7	170 $\pm$ 10	59.4 $\pm$ 4	0.80 $\pm$ 0.06	9.4 $\pm$ 0.2	0.34 $\pm$ 0.02	3.5 $\pm$ 0.4	14.0 $\pm$ 1.1	113 $\pm$ 8	0.7 $\pm$ 0.06		
	3.4	8.7 $\pm$ 0.8	27.7 $\pm$ 0.9	8.8 $\pm$ 0.8	126 $\pm$ 10	85.9 $\pm$ 7	1.0 $\pm$ 0.1	11.6 $\pm$ 0.8	0.62 $\pm$ 0.05	3.1 $\pm$ 0.2	12.8 $\pm$ 0.9	110 $\pm$ 8	0.9 $\pm$ 0.07		
	3.5	7.5 $\pm$ 0.1	29.0 $\pm$ 2.9	12.6 $\pm$ 0.7	126 $\pm$ 9	31.8 $\pm$ 2.1	0.80 $\pm$ 0.04	5.0 $\pm$ 0.1	0.59 $\pm$ 0.04	4.3 $\pm$ 0.2	18.2 $\pm$ 1.2	125 $\pm$ 9	4.1 $\pm$ 0.9		
4	3.6	7.3 $\pm$ 0.1	29.0 $\pm$ 0.8	11.7 $\pm$ 0.9	189 $\pm$ 12	31.8 $\pm$ 2.2	0.80 $\pm$ 0.05	6.9 $\pm$ 0.1	1.19 $\pm$ 0.1	2.9 $\pm$ 0.2	14.2 $\pm$ 1.2	117 $\pm$ 8	0.7 $\pm$ 0.05		
	3.7	8.1 $\pm$ 0.4	41.7 $\pm$ 2.1	16.0 $\pm$ 0.8	206 $\pm$ 10	47.5 $\pm$ 2.3	0.76 $\pm$ 0.03	7.6 $\pm$ 0.4	1.63 $\pm$ 0.08	2.0 $\pm$ 0.1	16.6 $\pm$ 0.8	92.0 $\pm$ 4.6	0.6 $\pm$ 0.03		
	3.8	8.2 $\pm$ 0.4	9.26 $\pm$ 0.5	9.6 $\pm$ 0.5	206 $\pm$ 9	39.7 $\pm$ 2.0	0.64 $\pm$ 0.02	5.9 $\pm$ 0.3	0.3 $\pm$ 0.01	3.7 $\pm$ 0.1	15.3 $\pm$ 0.7	109 $\pm$ 5	0.5 $\pm$ 0.02		
	3.9	8.1 $\pm$ 0.3	45.0 $\pm$ 2.2	12.6 $\pm$ 0.6	211 $\pm$ 10	52.0 $\pm$ 2.6	0.83 $\pm$ 0.04	8.7 $\pm$ 0.4	1.43 $\pm$ 0.07	1.7 $\pm$ 0.08	14.6 $\pm$ 0.7	85.0 $\pm$ 4.2	0.7 $\pm$ 0.03		
	3.10	8.1 $\pm$ 0.3	34.1 $\pm$ 1.7	15.7 $\pm$ 0.8	224 $\pm$ 11	44.8 $\pm$ 2.25	0.76 $\pm$ 0.03	8.3 $\pm$ 0.4	1.67 $\pm$ 0.08	1.6 $\pm$ 0.08	17.3 $\pm$ 0.8	87.8 $\pm$ 4.2	0.3 $\pm$ 0.01		
	3.11	8.0 $\pm$ 0.4	14.0 $\pm$ 0.7	8.4 $\pm$ 0.4	107 $\pm$ 6	104 $\pm$ 5	1.7 $\pm$ 0.08	17.3 $\pm$ 0.8	0.53 $\pm$ 0.02	2.9 $\pm$ 0.1	13.2 $\pm$ 0.6	109 $\pm$ 8	0.7 $\pm$ 0.03		
	3.12	8.0 $\pm$ 0.4	25.5 $\pm$ 1.3	10.8 $\pm$ 0.5	157 $\pm$ 7	76.3 $\pm$ 3.8	1.14 $\pm$ 0.06	9.7 $\pm$ 0.4	1.2 $\pm$ 0.06	2.4 $\pm$ 0.1	13.9 $\pm$ 0.7	102 $\pm$ 7	0.4 $\pm$ 0.02		
5	4.1	8.5 $\pm$ 0.8	31.1 $\pm$ 3.0	32.8 $\pm$ 2.2	260 $\pm$ 10	11.5 $\pm$ 0.4	0.20 $\pm$ 0.01	1.1 $\pm$ 0.01	0.68 $\pm$ 0.05	2.6 $\pm$ 0.1	8.7 $\pm$ 0.8	83.7 $\pm$ 6	1.1 $\pm$ 0.08		
	4.2	7.7 $\pm$ 0.1	30.0 $\pm$ 2.1	24.5 $\pm$ 1.9	246 $\pm$ 11	10 $\pm$ 0.9	0.30 $\pm$ 0.01	5.5 $\pm$ 0.1	0.36 $\pm$ 0.02	2.6 $\pm$ 0.2	8.5 $\pm$ 0.7	113 $\pm$ 9	0.5 $\pm$ 0.02		
	4.3	8.1 $\pm$ 0.3	30.0 $\pm$ 1.5	22.1 $\pm$ 1.4	230 $\pm$ 11	35.8 $\pm$ 1.8	0.41 $\pm$ 0.02	4.2 $\pm$ 0.2	1.07 $\pm$ 0.05	3.0 $\pm$ 0.1	10.5 $\pm$ 0.5	89.0 $\pm$ 4.4	0.5 $\pm$ 0.02		
	4.4	8.2 $\pm$ 0.1	30.0 $\pm$ 2.5	14.2 $\pm$ 1.7	203 $\pm$ 16	63.4 $\pm$ 2.1	0.61 $\pm$ 0.02	4.2 $\pm$ 0.1	0.86 $\pm$ 0.1	2.6 $\pm$ 0.2	4.0 $\pm$ 0.8	94 $\pm$ 8	0.5 $\pm$ 0.01		
	5.1	7.6 $\pm$ 0.1	24.7 $\pm$ 1.2	11.2 $\pm$ 0.6	244 $\pm$ 12	8.9 $\pm$ 0.4	0.53 $\pm$ 0.02	0.95 $\pm$ 0.04	0.23 $\pm$ 0.01	3.2 $\pm$ 0.1	12.2 $\pm$ 0.6	107 $\pm$ 9	0.18 $\pm$ 0.009		
	5.2	7.4 $\pm$ 0.2	69.5 $\pm$ 3.5	11.1 $\pm$ 0.5	243 $\pm$ 12	8.9 $\pm$ 0.3	0.53 $\pm$ 0.02	1.35 $\pm$ 0.09	0.28 $\pm$ 0.01	3.1 $\pm$ 0.1	12.2 $\pm$ 0.6	95.0 $\pm$ 4.7	0.16 $\pm$ 0.03		
	5.3	7.5 $\pm$ 0.2	67.9 $\pm$ 3.2	12.4 $\pm$ 0.6	224 $\pm$ 11	9.6 $\pm$ 0.4	0.61 $\pm$ 0.02	1.5 $\pm$ 0.09	0.32 $\pm$ 0.01	3.3 $\pm$ 0.1	12.4 $\pm$ 0.6	107 $\pm$ 5	0.35 $\pm$ 0.01		
5.5	5.4	7.6 $\pm$ 0.1	39.3 $\pm$ 1.9	10.7 $\pm$ 0.5	256 $\pm$ 11	8.5 $\pm$ 0.3	0.53 $\pm$ 0.02	0.86 $\pm$ 0.04	0.23 $\pm$ 0.01	1.2 $\pm$ 0.06	11.0 $\pm$ 0.5	99.0 $\pm$ 4.6	0.15 $\pm$ 0.03		
	5.5	7.7 $\pm$ 0.2	76.4 $\pm$ 3.8	11.5 $\pm$ 0.6	218 $\pm$ 10	9.9 $\pm$ 0.4	0.61 $\pm$ 0.01	1.65 $\pm$ 0.08	0.36 $\pm$ 0.01	1.4 $\pm$ 0.06	12.7 $\pm$ 0.6	104 $\pm$ 5	0.24 $\pm$ 0.01		
	5.6	7.6 $\pm$ 0.1	74.0 $\pm$ 3.7	11.6 $\pm$ 0.6	233 $\pm$ 10	9.4 $\pm$ 0.3	0.61 $\pm$ 0.03	1.16 $\pm$ 0.06	0.3 $\pm$ 0.01	1.3 $\pm$ 0.05	12.8 $\pm$ 0.6	104 $\pm$ 5	0.26 $\pm$ 0.01		

