Ecological risk assessment of heavy metals accumulation in soil and zygophyllum album album: a case study of industrial phosphate vicinity, Tunisia

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ECOLOGICAL RISK ASSESSMENT OF HEAVY METALS ACCUMULATION IN SOIL AND *ZYGOPHYLLUM ALBUM:* STUDY CASE OF INDUSTRIAL PHOSPHATE VICINITY, TUNISIA

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Abstract: Contents and spatial distribution of heavy metals (Zn, Cu, Cd, Ni, As, Pb, Al and Ba) in the fine fraction of surface sediments and in *Zygophyllum album* shrub of zones influenced by phosphate industry in the region of Gabès, as well as in a control site (Ejjehmi) were determined. Several parameters were calculated, including enrichment factor (EF), contamination factor (CF), Pollutant Load Index (PLI), Risk factor (Er), potential ecological Risk Index (Ri), Geoaccumulation Index (Igeo), Electrical Conductivity (Ec), Organic Matter (OM), pH, Bio-Concentration Factors (BCF) and Translocation Factors (TF). The soils of Gabès are characterized by a high average relative concentration of As, Ba, Cd, Cu, Ni, Pb, Al and Zn in all the study sites, indicating contributions from anthropogenic sources. The Igeo and the PLI of heavy metals show that all study sites are heavily polluted. All the EF values of all trace metals from Gabes sites (above 10), indicate a very significant enrichment in soils. The PCA, AC and correlation matrix suggest that soils are mainly polluted by As, Ba, Cd, Cu, Ni, Pb, Al and Zn. For all studied metals, the values of TF in *Z. album* from Gabes sites are greater than 1 except for Al at S2. All metals studied, except Cd, are more accumulated in shoots than in roots. Values of BAF are greater than 1, as well as TF values are greater than 1, so *Z. album* of Gabes can be considered as phytoremediator in the case of those studied metals. For Cd, TF is greater than 1 and BCF is less than 1, *Z. album* can be considered as a phytostabiliser for this metal.

Keywords: *Zygophyllum album*; Heavy metals; Soil contamination; Phytoremediation; Bio-Concentration Factors; Translocation factor.

1. INTRODUCTION

Soil is considered important natural resources because of its capability to act as a geochemical reservoir for various contaminants, including heavy metals resulting from aerosol deposition through urban and manufacturing activities (El-Sherbiny et al., 2019). Industrialization, extensive urbanisation and mining have been among the main causes of soil contamination which have a negative impact on the quality of the environment (Yaylali-Abanuz, 2011).The Gabes region in Tunisia hosts about twenty exporting factories, including units of the Tunisian Chemical Group (TCG), which transforms phosphate into phosphoric acid and fertilizer. The pollutants discharged by this industry damage the ecosystems in which the biotic components are modified and broken (Trasande et al., 2016; Wu et al., 2016). Phosphate industries are considered major emitters of dust and heavy metals (MTEs) such as Cd, Cr, Hg, Pb and Zn (Galfati, 2011). Even at low concentrations, some heavy metals are known to be toxic to animals and plants (Khan et al., 2008; Qureshi et al., 2016) due to their persistence and resistance to atmospheric degradation environment through chemical, biological and photolytic processes (Al-Kashman and Shawabkeh, 2006). These MTEs can spread over a large area by wind and rain, depositing in the topsoil, bioaccumulating, entering the food chain, and thus affecting human health. Many studies have shown that topsoil and plants near phosphate can be heavily contaminated with heavy metals (Orisunmibare, 2022), and although there are physical and chemical treatment strategies to eliminate metal pollutants, such methods are labor intensive. In addition, they are expensive and generate other pollutants. Therefore, the need for alternative technologies and the exploration of different biobased techniques, such as bioremediation has become imperative. The use of biological agents is safer, it has limited or no negative effects on the environment. Bioremediation methods include bio-augmentation, bioremediation, bioventilation, composting, and phytoremediation. Of these, phytoremediation proves to be the most viable and inexpensive alternative and has since attracted increased attention (Usman et al., 2019). Phytoremediation can be defined as the use of plants for containment, degradation or extraction of xenobiotics from water or soil substrates (USEPA, 2000).

The use of certain plants to remove heavy metals dates back hundreds of years (Usman et al., 2019). The best plants for phytoremediation purposes are native plants because of their greater chance of survival, growth and reproduction in environmental stress conditions than plants introduced from other environments (Adriano, 2001; Antonsiewicz et al., 2008). The halophyte *Zygophyllum album* (*Z. album*) chosen in this present work is a plant overrepresented in Tunisian arid rangelands because it is very adapted to arid conditions (Gamoun et al., 2018). The abundance of this plant, which grows naturally around Gabes Chemical Group and several other polluting industries in Tunisia, reflects its toxitolerant character (Jalali, 2018).

The present study is mainly focused on the evaluation of various concentrations of heavy metals (Al, Cd, Ni, As, Pb, Zn, Ba and Cu) in the soil around the phosphate industries and in remote sites. It is also focused on assessing the level of heavy metal contamination measured on the basis of different pollution indices. Finally, research the effectiveness of *Z. album* in the capture of ETMs for phytoextraction purposes. These results in turn, can be useful to different stakeholders such as urban development planners and especially, environmental risk managers (Hamdi et al., 2015).

2. MATERIALS AND METHODS

2.1. Study area description

The study area is located in the Gulf of Gabes in southern Tunisia (33_8802300N, 10_0909000E) (Figure 1). It is one of the most industrialized regions of the country. This area covers a surface of approximately 7166 km2, has an arid climate with low average rainfall (mean annual rainfall between 167 and 176 mm), an average annual temperature between 18.8 and 19.3 °C, and it is affected by strong easterly winds (Hamdi et al., 2015). In the industrial zone of Ghannouch was established the Tunisian Chemical Group (GCT), it is one of the major industrial sites associated with the exploitation of phosphate. This industrial activity has three main factories: The phosphoric acid factory (1972), the Di-Ammonium Phosphate (DAP) factory (1979) and the Ammonitrate (AN) factory (1983). In this region the majority of the vegetation is of the halophyte type. The study focused on a native dwarf shrub of the steppes *Zygophyllum album* (Floret and Le Floc'h, 1983). The control site (Sc) is located in Soliman at the level of Chat Ejjehmi in Tunisian Cap-Bon. It is a site far from all forms of pollution. Four sites were selected in the sampling area (Figure 1), their descriptions are summarized in Table 1.

