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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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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 (Sidi Ejjehmi) were determined. For the assessment of the level of sediment pollution, 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) and pH. Whereas, Bio-Concentration Factors (BCF) and Translocation Factors (TF) are calculated for the evaluation of pollution degree in *Zygophyllum album*. 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

Because of its capacity to serve as a geochemical reservoir for numerous pollutants, including heavy metals emerging from aerosol deposition through industrial and urban activities, soil is regarded as an important natural resource (El-Sherbiny et al., 2019). The main contributors to soil contamination that has a detrimental effect on the ecosystem are industrialization, significant urbanization, and mining (Yaylali-Abanuz, 2011). About twenty exporting facilities, including divisions of the Tunisian Chemical Group (TCG), which converts phosphate into phosphoric acid and fertilizer, are located in the Tunisian area of Gabes. The ecosystems in which the biotic components are altered and damaged are harmed by the pollutants released by this industry (Trasande et al., 2016; Wu et al., 2016). According to Galfati (2011), the phosphate industry is a significant source of dust and MTEs such Cd, Cr, Hg, Pb, and Zn. Due to their durability and resistance to atmospheric degrading environments through chemical, biological, and photolytic processes (Al-Kashman & Shawabkeh, 2006), several heavy metals are known to be hazardous to animals and plants even at low concentrations (Khan et al., 2008; Qureshi et al., 2016). Wind and rain have the ability to disperse these MTEs over a wide area, where they can accumulate in the topsoil, bioaccumulate, enter the food chain, and harm human health. The topsoil and plants close to phosphate have been shown in numerous studies to be susceptible to heavy metal contamination (Agbede, 2022). Physical and chemical treatment methods exist to get rid of metal pollutants, but these procedures are time-consuming. They also cost a lot and produce other pollutants. Alternative technologies are therefore required, and various biobased solutions like bioremediation must be investigated. Utilizing biological agents is safer and has little to no environmental impact. Bio-augmentation, bioremediation, bioventilation, composting, and phytoremediation are all types of bioremediation techniques. Phytoremediation stands out among them as the most practical and affordable option, and as a result, interest in it has grown (Usman et al., 2019). The use of plants for containing, degrading, or extracting xenobiotics from water or soil substrates is known as phytoremediation (USEPA, 2000).

Many different plants have been used to detoxify heavy metals for hundreds of years (Usman et al., 2019). Native plants have a better chance of surviving, growing, and reproducing under environmental stress circumstances than plants imported from other ecosystems, making them the best plants for phytoremediation (Adriano, 2001; Antonsiewicz et al., 2008). *Zygophyllum album* (*Z. album*), a halophyte that was selected for this study, is a plant that is overrepresented in Tunisian dry rangelands because it is exceptionally well-adapted to arid environments (Gamoun et al., 2018). The profusion of this plant, which naturally grows next to Gabes Chemical Group and a number of other polluting enterprises in Tunisia, is an indication of its toxitolerant nature (Jalali, 2018).

The current study focuses primarily on determining the various concentrations of heavy metals (Al, Cd, Ni, As, Pb, Zn, Ba, and Cu) in soil near phosphate processing plants and rural areas. Another key issue is the assessment of the level of heavy metal contamination as determined by several pollution indices. In order to envision *Z. album's* potential use in the field of phytoextraction, we will examine how well it can capture metal traces (ETM).