Table 2Trace element concentrations of soils from l'Escalette (g kg^{-1}), mean $\pm$ SD ($n = 3$).

Zone	Sampling points	Heavy metals and metalloids (g kg^{-1})				
		Pb	As	Sb	Cu	Zn
1	1.1	0.75 $\pm$ 0.08	<DL	0.04 $\pm$ 0.003	0.04 $\pm$ 0.002	0.21 $\pm$ 0.01
	1.2	0.58 $\pm$ 0.01	<DL	0.03 $\pm$ 0.003	0.03 $\pm$ 0.001	0.29 $\pm$ 0.02
	1.3	0.96 $\pm$ 0.08	0.26 $\pm$ 0.02	<DL	0.04 $\pm$ 0.003	0.35 $\pm$ 0.03
	1.4	3.64 $\pm$ 0.2	0.08 $\pm$ 0.007	0.16 $\pm$ 0.001	0.04 $\pm$ 0.004	1.6 $\pm$ 0.1
	1.5	8.5 $\pm$ 0.6	0.07 $\pm$ 0.006	0.3 $\pm$ 0.02	0.14 $\pm$ 0.001	7.0 $\pm$ 0.6
	1.6	6.04 $\pm$ 0.5	0.09 $\pm$ 0.008	0.24 $\pm$ 0.02	0.10 $\pm$ 0.001	4.0 $\pm$ 0.3
	1.7	8.7 $\pm$ 0.7	0.05 $\pm$ 0.004	0.4 $\pm$ 0.03	0.12 $\pm$ 0.001	6.5 $\pm$ 0.5
	1.8	1.64 $\pm$ 0.08	<DL	0.12 $\pm$ 0.006	0.085 $\pm$ 0.004	1.57 $\pm$ 0.07
	1.9	3.16 $\pm$ 0.16	0.02 $\pm$ 0.001	0.22 $\pm$ 0.01	0.1 $\pm$ 0.004	2.8 $\pm$ 0.1
	1.10	1.56 $\pm$ 0.07	0.016 $\pm$ 0.0008	0.09 $\pm$ 0.004	0.05 $\pm$ 0.002	0.94 $\pm$ 0.05
2	2.1	130 $\pm$ 9	5.8 $\pm$ 0.6	9.03 $\pm$ 0.8	0.30 $\pm$ 0.02	48 $\pm$ 3.2
	2.2	29.9 $\pm$ 2.1	1.8 $\pm$ 0.17	1.56 $\pm$ 0.1	0.10 $\pm$ 0.01	7.58 $\pm$ 0.7
	2.3	66.6 $\pm$ 4.2	4.0 $\pm$ 0.4	4.83 $\pm$ 0.4	0.14 $\pm$ 0.01	21.1 $\pm$ 0.9
	2.4	83.1 $\pm$ 4.5	4.1 $\pm$ 0.3	4.42 $\pm$ 0.35	0.24 $\pm$ 0.02	24.6 $\pm$ 0.8
	2.5	43.3 $\pm$ 1.3	7.0 $\pm$ 0.65	3.10 $\pm$ 0.27	0.04 $\pm$ 0.03	7.7 $\pm$ 0.6
	2.6	12.8 $\pm$ 0.8	2.1 $\pm$ 0.19	1.28 $\pm$ 0.1	0.02 $\pm$ 0.01	2.8 $\pm$ 0.15
3	3.1	13.7 $\pm$ 0.8	0.49 $\pm$ 0.04	1.6 $\pm$ 0.1	0.9 $\pm$ 0.08	10.6 $\pm$ 0.12
	3.2	24.7 $\pm$ 0.9	0.22 $\pm$ 0.02	1.5 $\pm$ 0.1	2.4 $\pm$ 0.2	30.9 $\pm$ 1.2
	3.3	51.4 $\pm$ 3.2	0.41 $\pm$ 0.03	2.0 $\pm$ 0.2	7.9 $\pm$ 0.7	36.3 $\pm$ 1.3
	3.4	60.4 $\pm$ 4.1	0.36 $\pm$ 0.03	1.1 $\pm$ 0.1	6.4 $\pm$ 0.6	52.0 $\pm$ 3.2
	3.5	21.4 $\pm$ 1.5	0.23 $\pm$ 0.02	0.32 $\pm$ 0.02	1.1 $\pm$ 0.1	8.7 $\pm$ 0.7
	3.6	34.3 $\pm$ 1.6	0.80 $\pm$ 0.08	1.86 $\pm$ 0.15	2.2 $\pm$ 0.2	30 $\pm$ 2.1
	3.7	16.2 $\pm$ 0.8	0.12 $\pm$ 0.006	1.72 $\pm$ 0.08	2.1 $\pm$ 0.1	16.2 $\pm$ 0.8
	3.8	24.4 $\pm$ 1.2	0.24 $\pm$ 0.01	1.0 $\pm$ 0.05	4.6 $\pm$ 0.2	24.4 $\pm$ 1.2
	3.9	18.9 $\pm$ 0.9	0.31 $\pm$ 0.01	1.1 $\pm$ 0.05	2.3 $\pm$ 0.1	18.9 $\pm$ 0.9
	3.10	11.7 $\pm$ 0.5	0.10 $\pm$ 0.005	1.28 $\pm$ 0.05	1.5 $\pm$ 0.07	13.6 $\pm$ 0.6
	3.11	71.7 $\pm$ 3.5	0.25 $\pm$ 0.01	1.01 $\pm$ 0.05	7.1 $\pm$ 0.3	65.6 $\pm$ 3.2
	3.12	44.5 $\pm$ 2.2	0.29 $\pm$ 0.01	1.21 $\pm$ 0.05	5.5 $\pm$ 0.2	41.3 $\pm$ 2.0
4	4.1	0.075 $\pm$ 0.002	<DL	<DL	0.06 $\pm$ 0.005	0.26 $\pm$ 0.02
	4.2	6.45 $\pm$ 0.7	0.07 $\pm$ 0.006	0.70 $\pm$ 0.06	0.5 $\pm$ 0.004	15.5 $\pm$ 1.2
	4.3	0.72 $\pm$ 0.03	<DL	0.032 $\pm$ 0.001	0.12 $\pm$ 0.006	1.03 $\pm$ 0.05
	4.4	5.8 $\pm$ 0.4	0.06 $\pm$ 0.005	0.26 $\pm$ 0.02	0.83 $\pm$ 0.07	7.9 $\pm$ 0.7
5	5.1	1.56 $\pm$ 0.07	0.02 $\pm$ 0.001	0.06 $\pm$ 0.003	0.07 $\pm$ 0.003	1.56 $\pm$ 0.07
	5.2	1.76 $\pm$ 0.08	0.02 $\pm$ 0.001	0.09 $\pm$ 0.004	0.07 $\pm$ 0.003	1.76 $\pm$ 0.08