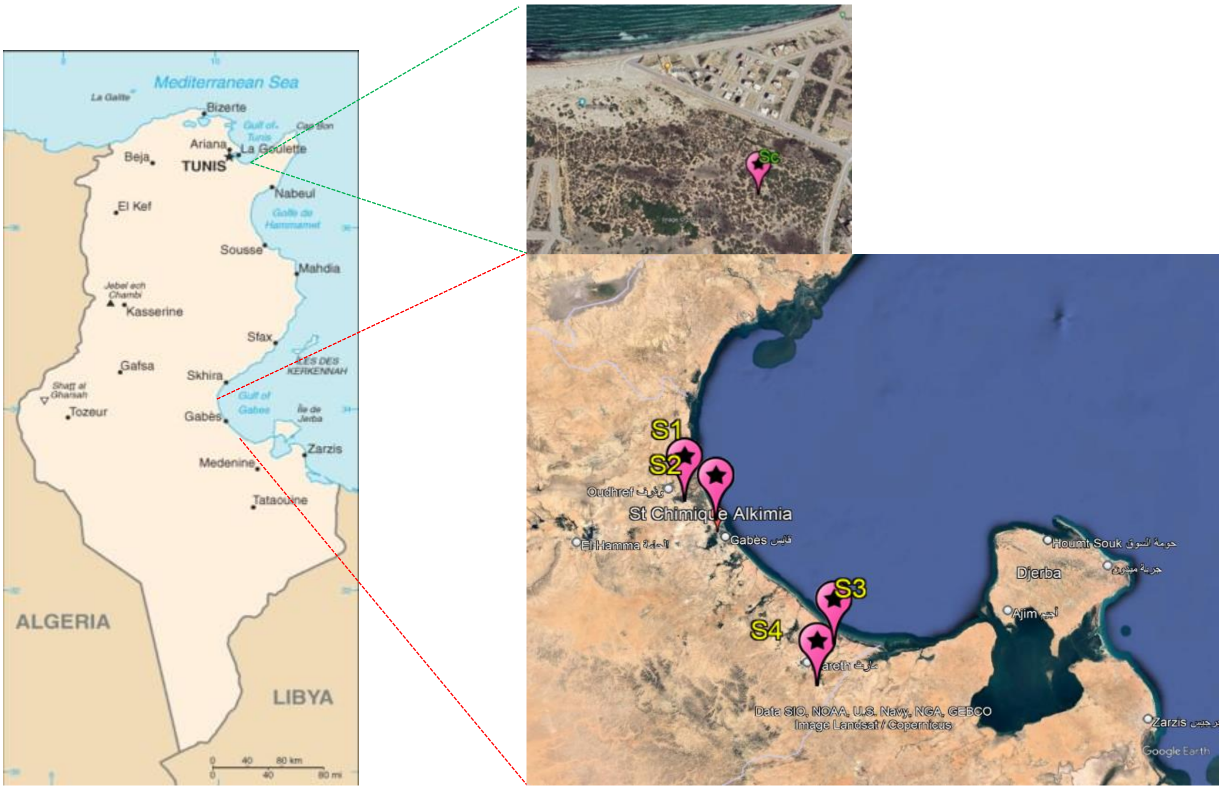

Figure 1. Map showing sampling sites (Sc: Ejjehmi, Contol site; S1, S2, S3 and S4: Gabès (Polluted sites).

Table 1. Locations and description of sampling sites.

Sites	Stations	Coordonates	Description
Ejjehmi (Contol site)	Sc	36°43′00.79″N 10°26′15.38″E	Located at 250m from sea Natural site far from any form of industrial pollution
Gabès (Polluted sites)	**S1 :** Ghanouch	33°56′17.21″N 10°04′35.26″N	Close to several mainly chemical industries. - 4 km from the Matwiyah Chemical Plant, - 2 km from the oil and natural gas company GPL AGIL of Ghannouch, - 1.7km from the TIMAB Tunisia chemical plant in Ghannouch, - 2 km from the Groupe Crystal chemical plant in Bouchema and 1.6 km from the Ghannouch plant - 2 km from Al Kimia Chemical Campany de Ghannouch
	S2: Gabes Chemical Group	33°55′08.54″N 10°5′4.79″NS	Located 1 km from Alkimia Chemical Campany, 800m from the ICF fluorine production plant and close to several other industries.
	S3 : Zarat	33°40′05.10″N 10Sc°21′55.19″N	Site located 37 km from the GCG
	S4 : Arram	33°34′51..64″N 10°19′13.26″N	Site located 58 km from the GCG

2.2. Sampling and analytical procedures

Sampling was carried out during September 2021. To evaluate the soil contamination, samples of composite soils were obtained from both polluted sites (Gabes: S1, S2, S3 and S4) and control sites (Ejjehmi: Cs). From each site, about one kg of soil sample was collected from the surface 0-20 cm soil layer using an auger. The soil samples were immediately placed in plastic bags and kept at 4 °C until analysis in the laboratory. Samples of *Zygophyllum album* were collected from their natural vegetation and washed with distilled water in order to remove the attached fine sediment particles. Samples of sol and plant were replicated three times over space.

Al, Cd, Ni, As, Pb, Zn, Ba, and Cu concentrations were measured by flame atomic absorption spectrometry (FAAS, PerkinElmer 1100). The sulphates were determined using a UV spectrophotometer (Uvikon XL, Secomann, ALES Cetex, France). All samples were filtered through a 0.22-μm nylon filter before metal determination. To assess the metal bioavailability potential, 5 g of soil samples were air dried, extracted in 50ml of 0.01M-$CaCl_2$ solution, and mechanically shaken for 5 h. The extracts were filtered before instrumental heavy metal quantification. Sample treatment was performed in triplicate (Bayouli et al., 2020).

2.3. Risk assessment

To assess the degree of pollution, we computed the enrichment factor (EF), degree of contamination (Dc), contamination factor (CF), pollution level index (PLI), geoaccumulation index (Igeo), risk factor (Er) and potential ecological risk index (Ri). The significance of index values in terms of degree of contamination is summarized in Table 2.

Table 2. Degree of trace metal contamination according to different indices: contamination factor (CF), geoaccumulation index (Igeo), and pollution level index (PLI), Enrichment factor (EF), Risk factor (Er) and Potential ecological risk index (Ri).