2. MATERIALS AND METHODS

2.1. Study area description

Near southern Tunisia, near the Gulf of Gabes, the research region is situated (33°53'28.38"N, 10°6'33.44"E) (Figure 1). One of the most industrialized sections of the nation is this one. This area has a surface area of about 7166 km^2, a dry climate, low average rainfall (between 167 and 176 mm annually), an average annual temperature between 18.8 and 19.3°C, and is exposed to strong easterly winds, according to Hamdi et al., (2015). The Tunisian Chemical Group (GCT), one of the biggest companies engaged in phosphate mining, is based in the Ghannouch industrial zone. The three primary factories for this industrial activity, one for phosphoric acid, one for di-ammonium phosphate (DAP), and one for ammonitrate (AN) were constructed in 1972, 1979, and 1983, respectively. However, phosphate mining and processing facilities can produce accidental releases of chemicals used in the process. These chemicals can seep into the ground, reach surface waters (rivers, lakes, etc.) and contaminate sediments. Liquid wastes from the treatment process can also be discharged into waterways, increasing the risk of contamination. Additionally, phosphate mining sites, especially surface mines, can disturb the natural soil and increase the risk of erosion. When it rains, the water can wash away sediment contaminated with chemicals and carriers to nearby waterways or wetlands, potentially affecting plants and aquatic ecosystems. Furthermore, tailings from phosphate mining and processing, such as sludge and waste, may be dumped in specific areas, such as tailings ponds. If these wastes are not properly managed, they can lead to contamination of the surrounding sediments. Chemicals used in phosphate processing can leach into the soil and be taken up by plant roots, potentially contaminating plants grown in the area. The halophyte kind of plant predominates in this area. The study was focused on *Zygophyllum album*, a native dwarf plant of the steppes (Floret & Le Floc'h, 1983). The study of both sediments and the plant *Zygophyllum album* in the vicinity of the phosphate industry located in the Gulf of Gabes, can provide a more complete and in-depth picture of the level of contamination, as well as its potential effects on the environment ecosystem and human health. Indeed, sediments and plants can act as complementary indicators of contamination. Sediments are often the last deposition of pollutants in aquatic and terrestrial ecosystems, reflecting the buildup of contaminants over time. Plants, on the other hand, can absorb and accumulate chemicals from soil and water, making them indicators of the presence of contaminants in the environment. Additionally, the study of sediments can help assess the persistence of pollutants in the environment over the long term, while the study of plants can reveal how contaminants are absorbed, entrained and transported through the food chain. Some plants, such as *Zygophyllum album*, have accumulative properties that can make visible the effects of contamination on vegetation. By studying both sediments and plants, it is possible to better understand how contamination can affect local biodiversity.

The control site (ST) is located at the level of Chat Ejjehmi in Soliman, Tunisian Cap-Bon. It is a place where there are no contaminants of any kind. Four locations were picked within the sampling area (Figure 1), and Table 1 compiles information about them.

2.2. Sampling and analytical procedures

In September 2021, the sampling process was finished. In order to evaluate the soil contamination, composite soil samples were taken from both polluted locations (Gabes: S1, S2, S3, and S4) and control sites (Ejjehmi: ST). From the top 0–20 cm of soil at each location, a sample of soil weighing about one kilogram was obtained using an auger. As promptly as practical, the soil samples were placed in plastic bags and kept at 4°C until a laboratory analysis. Samples of *Zygophyllum album* were extracted from their natural vegetation, and