	5.3	1.85 $\pm$ 0.08	0.01 $\pm$ 0.0005	0.11 $\pm$ 0.005	0.07 $\pm$ 0.002	1.85 $\pm$ 0.09
	5.4	1.35 $\pm$ 0.02	0.03 $\pm$ 0.001	0.05 $\pm$ 0.002	0.07 $\pm$ 0.003	0.6 $\pm$ 0.03
	5.5	1.64 $\pm$ 0.05	<DL	0.04 $\pm$ 0.001	0.074 $\pm$ 0.002	0.66 $\pm$ 0.03
	5.6	1.95 $\pm$ 0.08	0.05 $\pm$ 0.002	0.1 $\pm$ 0.005	0.08 $\pm$ 0.003	0.82 $\pm$ 0.04

<DL: lower than the detection limit for As 0.0008 and Sb 0.0005 g kg^{-1} .

did not only depend on the natural environment, but reflected historical land use in the studied area. A multi-contamination by trace elements was demonstrated (Table 2). Soils were heavily contaminated by As, Pb, and Sb with concentrations up to 7.0, 130, and 9 g kg^{-1} respectively. Abnormal concentrations of Cu and Zn were also observed, with concentrations up to 7.9 and 65 g kg^{-1} respectively. For comparison, the concentrations of the most contaminated sampling points were up to 5000 times for Pb, between 500 and 900 times for Cu and Zn, the respective median concentrations of French agricultural soils that are of 25.6, 13.8, and 59.0 mg kg^{-1} respectively [11]. A mapping of element concentrations in an extended area around the factory site was conducted in parallel, comparing the percentiles 0.05 ($n = 250$) that are of 40, <10 and 53 mg kg^{-1} for Pb, Cu and Zn respectively, with the result that the soil concentrations in the factory immediate vicinity clearly confirm its important contamination role.

In order to better understand soils physico-chemical characteristics, a PCA was performed. In a first step, all the analytical parameters were considered for the 38 soils (PCA1). Then, in order to have a better view of soil contamination by trace elements, a second stepwise principal component analysis (PCA2) was realized, considering only 9 parameters i.e. Fe, Mn, Zn, S, Cu, Pb, As, Sb and TOC.

In PCA1, the first four components had Eigenvalues > 1 and accounted for 80.6% of the total variance. The rotated component

matrix for these 4 components is presented in Table 3 (supplemental material).

The first principal component explained 32.43% of the total variance. It had high positive loadings of Fe, S, Cu (>0.90), Zn and Mn (>0.80) and a moderate negative loading of TOC. The second principal component explained 22.30% of the total variance. It had high positive loadings of Si, Al, K (>0.92) and high negative loading of Ca (−0.89). The third principal component explained 18.68% of the total variance. It had high positive loadings of Sb, As, Pb (>0.84), a moderate negative loading of TOC (−0.511) and a moderate positive loading of Zn (0.488). The fourth principal component explained 7.19% of the total variance. It had high positive loadings of Mg (0.869) and a moderate positive loading with P (0.604).

Regarding results of PCA1, five groups of parameters could be identified.