Index	**Value**	**Probability of toxicity**
Contamination factor (CF): $CF_{metal} = \frac{C_{metal}}{C_{background}}$	< 1 1-3 3-6 > 6	Low contamination, Moderate contamination, considerable contamination, Very high contamination (Tomlinson et al. 1980).
Pollution load index (PLI): $PLI = \sqrt[n]{CF_1 \times CF_2 \times ...CF_3})$	< 1 1-2 2-3 > 3	No metal pollution Moderate pollution Heavy pollution Extremely heavy pollution (Zarei et al. 2014).
Geo-accumulation index (Igeo): Igeo = $Log_2 (C_n)/1.5(B_n)$	<0 0–1 1–2 2–3 3–4 4–5 >5	Uncontaminated Uncontaminated to moderately contaminated Moderately contaminated Moderately to strongly contaminated Strongly contaminated Strongly to extremely contaminated Extremely contaminated (Muller 1969).
Enrichment factor (EF) EF = (M/Al) sample/(M/Al) background Where (M/Al) sample is the ratio of metal and Al concentrations in the sample, and (M/Al) crust is the ratio of metal and Al concentrations in the Earth's crust	< 1 >1 1.5–3 3–5 5–10 > 10	A possible mobilization or depletion of elements (Zsefer 1996). The element is of anthropogenic origin, Minor contamination, Moderate contamination, Severe contamination, Very severe contamination,
Degree of contamination (Dc) The sum of all values of contamination factors	< 7 7-14 14-28 > 28	Referring to Hokanson (1980) the degrees of contamination are classified into four classes: Low Dc, Moderate Dc, Considerable Dc, Very high Dc.
Risk factor (Er) Er = Tr* CF Where Tr is the toxic-response factor for a given substance, and CF is the contamination factor.	< 40 40-80 80-160 160-320 ≥ 320	Hokanson (1980) recommended the following classes: Low, Moderate Considerable, High, Very high.
Potential ecological risk index (Ri) The sum of all values of risk factors.	< 150 150-300 300-600 > 600	Hokanson (1980) recommended the following classes: Low, Moderate, Considerable, Very high.

2.4. Phytoextraction potential: BCF and TF

Bioconcentration factor (BCF) and translocation factor (TF) are important parameters in heavy metal uptake studies (Marchiol et al., 2004). In order to evaluate the phytoextraction potential of the selected plants, the bioconcentration factor was calculated

$$BCF_{metal} = \frac{C_{\text{harvested tissue}}}{C_{soil}}.$$

Where C harvested tissue is the metal concentration in harvested tissues and C soil is the metal concentration in soil. Plant species are considered to exhibit removal potential for an element when the BCF value exceeds 1. However, when the BCF<1, the plant species are qualified as excluder (Sun et al., 2009). Plants characterized by a BCF value higher than 1 can be considered appropriate for phytoextraction (Napoli, 2018).

The translocation factor (TF) evaluates the heavy metal translocation along the plant (from roots to shoots) and it is defined as the ratio between the metal concentrations in shoots and in roots (Arrivabenes et al., 2016)

$$TF_{metal} = \frac{C_{shoots}}{C_{roots}}.$$

Translocation factor (TF) indicates the ability of plant to translocate heavy metal from roots to aerial tissues and then the potential of plants to accumulate heavy metal in aerial organs. High value of TF (TF > 1) indicates a great capacity of plant to translocate heavy metals from roots to aerial tissues. At the opposite, a low value (TF < 1) indicates a limited capacity of plant to translocate the metal to aerial tissues (Lam et al., 2017).

2.5. Statistical Analysis

Statistical analyses were performed with STATISTICA 8.0. For $p < 0.05$ the analysis of variance (ANOVA) helped identify the significant spatial differences. Cluster (CA) was used for a multivariate analysis of the stations data set and Pearson correlation was used for the elements treated of sediment.

3. RESULTS AND DISCUSSION

3.1. Metal concentrations in soil and vegetation samples

Nine heavy metal concentrations (As, Ba, Cd, Cu, Hg, Ni, Pb, Al and Zn), OM, pH and EC in the industrial phosphate vicinity soil samples are listed in Table 3. Heavy metal concentrations (g/kg) were found in the range of 22.544–39.22 for As, 308–682 for Ba, 13.58–25.22 for Cd, 76.25–110 for Cu, 142–190.21 for Ni, 41.53–78.88 for Pb, 3780–4900 for Al, and 172.35–188.22 for Zn.

Mean pH value was relatively high in S3 and S4 (8–8.4), whereas quite low in S1 and S2 (5.5–5.8) sites. However, the electrical conductivity showed comparatively higher values at the S2 site (20.1 dSm-1), which is located next to the main GCT plants and the lowest value is recorded at Arram (S4) (1 .8 dSm^{-1}), the furthest site from the TCG. At the control site, the EC value does not deviate too much from that of S4 (2.6 dSm^{-1}). The concentration of OM in S2 and S1 is relatively high (75.03–66.75 g/kg MS) than that of S3 and S4 (32.37–30.73 g/kg MS). Spatial distributions of heavy metals show the increases in As, Ba, Cd, Cu, Hg, Ni, Pb, Al and Zn for S1, and the concentrations of most metals in the S4 tend to have decreases, reflecting both natural and anthropogenic source material inputs (Li and Zhang, 2010). The mean concentrations of heavy metals in soil samples are in decreasing order as follows: Al> Ba> Ni> Zn> Cu> Pb> As> Cd. For each study site, the mean heavy metal contents are relatively high. In this study, total metal concentrations followed the order of site-2 > site-3 > site-1 > site-4. However, high contents of these heavy metals in the soil samples indicate an anthropogenic source input to the investigated area. High abundance of all elements in the soil samples for study sites suggests industrial effluent as well as clay mineral control.

Table 3. Concentrations (mg/kg) of heavy metals with pH, EC (lS/cm) and OM (%) in soils from the phosphate industrial zone and control site, Tunisia

Sample	Zn	Cu	Cd	Ni	Hg	As	Pb	Al	Ba	Ec	OM	pH
Sc	0,124	0,55	0,11	0,78	b.d.l	0,341	0,34	4170	55,8	2,6	2,54	7,7
S1	188,22	109,88	24,34	188	b.d.l.	29	78,53	3780	682	17,2	66,75	5,5
S2	188,22	110	25,22	190,21	b.d.l.	39,22	78,88	4900	513	20,1	75,03	5,8
S3	172,35	98,36	15,28	163,75	b.d.l.	25,3	52,42	4620	308	4,7	32,37	8
S4	175,88	76,25	13,58	142	b.d.l.	22,44	41,53	4080	351	1,8	30,73	8,4
Min	172,35	76,25	13,58	142	-	22,44	41,53	3780	351	1,8	30,73	5,5
Max	188,2	110	25,22	190,21	-	39,22	78,53	4900	682	20,1	75,03	8,4
Mean	181,16	98,62	19,60	171	-	29	62,84	4345	463,5	10,95	51,22	6,92

b.d.l. below detection limits (<0.000012)

The I_{geo} is widely used to evaluate the degree of metal contamination in geologic samples (Hossain et al., 2015). The statistical values of I_{geo} in the soil samples are shown in Table 4. The mean Igeo value for Zn and Pb are 1.21 and 1.24, respectively, suggesting moderately contaminated of the metals. Consequently, mean Igeo value is < 0 for Al (-4.75) reflecting that investigated soil samples are practically uncontaminated. However, group-wise mean I_{geo} values for Cu (2.18) and Ni (2.6) indicating that sample soils are moderately to strongly contaminate. In addition, the mean Igeo value for As (3.23) and Cd (6.97) suggesting strongly and extremely contaminated respectively, due to anthropogenic source materials input, confirmed by high industrial activity of the area.

The CF and PLI are widely used to evaluate the degree of heavy metal pollution in the soils (Bhuiyan et al., 2010). The calculated CF and PLI are listed in Table 5. In all sites of Gabes CF values are upper than 3, it shows at less a considerate contamination. In fact, The CF values for Zn, Cu, Cd, Ni, and As at sites 1 and 2 soils were > 6, thus showing a “very high contamination” as well as a “considerable contamination” for Pb and a “low contamination” for Al. In all sites of Gabes CF values of Pb shows a low contamination by this metal. The values of CF> 6 for Cd, Ni, and As of the sediment at Site 4 furthest from the phosphate industries indicate a “very high contamination” and those for Zn and Cu indicate a “considerable contamination”. The mean CF values for the metals in the Gabes Golf are following this decreasing order Ba > Cd > As > Ni > Zn > Cu > Pb > Al. However, incredibly high mean PLI value (9.56) in the study area is ascribed to be extremely heavy pollution (Zarei et al., 2014).

Most often the EF of heavy metals is used to evaluate human-made contamination. However, EF values of 0.5–1.5 reveal regional rock compositions, while EF values that are > 1.5 signify non-crustal contributions and/or non-natural weathering processes (e.g., anthropogenic influences) (Zhang and Shan, 2008). The calculated EF and DC is listed in Table 6. In this work, EF ranges of the studied metals are: Ba, 3943,7–8732,48; Zn, 67,9–74,15; Cu, 109,23–157,59; Ni, 156,4–209,5; Cd, 2727,55– 5065,45, As, 229,86–401,74 and Pb, 50,04–94,63. The mean EF values of Ba (5934,75), Cu (141,28), Zn (71,37), Cd (3937,67), Ni (188,33), Pb (75,72) and As (291,83) propose anthropogenic impact on the metal levels in the phosphate industrial zone. The EF value of all heavy metals denotes very severe enrichment in the soils of all sampling sites. Total EF values followed the order of site-1 > site-2 > site-4 > site-3.

The values of degree of contamination (Dc) extended from 377.07 at site 3 to 715,41 at site 1 an average 524,68 (Table 6). Referring to Hokanson (1980), all studied sites are situated in the fourth class which represents a very high Dc value.

Table 4. Geo-accumulation index (I_{geo}) values in soils from the phosphate industrial zone and control site, Tunisia

Station	Zn	Cu	Cd	Ni	As	Pb	Al	Ba	Hg
CS	-9,38	-5,32	-0,45	-1,83	-3,18	-6,64	-5,05	4,54	b.d.l
S1	1,27	2,35	7,34	2,75	3,27	1,62	-5,05	8,15	b.d.l
S2	1,27	2,35	7,4	2,76	3,7	1,62	-4,46	7,74	b.d.l
S3	1,13	2,2	6,67	2,55	3,07	1,03	-4,46	7	b.d.l
S4	1,17	1,82	6,5	2,34	2,9	0,7	-5,05	7,2	b.d.l
Min	1,13	1,82	6,5	2,34	2,9	0,7	-5,05	7	b.d.l
Max	1,27	2,35	7,4	2,76	3,7	1,62	-4,46	8,15	b.d.l
Mean	1,21	2,18	6,97	2,6	3,23	1,24	-4,75	7,52	b.d.l

b.d.l. below detection limits (<0.000012)

Table 5. Contamination factors (CFs) and pollution load indices (PLIs) of soil heavy metals from the phosphate industrial zone and control site, Tunisia

Sample	CF								PLI
	Zn	Cu	Cd	Ni	As	Pb	Al	Ba	
CS	0,002	0,038	1,07	0,04	0,17	0,02	0,05	34,87	0,11
S1	13,6	7,68	238,62	10,1	14,5	4,62	0,04	426,25	11,41
S2	13,6	7,69	247,25	10,22	19,61	4,64	0,06	320,62	12,11
S3	3,31	6,87	149,8	8,8	12,65	3,08	0,06	192,5	7,78
S4	3,38	5,33	133,13	7,63	11,22	2,44	0,05	219,37	6,96
Min	3,31	5,33	13,13	7,63	11,22	2,44	0,04	192,5	6,96
Max	13,6	7,69	247,25	10,22	19,61	4,64	0,06	426,25	12,11
Mean	8,47	6,9	192,2	9,18	14,5	3,7	0,05	289,7	9,56

Table 6. Values of EF for the measured metals in soils of the phosphate industrial zone and control site, Tunisia

Sample	EF							DC
	Zn	Cu	Cd	Ni	As	Pb	Ba	
S1	74,15	157,41	4888,7	207,07	276,57	94,63	8732,48	715,41
S2	74,15	157,59	5065,45	209,5	401,74	95,05	6568,57	623,69
S3	67,9	140,91	3069	180,36	259,15	63,17	3943,7	377,07
S4	69,29	109,23	2727,55	156,4	229,86	50,04	4494,28	382,55
Min	67,9	109,23	2727,55	156,4	229,86	50,04	3943,7	377,07
Max	74,15	157,59	5065,45	209,5	401,74	94,63	8732,48	715,41
Mean	71,37	141,28	3937,67	188,33	291,83	75,72	5934,75	524,68