Groups 1 to 5 were characterized by elements with communalities ≥ 0.8 and whose variance was principally explained by the same component:

- Group 1 gathered major elements Al, Si, K (component 2) and Ca (component 2 then 1),
- Group 2 only composed of Mg (component 4),
- Group 3 including elements Cu, Fe, S (component 1), Mn (components 1 then 2), Zn (component 1 then 3),

- Group 4 composed of As and Sb (component 3), Pb (components 3 then 1),
- Group 5 included TOC, pH and elements Cl and P, parameters with low values of communalities (respectively 0.465, 0.471, 0.644, 0.481) and whose variance was consequently poorly explained.

Groups 1 and 2 gathered the major elements. Ca, Al, Si and K naturally occur on the site but negative correlations ($p < 0.001$) were noted between Ca in one hand and Al, Si, K on the other hand. This result added to the large ranges of concentrations encountered seems to indicate an exogenous origin of Al, Si and K, related to gangue crushing or construction wastes. Mg is certainly more specific of the mineralogy of the site where it can be found in dolomite and gypsum.

Parameters characterizing the contamination by the smelting activities were divided in two groups: groups 3 and 4 which could indicate the presence of at least two major sources.

Considering PCA2 only components 1 and 2 had Eigenvalues > 1 . They explained 83.4% of the total variance.

Representation of individual scores in the plane PC1–PC2 of PCA1 (Fig. 2) allowed a global description of the studied zones while the same representation for PCA2 (Fig. 3) permitted to precise the type of contamination. The individual scores of sampling points located in the North of the factory (zone 1) were dispersed along axis 2 in the plane PC1–PC2 of PCA1 (Fig. 2) and were located in the negative part of the one of PCA2 (Fig. 3). This indicated that this zone was characterized by a large range of Al, Si, K and Ca concentrations, by the opposition between Al, Si, K in one hand and Ca in the other, and as being one of the less contaminated. Al, Si, and K concentrations were significantly correlated ($p < 0.001$), aluminosilicates of potassium were likely present. Zone 1 was mainly impacted by random deposits of scrap materials containing aluminosilicates such as tiles and bricks. Zone 5, of which individual scores of sampling points were located in the negative part of PCA1 and PCA2 could be considered as having characteristics closest to the natural conditions ones, i.e. high calcium and TOC concentrations and as being among the least contaminated zones, although despite its location under the dominant wind regarding the factory.

From Fig. 3b, it is obvious that the more contaminated soils were located near the chimney (zone 2) or on the slag heaps (zone 3). Soils sampled along the horizontal chimney (zone 2) were characterized by a more or less important presence of Al, Si, K and, even if highly polluted by Pb and locally by Zn, by a contamination differing from that of other zones by higher As and Sb concentrations (Figs. 2 and 3b). As and Sb belonging to the same periodic group were likely to have similar behaviour during ore treatment and after in soils. Pb and As were significantly correlated ($p < 0.001$), lead arsenate was likely to be present. Results indicated the presence of aluminosilicates that could be put in relation with the presence of materials, such as mortar or vault bricks, issuing from the degradation of the horizontal chimney. These degradation materials were rich in contaminants. Fumes emitted during the roasting of galena or smelting reduction processes contained volatile compounds and fly ashes which could be deposited during flue gas cooling and formed crusting rich in As, Sb, Pb and Zn all along the chimney. Damaged chimney sections could have released contaminated material, which, by weathering, have contaminated the soils located beyond the chimney.

The dispersion of individual scores of soils formed on slag heaps (zone 3) along PC1 in plane PC1–PC2 of PCA1 and PCA2 (Figs. 2 and 3) indicated that these soils were characterized by high concentrations of Cu, Fe, Mn and S, and by the large range of TOC encountered in the samples, from 0.9 to 4.5%. The presence of the elements Cu, Mn and S could be put in relation with the composition of the ores that were treated at the site, and with the reduction process with iron addition to explain the presence of Fe. Trace elements

can remain in slag as oxides, carbonates, sulphides or sulphates or more complex mineralogical forms including silicates. High significant correlation of S concentrations with those of Fe, Cu, and Zn ($r = 0.922$, $r = 0.886$, $r = 0.741$, $p < 0.001$ respectively) corroborated the presence of sulphides or sulphates. These results certainly could be linked to some specific micro- and macro- biological activities adapted to the extreme conditions on slag heaps. The TOC dispersion in soil developed on slag heaps might be related to topography and to plant cover but also to biolixivation processes. Generally Cu and Zn are considered to have high affinity for organic matter, but in this study, Cu and Zn concentrations were significantly negatively correlated to TOC ($r = -0.483$ and $r = -0.556$ for $p < 0.001$ respectively). This indicates that binding of these elements to organic matter remains marginal however, even in low concentrations in soil solutions, where low-molecular-weight organic acids can promote the dissolution of solids, mobility of elements and uptake of these into plants. Leaching tests in multiple organic acid solutions, simulating the rhizospheric environment would be required as previously reported in other studies [12,13].

Pb and Zn, even if encountered at high concentrations, did not seem to discriminate zone 2 from zone 3. However, regarding the results, it could be hypothesized that their major physico-chemical forms could be different according to the zone. Soils sampled in the small valley (zone 4) were rich in Ca and organic matter and approached the natural conditions regarding these parameters but a low dispersion of their individual scores towards the positive part of PC1 axes of PCA1 and PCA2 (Figs. 2 and 3) reflected the impact of the two slag heaps located on each side of the valley.

3.2. Metal concentrations in plants

Results of trace element concentrations in *G. alypum* and *R. officinalis* showed a great variability that was generally greater in roots than in shoots.

For *G. alypum*, concentrations ranged in roots and shoots, respectively:

- for arsenic, 0.001–0.38 g kg⁻¹ and 0.001–0.18 g kg⁻¹,
- for copper, 0.007–0.088 g kg⁻¹ and 0.006–0.011 g kg⁻¹,
- for lead, 0.020–2.64 g kg⁻¹ and 0.014–1.35 g kg⁻¹,
- for zinc, 0.024–0.77 g kg⁻¹ and 0.030–1.023 g kg⁻¹.

For *R. officinalis*, concentrations ranged in roots and shoots, respectively:

- for arsenic, 0.002–0.029 g kg⁻¹ and <0.0008–0.033 g kg⁻¹,
- for copper, <0.0001–0.041 g kg⁻¹ and <0.0001–0.017 g kg⁻¹,
- for lead, 0.038–1.15 g kg⁻¹ and <0.0002–0.153 g kg⁻¹,
- for zinc, 0.015–0.98 g kg⁻¹ and 0.027–0.115 g kg⁻¹.