3.2. Ecological risk factor (Er) and Potential ecological risk index (Ri)

The calculated Er and Ri are listed in Table 7. Referring to Hokanson (1980) all studied sites exhibited low values of Er for Zn (3.31- 13.6 average = 8.47), Cu (26.65- 38.45, average = 34.462), and Pb (12.12 – 23.20, average = 18.475). Otherwise, all sites show very high values for Cd (3993.90 – 7417.50, average = 5766). For Ni, all values are greater than 40 but less than 80 (38.15 – 51.10, average = 45.937) indicating a moderate ecological risk. The Er value for As ranged from considerable contaminated (112.20) to very high contaminated (196.10) in terms of ecological risk factor. In order to identify the sensitivity of the biota to the toxic elements, Ri was calculated. Håkanson (1980) described RI as the index that determines the heavy metal toxicity and the subsequent environmental response to all six risk factors (Zn, Cu, Cd, Ni, As and Pb) in soils. All the study sites of Gabes had very high values of Ri (4186.48 – 7739.95, average = 6018.298), suggesting that they are at a very high-risk level.

Table 7. Ecological risk factor (Er) and Potential ecological risk index (Ri)

Sample	Er						Ri
	Zn	Cu	Cd	Ni	As	Pb	
CS	0,00	0.19	32.1	0.2	1.7	0.1	34,29
S1	13,60	38,40	7 158,60	50,50	145,00	23,10	7 429,20
S2	13,60	38,45	7 417,50	51,10	196,10	23,20	7 739,95
S3	3,31	34,35	4 494,00	44,00	126,50	15,40	4 717,56
S4	3,38	26,65	3 993,90	38,15	112,20	12,20	4 186,48
Min	3,31	26,65	3 993,90	38,15	112,20	12,20	4 186,48
Max	13,60	38,45	7 417,50	51,10	196,10	23,20	7 739,95
Mean	8,47	34,46	5 766,00	45,94	144,95	18,48	6 018,30

3.3. Principal component analysis/factor analysis

PCA was performed on the normalized data to compare the compositional pattern between the sediment samples and to identify the factors influencing each one. PCA of the entire data set (Table 8) revealed three PCs with eigenvalues >1 that explained about 96.65% of the total variance in the sediment quality data set. The scores and loadings of the three PCs for the heavy metals are shown in Figure 2. The first PC accounting for 82.29% of the total variance was correlated with Cd, Cu, As, Pb, Ec, Ba and Ni. The second PC accounting for 14.35% of total variance was correlated with Al. whereas the third PC accounted for the total variance of 3.34%, it correlated with none of the metal parameters.

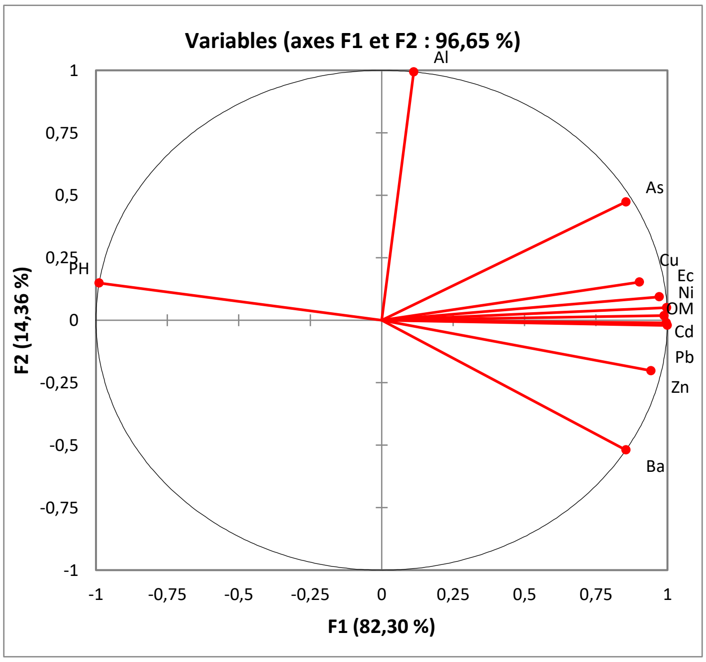

Figure 2. Principal component analysis of heavy metal concentrations in the sediments of the phosphate industrial zone and control site.

Table 8. Principal component analysis for heavy metals in soils from the phosphate industrial zone and control site, Tunisia

Parameter	Principal component		
	F1	F2	F3
Zn	0,943	-0,202	-0,266
Cu	0,901	0,153	0,405
Cd	0,999	-0,021	-0,039
Ni	0,971	0,093	0,221
As	0,854	0,474	-0,214
Pb	0,996	-0,011	0,093
Al	0,112	0,993	-0,030
Ba	0,854	-0,519	-0,008
Ec	0,997	0,050	-0,057
OM	0,988	0,019	-0,155
PH	-0,989	0,149	-0,021
Eigenvalue	9,053	1,579	0,368
Total variance (%)	82,299	14,356	3,346
Cumulative variance (%)	82,299	96,654	100,000

3.4. Cluster analysis

For spatial variability (clustering of similar study sites), a group analysis (CA) was used. This is a common method in results analysis studies of soil/sediment pollution (Ghannem et al., 2018; Touaylia et al., 2016; Karbassi et al., 2016). In general, the study of a dendrogram is important to know the level of similarity between the environment and the origin of various elements of the sampling stations. However, at 97% similarity, a statistically significant cluster groups the four study sites into two groups (Figure 3). The highly polluted region is represented by the site 1 and site 2 (Cluster 1) marked by the strong metal rejection from industrial phosphate. Cluster 2 (sites 3 and 4) represent a moderately polluted province.

Likewise, CA was applied to cluster the analyzed elements. In addition, a grouping of the studied parameters was represented by a dendrogram (Figure 4). However, with 79% similarity, a cluster grouping three statistically significant groups was observed. Cluster 1 included Cd and As (pollutants from anthropogenic sectors: waste from the industrial zone). Cluster 2 contained Cu, Pb, Zn, Ni, and Ba (also from anthropogenic sources: waste from phosphate plant, and industrial and domestic waste). Cluster 3, which contained Al, derived from lithogenic sources.

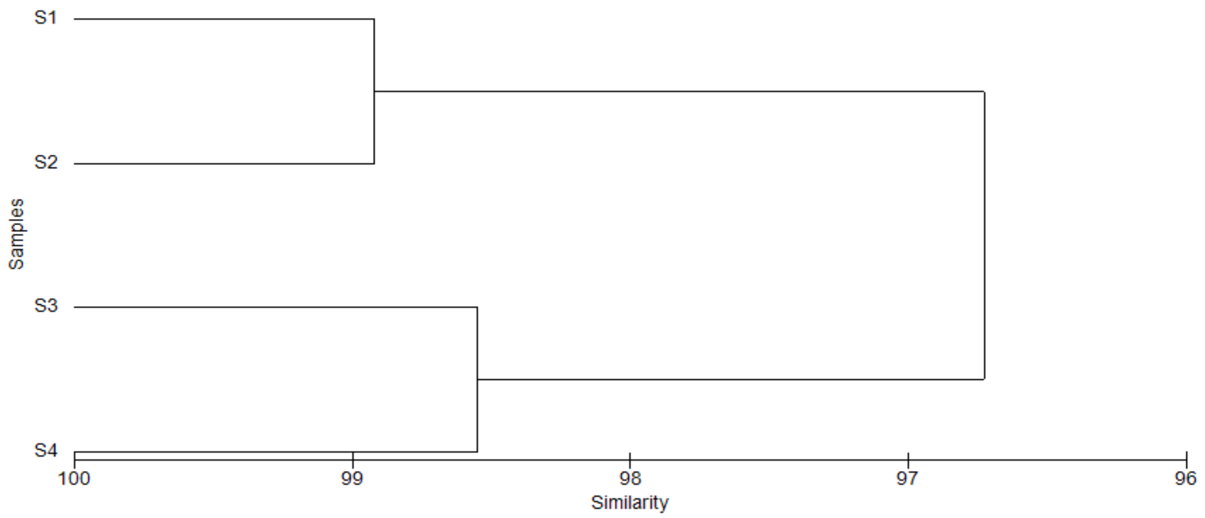

Figure 3. Dendrogram showing clustering of sampling sites in the vicinity of the phosphate industrial zone and control site

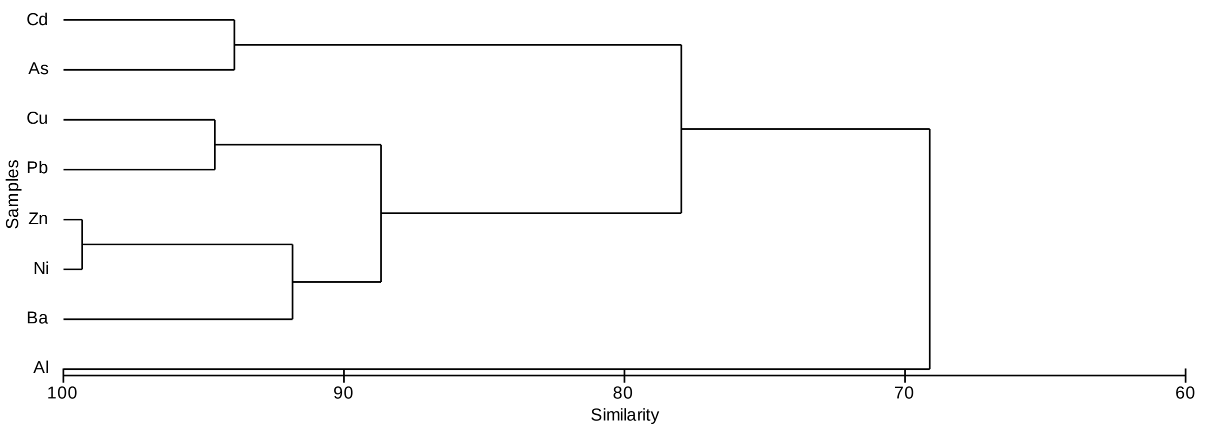

Figure 4. Dendrogram showing clustering of the analyzed parameters

3.5. Correlation matrix

A significant positive correlation was found between the toxic elements based on the values of the Pearson correlation coefficients (Table 9). Heavy metals with significant correlations may have common sources and similar behavior during transformation or migration (Wang et al., 2012). In this study, Al does not show a significant correlation with all the elements. This confirms also its suitability to be a reference element for EF calculation. OM is positively correlated with Zn ($r = 0,96$, $p < 0.05$), Cu ($r = 0,83$, $p < 0.05$), Cd ($r = 0.99$, $p < 0.05$), As ($r = 0.88$, $p < 0.05$), Ni ($r = 0.92$, $p < 0.015$), and Pb ($r = 0. 96$, $p < 0.05$) suggesting that these elements are largely controlled by soil OM. EC positively correlated with Cd ($r = 0.99$, $p < 0.05$), Ni ($r = 0.96$, $p < 0.05$) and Pb ($r = 0.98$, $p < 0.05$).

The hierarchical clustering was carried out in standardized data applying Ward's method (Li et al., 2013), and the squared Euclidean distance as a similarity measure (Bhuiyan et al., 2010; Li et al., 2013). CA is commonly used to assess metal variables to show a spatial sampling strategy (Li and Zhang, 2010; Li et al., 2013). However, CA performed by sampling sites was also organized and the dendrogram obtained showed three statistically significant clusters, i.e., cluster 1 (S 1 and S 2), and cluster 2 (S 3 and S 4) (Figure 3). The clusters show high degree of pollutions derived from anthropogenic sources. Most of the sampling sites in Ghannouch and Gabes belonged to the clusters 1 and cluster 2 corresponding to extremely heavy pollution regions. The clusters 1 and 2, which contain relatively high Pb, Al, As, Zn, Br, Cu, Ni and Cd ascribed to be highly polluted confirming that these heavy metals were probably derived from industrial effluents.

In order to establish relationships among metals and determine the common source of metals in the vicinity of industrial phosphate of Gabes, a correlation matrix was calculated for toxic elements in soils. The data suggest that the distributions of the elements were determined by a common factor, they were derived from waste discharges of industrial phosphate and also moving together. It is also clear that the correlation pattern is strongest at the most polluted site. Al was significantly correlated with As ($r = 0.573$, $p < 0.05$), indicating that the elements were derived from lithogenic sources. OM is positively correlated with all toxic elements suggesting that these elements are largely controlled by soil OM (Zhang et al., 2009, 2008; Hossain et al., 2015). Tume et al. (2011) reported that soil OM positively correlated with Cr, Ni, Pb and Zn, implying that OM has a high adsorption capacity towards these heavy metals (Yin et al., 2002; Quenea et al., 2009). Dragovic´ et al. (2008) reported that heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) are positively correlated with OM inferring a common affinity for clay minerals. EC positively correlated with Cd, Ni, and Pb suggests a large amount of soluble salts in aqueous solution of the soil.