The highest concentrations of As and Pb were found in *G. alypum*. However, no data on *R. officinalis* in zone 2, where the highest concentrations in soil were detected for these elements, were obtained. Thus no conclusion on the better phytoremedial performance of one of these plant species is possible. The lack of *R. officinalis* individuals on zone 2 may be due to either a lower metal tolerance or a less convenient habitat.

For similar Cu and Zn concentrations in soil, concentrations of these elements in both plant species were of the same order of magnitude (except for Zn in shoot of *G. alypum* collected on site 3.2). The highest As concentrations in roots and shoots of *G. alypum* did not drastically differ from those observed by Baroni et al. [14] in roots and leaves of *Mentha aquatica* (0.540 and 0.216 g kg⁻¹ respectively) and in roots of *Phragmites australis* (0.688 g kg⁻¹). The two latter exhibiting the highest concentrations among 64 plant species grown on two former Sb-mining and old quarry areas with

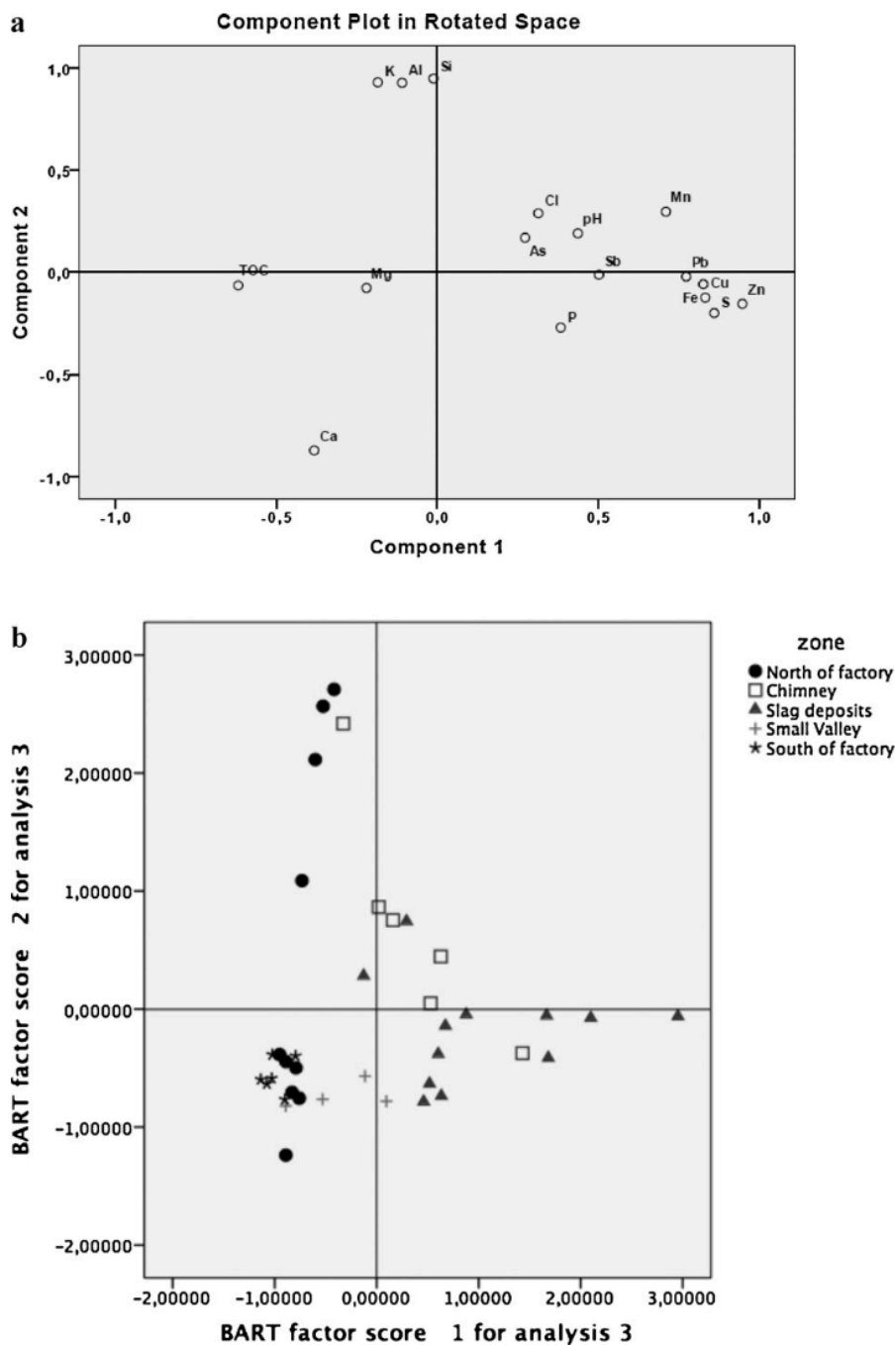


Fig. 2. PCA (PCA1) of 17 chemical properties of soils of the former industrial site of l'Escalette (France) represented by factors 1 and 2 (a) as loads, and (b) as individual scores.

As soil concentrations ranging from 0.0053 to 2.035 g kg⁻¹. Analyzing 36 individuals from 17 different plant species from a site contaminated by Pb, Cu and Zn, Yoon et al. [10] found concentration in roots and shoots, ranging respectively nd–1.183 g kg⁻¹ and nd–0.453 g kg⁻¹ for Pb, 0.025–0.598 g kg⁻¹ and 0.017–0.453 g kg⁻¹ for Zn, nd–0.460 g kg⁻¹ and 0.006–0.352 g kg⁻¹ for Cu. In our study, only *G. alypum* showed higher maximum concentrations of Pb and Zn (roots and shoots) than in the previous study by Yoon et al. These results seem congruent, Pb and Zn concentrations in soils in our study were from 4 to 30 and 2 to 10 times, respectively, higher than in the above-mentioned study. Cu concentrations in roots and shoots of *G. alypum* and *R. officinalis* were clearly lower than those

shown in Yoon et al. study [10], even when Cu concentrations in soil were higher than those in the previously cited study. Our results are similar to those reported by Wang et al. [1], with Cu concentrations ranging from 0.0037 to 0.123 g kg⁻¹ in roots and from 0.0011 to 0.0418 g kg⁻¹ in shoots in 9 plant species collected on Mn mining contaminated soil, but with only a Cu soil contamination of 0.093 g kg⁻¹.