PCA is widely used as a tool for evaluation of metal contamination as well as source identification in soils (Dragovic´ et al., 2008; Chabukdhara and Nema, 2013). PCA and CA distinguish factor of anthropogenic and natural sources of heavy metals.

3.6. Heavy metal concentrations in *Zygophyllum album*

In this study, 8 ETMs were studied in 4 sites (S1, S2, S3 and S4) related to the industrial activity of the Gabes region, including mainly the units of the Tunisian chemical group (TCG). The control site being the Cs site far from any industrial activity and especially that of the phosphate industry. The metal concentration in the samples varied according to two parameters; the sampling site and the part of the *zygophyllum album* analyzed for this purpose.

In the control site, all the concentrations of the ETMs studied are either deficient or much lower than the normal concentrations (Table 10) (Pandias and Pandias, 1992).

In Gabes sites, total Zn concentrations in tissues of *Z. album* range from 99 to 136,221 ppm. Whatever, the sampling site, the highest Zn concentrations are recorded in the shoots and not in the roots (Figure 5). The lowest concentration for the root part is recorded at S4, the highest one at S3 (respectively of 99 and 111.38 ppm). Likewise for the shots the lowest value is recorded at S4 and the highest at S3 (respectively of 120.08 and 136.221 ppm).

Zn concentrations in *zygophyllum album* reach phytotoxic levels. In fact, according to Pandias and Pandias (1992), Zn levels in the tissues of

Table 9. Pearson's correlation matrix of heavy metals in the soil samples of industrial phosphate vicinity, Tunisia

Variables	Zn	Cu	Cd	Ni	As	Pb	Al	Ba	Ec	OM	PH
Zn	**1**										
Cu	0,711	**1**									
Cd	**0,956**	0,881	**1**								
Ni	0,838	**0,979**	**0,959**	**1**							
As	0,766	0,756	0,852	0,827	**1**						
Pb	0,916	0,934	**0,991**	**0,986**	0,826	**1**					
Al	-0,087	0,240	0,092	0,195	0,573	0,098	**1**				
Ba	0,913	0,688	0,865	0,779	0,486	0,855	-0,420	**1**			
Ec	0,945	0,883	**0,997**	**0,960**	0,888	**0,987**	0,164	0,826	**1**		
OM	**0,968**	0,831	**0,992**	0,927	0,886	**0,969**	0,134	0,836	**0,995**	**1**	
PH	**-0,956**	-0,877	**-0,990**	**-0,951**	-0,770	**-0,988**	0,038	-0,922	**-0,977**	**-0,970**	**1**

In bold significance at the 0.05 probability level

Z. album are within the range of concentrations toxic to plant tissues (Table 10).

In the roots, the lowest Cu content is recorded at S1 (29.66 ppm), the highest at S3 (45.46 ppm). The highest concentration in the shoots is recorded at S1 (85.45 ppm) and the lowest at S4 (78.05 ppm). Both in roots and in shoots, the Cu concentrations are within the range of toxic concentrations for plant tissues (Table 10).

In all the Gabes sites, the Cd levels are within the range of toxic concentrations for plant tissues. The lowest content is recorded in the shoots at S3 (6,237 ppm) and the highest in the roots at S1 (17,957 ppm).

Similarly for Ni, all values are within the toxicity range. *Zygophyllum* roots from S4 contain the lowest concentration (12.2 ppm) and shoots of S2 contain the highest value (27.8 ppm).

Concerning Pb, site 4 presents the lowest Pb contents for both roots and shoots (respectively of 20,731 and 21,864 ppm). These values are below the toxicity limits. The Pb contents reach toxic values at S1 and S2 where the metal seems to be concentrated in the roots. Indeed, at S2, we recorded a content of 38,098 ppm and a higher content is also recorded at S1 (46,647 ppm). As concentrations are within the standards except in shoots at S2 where it's slightly exceeds the lower limit of the toxicity range (5.2 ppm).

The concentration of aluminum ions in the soil solution increases sharply with the drop in pH and becomes toxic from 5.5 (Hasni, 2015). This is the case of sites S1 and S2 where the respective pH values are 5.5 and 5.8.

According to several studies, Ba is not particularly toxic to plants (Elluin, 2005). According to (Pendias, 2001) the toxic concentration would be from 500 ppm. In our work, this value is slightly exceeded in the roots and shoots of *zygophyllum* at S4 (respectively of 527.4 and 798.1 ppm). However, this toxic content is largely exceeded at S2 (in roots: 1120 ppm) and at S1 (in shoots: 1654.26 ppm). Probably because of the proximity of these two sites to the phosphate industries and the polluting impact of these industries on the environment. These relatively high values could hide Ba contamination of groundwater in the Gabes region and therefore a risk to human health (Dridi, 2009).

Bioconcentration and translocation factors (BCF and TF)

BCF values for heavy metals are ranked on the following sequence: Ba > Cu > Zn > Cd > Pb > Al > Ni > As (Table 11). *Zygophyllum album* was qualified as excluder for Ni, As and Al (BCF < 1), (Table 11). Moreover, it exhibited good removal potential for Zn, Cu, Cd, Pb and Ba (BCF > 1).

The potential mobilization of trace elements (TF) seems to decrease as follows: Cu > Al > Zn > Ba > Ni > Pb > As>Cd. The translocation factor is a crucial factor for selecting plant species as candidates for phytoremediation. By comparing BCF and TF, we can compare the ability of different plants in taking up metals from soils and translocating them to the shoots (Fitz and Wenzel, 2002). Species that show values of BCFs and TFs greater than 1, have the potential to be used for the phytoextraction (Yoon et al., 2006). It should be noted that for Zn, Cu, Pb and Ba the BAF is greater than 1, TF is greater than 1 so *Z. album* in the case of these 4 metals can be considered as phytoremediator. For Cd and since the TF is greater than 1 and the BAF is less than 1, the plant can be considered as a phytostabiliser for this metal.

For all the studied metals, the values of TF in the Gabes sites are greater than 1 except for Al at S2. And Except for Cd, all the studied metals are more accumulated in the shoots than in the roots (Figure 5). Thus, it can be concluded that these heavy metals probably have a coherent transport medium in the *zygophyllum album* plant and that the latter can play a very important role in minimizing the harmful effects of MTEs.

Table 10. Normal, deficiency, excessive and phytotoxic values (mg·kg–1) of heavy metals in vegetation (Kabata Pendias & Pendias, 1992)

Heavy metals	Sufficient or normal	Excessive or toxic
Zn	27-150	100-400
Cd	0.05-0.2	5-30
Cu	5-30	20-200
As	1-1.7	5-20
Ni	0.1-5	10-100
Pb	5-10	30-300

4. CONCLUSION

Soils pollution at the industrial phosphate vicinity in Gabes from Tunisia has been studied using various tools and methods along with evaluation indices and guidelines. The highest values of the toxic elements were recorded at site 2, mainly from metallic wastewater discharge from industrial areas in the chemical group province. Site 1 (Ghannouch province), site 3 (Zarat) and site 4 (Arram) also have strong metal concentrations, received by industrial and domestic wastewater. The total ranking of the concentration of metals is: Al> Ba> Ni> Zn> Cu> Pb> As> Cd.

The Gabes soils are characterized by high mean relative concentration of As, Ba, Cd, Cu, Ni, Pb, Al and Zn in all study sites, indicating inputs from anthropogenic sources. The Igeo and PLI of the heavy metals show that the all study sites are highly polluted. PCA, CA and correlation matrix suggest that the soils are mainly polluted by As, Ba, Cd, Cu, Ni, Pb, Al and Zn. However, high abundances of these heavy metals in the studied soil samples reflect an influx from anthropogenic sources.

BCF values for heavy metals are ranked on the following sequence: Ba > Cu > Zn > Cd > Pb > Al > Ni > As. *Zygophyllum album* exhibited removal potential for Cu and Zn, Cu, Cd, Pb and Ba (BCF > 1). This result is consistent with those of Jalali et al. (2019) which stated that this species is effective in soil phytoextraction contaminated, and Morsy et al. (2012) which showed that this plant, when facing heavy metal pollution, has the capability to increase antioxidant enzyme activities, and alter root plasma membrane lipid composition. Therefore, in a subsequent study, we will investigate the physiological response of *Z. album* to ETMs in the region of Gabes contaminated by industrial phosphate pollution.

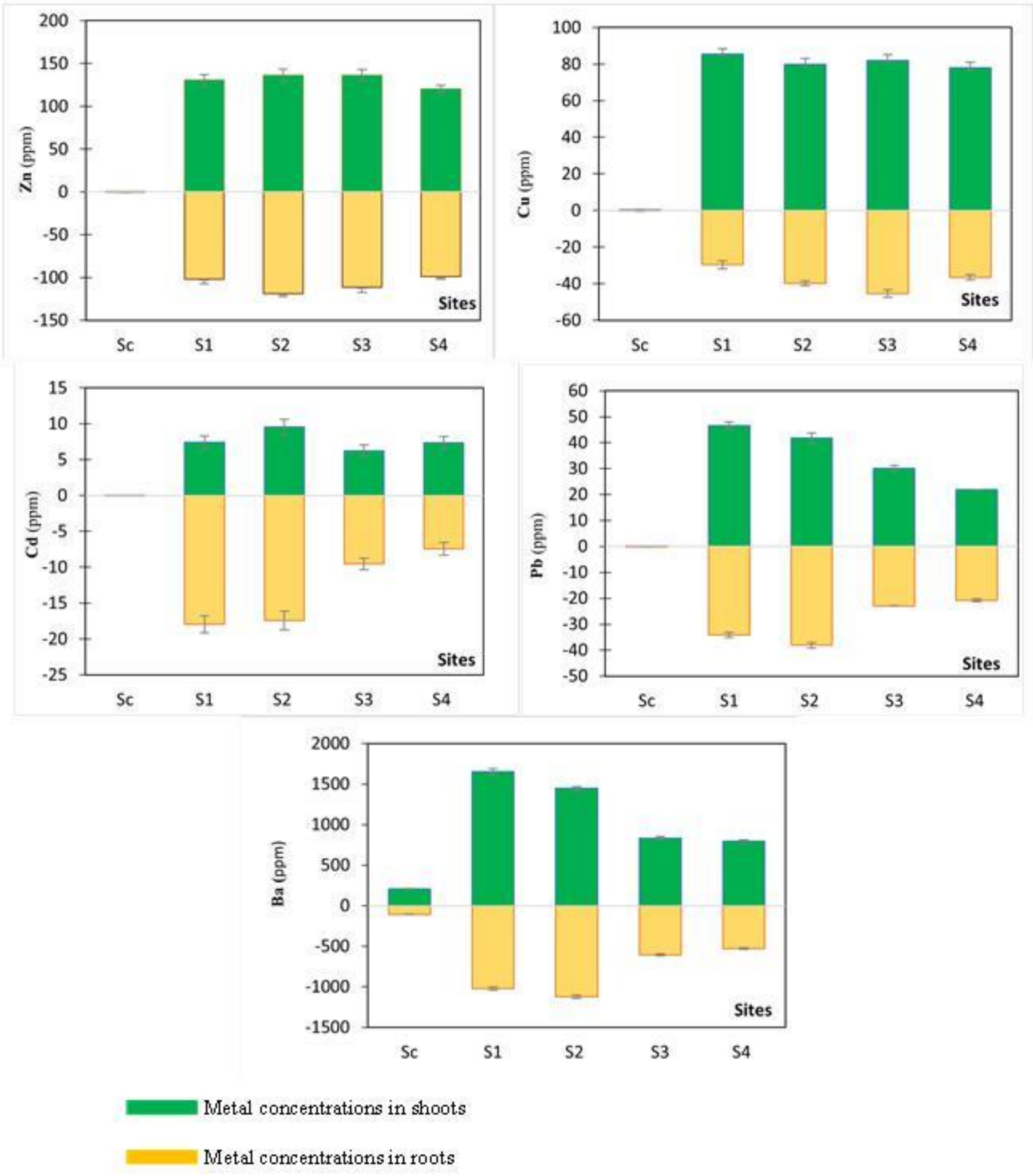

Figure 5: Concentration of heavy metals (Zn (a), Cu (b), Cd (c), Pb (d) and Ba (e)) in shoots and roots of *zygophyllum album.*

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of the paper

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