Few works deal with trace element transfer to *R. officinalis* in the context of a contaminated site. For As concentrations in soils of the same order of magnitude (0.049–0.339 g kg⁻¹) than the ones of soil collected in the root zone of *R. officinalis* of Escalette, Domínguez et al. [15] observed concentrations in leaves

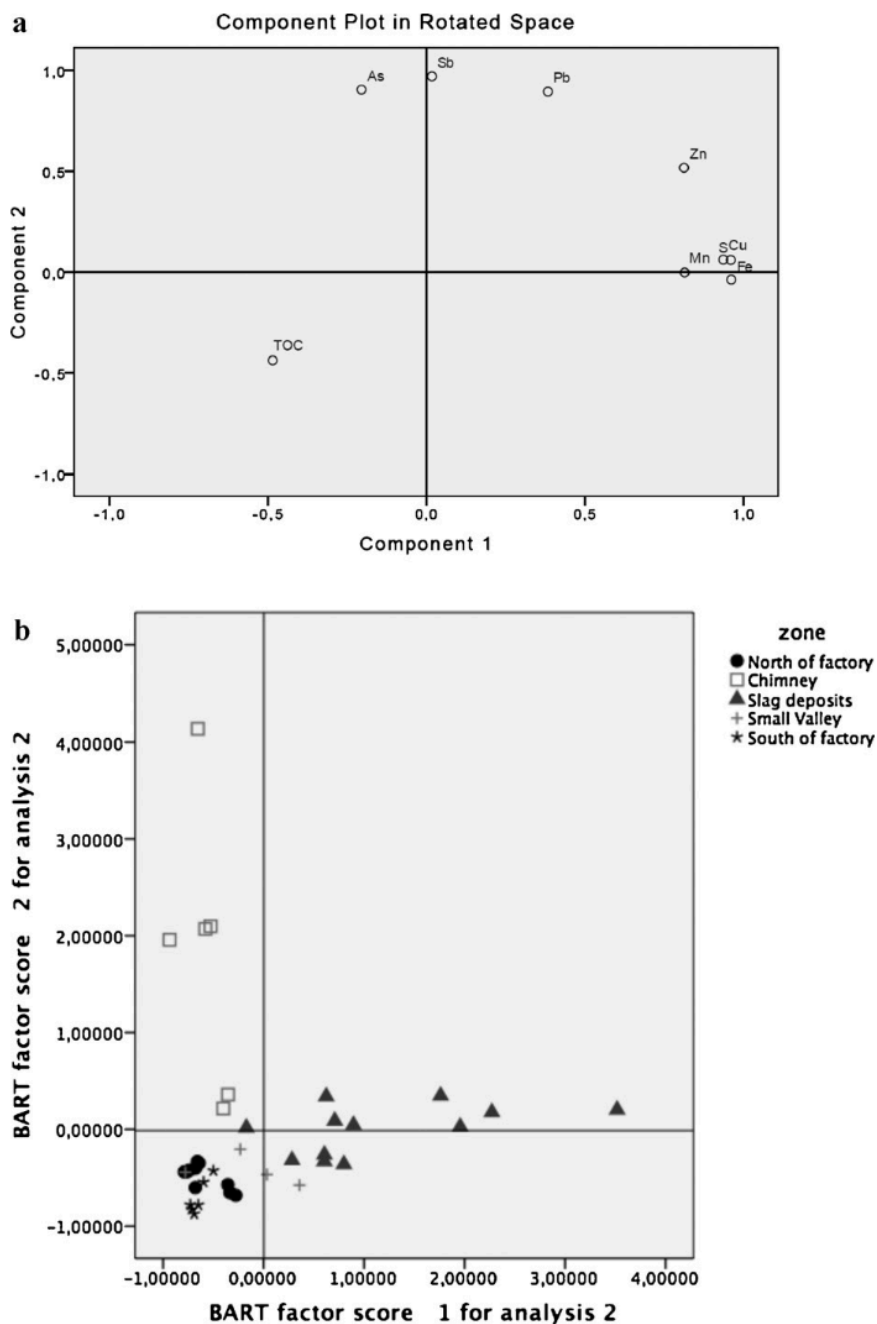


Fig. 3. PCA (PCA2) of 9 chemical properties of soils of the former industrial site of l'Escalette (France) represented by factors 1 and 2 (a) as loads, and (b) as individual scores.

($0.00079 \pm 0.00018 \text{ g kg}^{-1}$) lower than those observed in this study for the whole shoots. However, these concentrations are coherent with complementary results obtained by analyzing separately roots, stems and leaves of some plants, the results showing As concentration in stem significantly higher than in the leaves, 0.00191 to 0.0024 and $<0.0008 \text{ g kg}^{-1}$, respectively. Same results were observed for Pb.

In order to better understand the role of soil and type of contaminated zone on transfer of trace elements to *G. alypum* and *R. officinalis*, another PCA was performed. COT, Fe, Mn, S, P, concentrations of trace elements in soil, in root and shoot parts for 21 soil-plant couples, were considered. The first four components had Eigenvalues > 1 and accounted for 81.18% of the total variance. Rotated component loadings of chemical soil properties and trace

elements in soils, roots and shoots of *G. alypum* and *R. officinalis* on these principal components are given in Table 4 (supplemental material). The first principal component explained 38.71% of the total variance. It had high positive loadings (>0.92) of As in soil, As in roots, Pb in soil and positive loadings (>0.80) of Zn in soil, Pb in roots, As in aerial parts, Pb in aerial parts. Component 2 explained 25.57% of the total variance and had high positive loading of Fe, S and P in soil (>0.90) and a moderate loading of Cu and Mn in soil (respectively 0.688 and 0.637). Component 3 explained 9.07% of the total variance; it had a moderate positive loading of Cu in root and Zn in aerial part, a moderate negative loading of TOC. Component 4 explained 7.83% of the total variance; it had a positive loading of Cu in aerial parts (0.859).

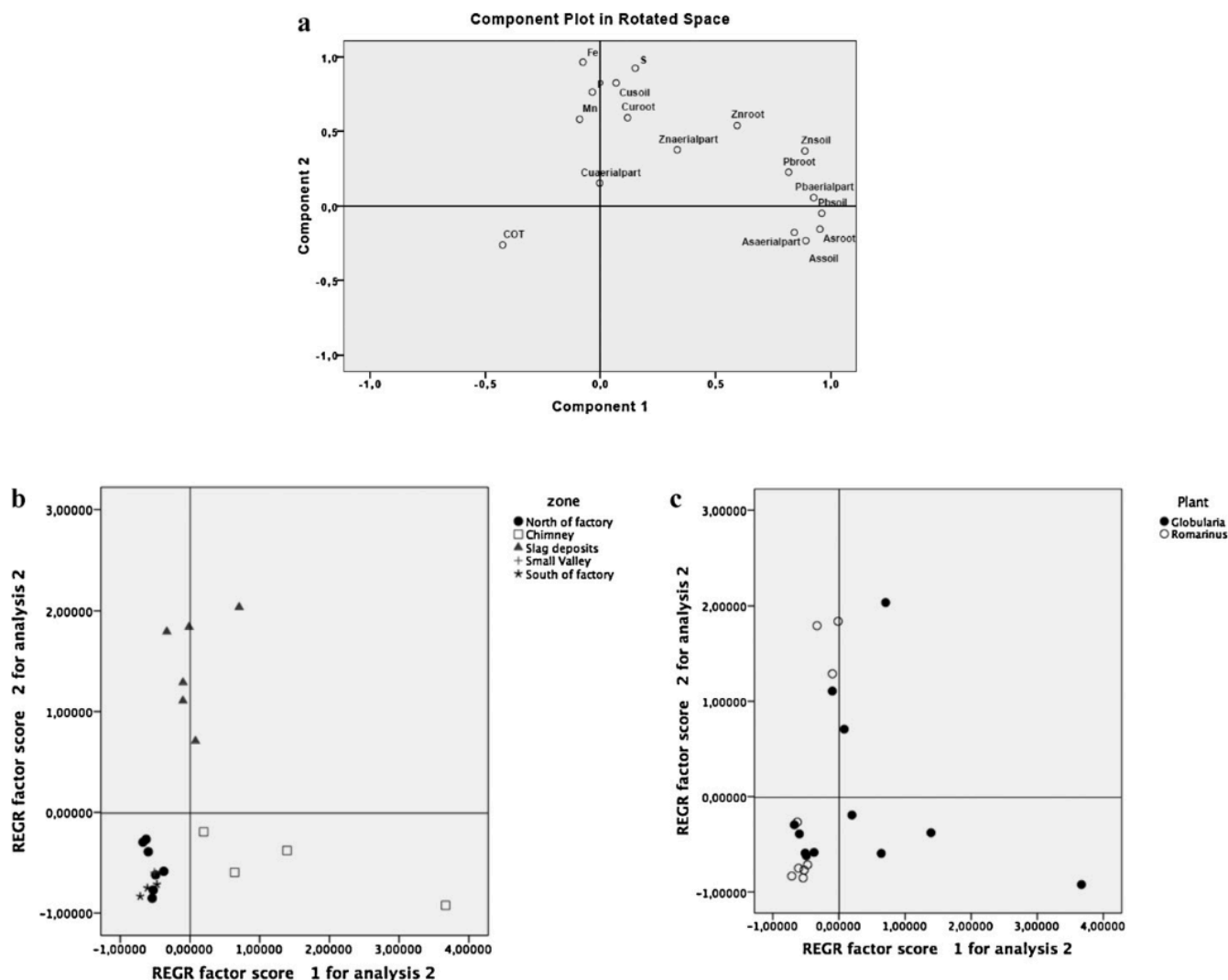


Fig. 4. PCA (PCA3) of chemical soil properties and trace elements in soils, roots and shoots of *Globularia alypum* L. and *Rosmarinus officinalis* L. of the former industrial site of l'Escalette (France) represented by factors 1 and 2, (a) as loads, (b) and (c) as individual scores, sampling points and plants respectively.

The influence of soils characteristics that distinguish the different sites appeared clearly in this description of the loadings of the four main components with the association Pb, As, in one hand, and the singularity of Cu and to a lesser extent Zn, on the other hand. Representation of individuals scores (Fig. 4) showed that the influence of the typology of the contamination of sampling sites was dominant in regard to the nature of the plant species (note that *R. officinalis* is not present on site 2).

No significant correlations were observed between As, Pb, Cu or Zn concentrations in roots or shoots and Fe, Mn, P or S concentrations in soils. Though As is an analogue of P and, Pb an analogue of Zn and Fe, no antagonism could be observed because the transporters were saturated by the high concentrations of bioavailable P, Zn and Fe, which could cancel symplastic transport for As and Pb [16]. As and Pb concentrations in roots were significantly correlated to the respective concentrations in soils ($r=0.840$, $r=0.772$ $p<0.001$ respectively). Pb concentrations in roots were significantly correlated with As ones ($r=0.703$, $p<0.001$) and with those of Zn ($r=0.831$ $p<0.001$), but an absence of correlation between Zn and As concentrations in roots was noted. Only As and Pb concentrations in shoot were significantly correlated to their respective root concentrations ($r=0.927$ and $r=0.707$, $p<0.001$) and were

significantly correlated with each other ($r=0.754$ $p<0.001$). Contrasting with the point of view by Reglero et al. [5], who associated metals in leaves to particular deposits, this correlation could reflect more a translocation than an aerial deposit, even if the hypothesis of incorporation of soil particles into the foliar tissues could not be excluded. It could be presumed that As and Pb could be transferred as lead arsenate and that passive translocation through the apoplastic compartment under the gradient of concentration, could be involved in the processes [17,18].

Correlation of concentrations in roots with those of soil were low for Zn ($r=0.621$ $p=0.001$) and for Cu ($r=0.462$ $p=0.017$). A weak transfer of Cu from soil to plant could find its origin in a regulation by the considered plants or in the copper speciation in slag. A low negative correlation between Cu concentrations in roots and TOC ($r=-0.417$, $p=0.03$) suggests that the weak lability of copper could be further reduced in the presence of organic matter. No significant correlations were observed between Zn or Cu concentrations in root and their respective concentrations in shoots. The concentrations of Zn and Cu and other metals were abnormally high so that a plateau response in plant uptake of metals could be reached. Plant physiological factors are suspected to be responsible for the plateau in plant metal concentrations observed [19,20].

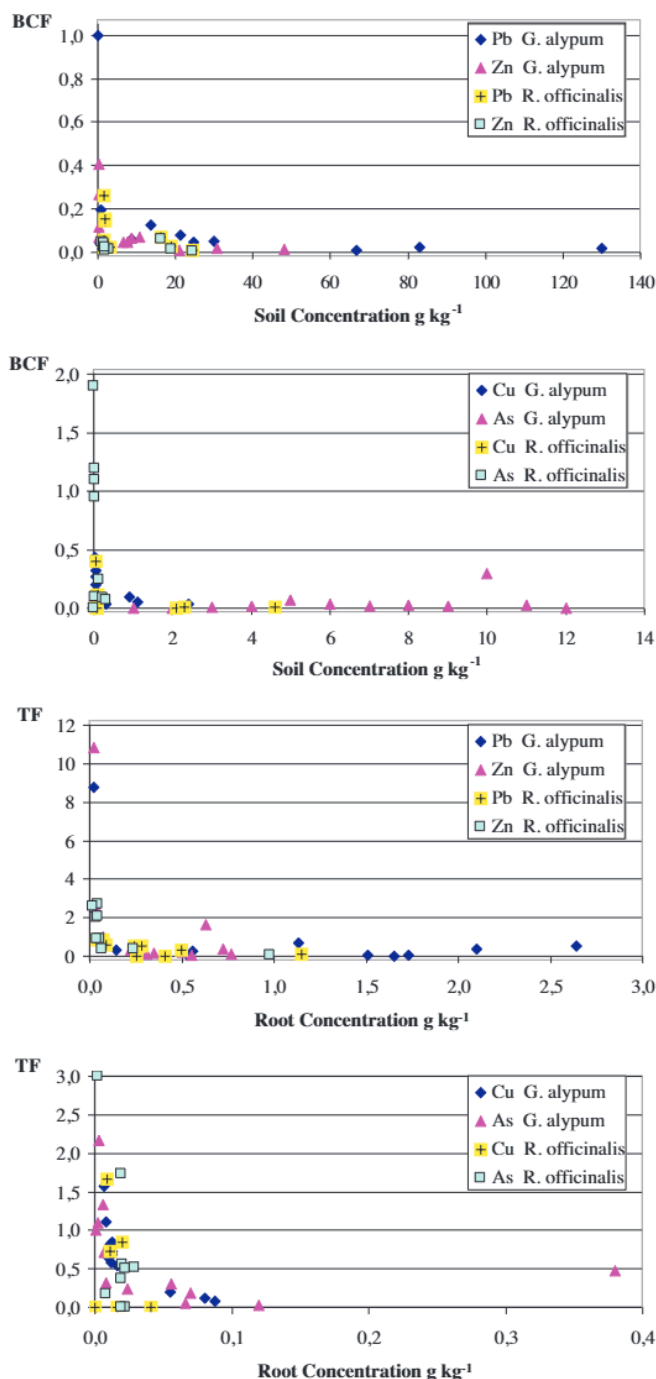


Fig. 5. BCF (bioconcentration factor) and TF (translocation factor) values for As, Cu, Pb and Zn in *Globularia alypum* L. and *Rosmarinus officinalis* L. of the former industrial site of l'Escalette (France).

Bioconcentration factors (BCF) and translocation factor (TF) are used in estimation of the phytoremediation potential of plants [2,21–23]. For *G. alypum* BCF were <1 for all trace elements except for Pb in plants collected on site 4.1 for which BCF=1.0, however this value corresponded to the lower Pb concentration in soil (0.075 g kg⁻¹, Fig. 5). For *R. officinalis*, As, Cu, Pb and Zn BCF were <1, except for As in plants collected on locations 1.10 (BCF=1.2), 5.1 (BCF=1.1), 5.2 (BCF=1.0) and 5.3 (BCF=1.7). A general decrease of BCF with increasing As, Cu, Pb or Zn concentrations in soils was

observed (Fig. 5) making in evidence a soil – root transfer restriction.

In this study, no plant exhibited concentrations in shoots higher than 1.0 g kg⁻¹ for Cu, Pb or As, and higher than 10.0 g kg⁻¹ for Zn, except *G. alypum* collected on site 2.1 with Pb concentration in shoot of 1.35 g kg⁻¹ but with a BCF=0.02 (for a soil concentration of 130 g kg⁻¹). *G. alypum* and *R. officinalis* cannot be considered as hyperaccumulators according to the criteria set by Baker and Brooks [24]. It was also observed that the higher values of TF were only observed for the lower concentrations in roots (Fig. 5). When concentrations in roots increased, translocation into the above biomass seemed to be restricted. *G. alypum* and *R. officinalis* exhibiting BCF ≤ 1 and TF < 1 for the highest concentrations in roots are unsuitable for phytoextraction. They tend to restrict soil-root and root-shoot transfers. With TF < 1, they could be termed as excluders even they show elevated concentrations in shoots [25]. However, *G. alypum* and *R. officinalis* can be considered as metal-tolerant plant species and could be considered as good candidates for phytostabilization, preventing a metal transfer to the food web.

4. Conclusions

A multi-element contamination by Pb, As, Sb, Zn, Cu was observed throughout the studied area, however two zones were more impacted by the former industrial activity: one was located along the horizontal chimney and the other corresponded to the slag deposits. They differed from each other: soils collected in the area along the chimney were marked by occurrence of aluminosilicates from degraded materials highly contaminated by Sb and As, since soils on slag heaps were characterized by their concentrations in Cu, Fe, Mn and S.

Pb and Zn concentrations together did not discriminate the different zones, however it could be hypothesized that their major physico-chemical forms could be different according to the zone. Our results showed that remediation processes have to be adapted to the various physico-chemical characteristics of the site and allow defining priority for actions. The two selected native plant species i.e. *G. alypum* and *R. officinalis* were metal-tolerant and could accumulate contaminants; the influence of the contamination typology was dominant in regard to the plant species. Concentrations in roots were significantly correlated with concentration in soil except for copper. Particularly due to the high analyzed concentrations, especially for Cu, Pb and Zn, and to BCF values ≤ 1, *G. alypum* and *R. officinalis* are not suitable for phytoextraction but these perennials, adapted to the extreme Mediterranean climatic and soil conditions, can play an important role in soil stabilization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.12.039>.

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