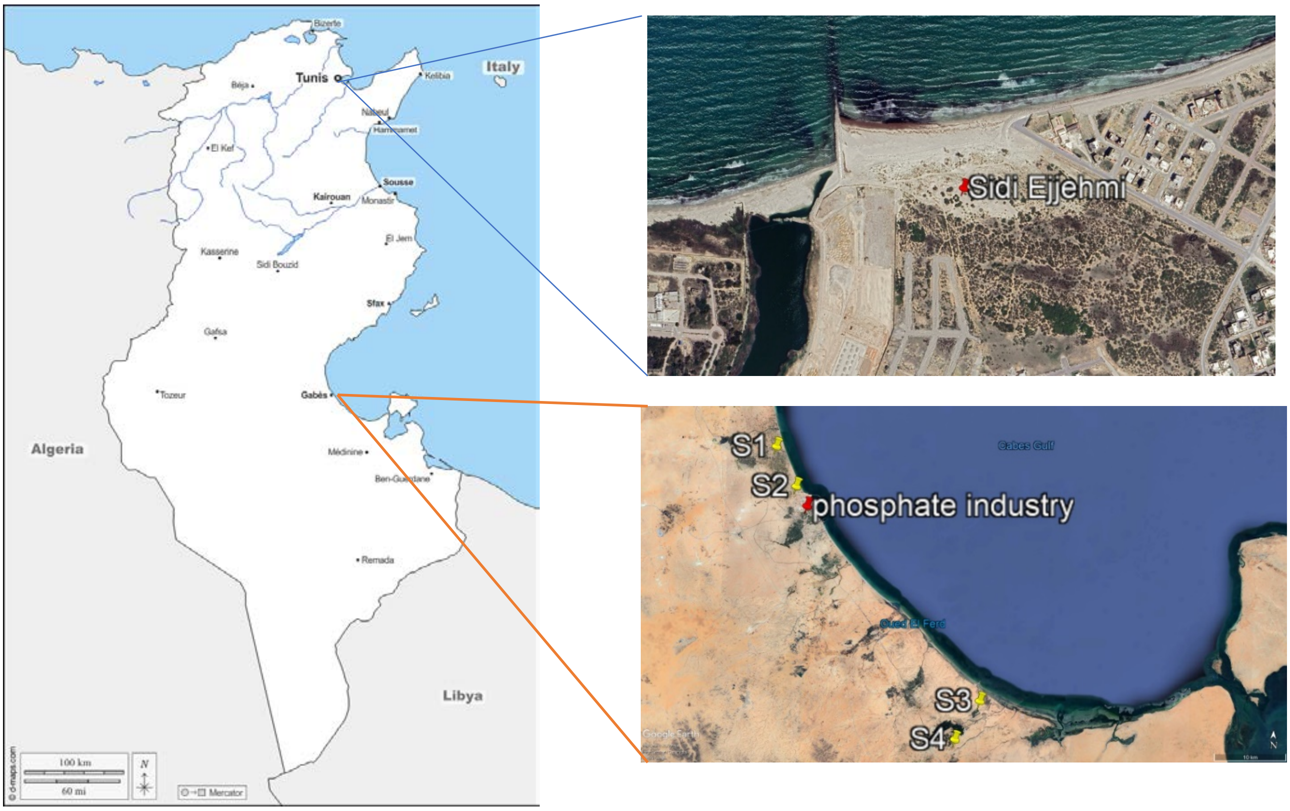

Figure 1. Map showing sampling sites (ST: Sidi Ejjehmi, Control site; S1, S2, S3 and S4: Gabes (Polluted sites).

Table 1. Locations and description of sampling sites.

Sites	Stations	Coordinates	Description
Sidi Ejjehmi (Control site)	ST	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°58'37.03"N 10° 2'24.40"E	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 Company de Ghannouch
	S2: Gabes Chemical Group	33°55'55.56"N 10° 4'30.85"E	Located 1 km from Alkimia Chemical Company, 800m from the ICF fluorine production plant and close to several other industries.
	S3 : Zarat	33°39'58.17"N 10°21'39.09"E	Site located 37 km from the GCG
	S4: Arram	33°36'54.80"N 10°19'35.91"E	Site located 58 km from the GCG

the small silt particles that had adhered to them were subsequently rinsed away with distilled water. Samples of soil and plant were replicated three times over space. The concentrations of Al, Cd, Ni, As, Pb, Zn, Ba, and Cu were determined using FAAS, a PerkinElmer 1100 device. The sulphates were measured using a UV spectrophotometer (Uvikon XL, Secomann, ALES Cetex, France). All samples were passed through a 0.22-m nylon filter before metal content was determined. To ascertain the possible metal bioavailability, 5 g of soil samples were air dried, extracted in 50 ml of 0.01 M CaCl2 solution, and mechanically stirred for 5 hours. The extracts were filtered before instrumental heavy metal measurement. There were three separate sample treatments (Bayouli et al., 2020).

2.3. Risk assessment

To assess the severity of sediment pollution, we looked at the enrichment factor (EF), 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 relation to the degree of pollution 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 Hakanson (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	Hakanson (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	Hakanson (1980) recommended the following classes: Low, Moderate, Considerable, Very high.

2.4. Phytoextraction potential: BCF and TF

The bioconcentration factor (BCF) and the translocation factor (TF) are important variables in studies of heavy metal uptake (Marchiol et al., 2004). To evaluate the potential for phytoextraction of the selected plants, the bioconcentration factor was determined.

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

The bioconcentration factor (BCF) and the translocation factor (TF) are important variables in studies of heavy metal uptake (Marchiol et al., 2004). To evaluate the potential for phytoextraction of the selected plants, the bioconcentration factor was determined.

In order to evaluate the heavy metal translocation along the plant (from roots to shoots), the translocation factor (TF), which is defined as the ratio between the metal concentrations in shoots and in roots, is used (Arrivabenes et al., 2016).

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

Translocation factor (TF) measures a plant's ability to transport heavy metal from roots to aerial tissues, suggesting a plant's capacity to accumulate heavy metal in aerial organs. A plant with a high TF value (TF > 1) has a significant ability to transport heavy metals from the roots to the aerial tissues. The plant's capacity to transport the metal to aerial tissues is constrained, on the other hand, if the value is low (TF 1) (Lam et al., 2017).

2.5. Statistical Analysis

STATISTICA 8.0 was used to conduct the statistical analysis. The analysis of variance (ANOVA) assisted in determining the significant spatial differences for $p < 0.05$. For a multivariate analysis of the stations' data set, cluster (CA) was used, and Pearson correlation was applied for the sediment-related aspects.

3. RESULTS AND DISCUSSION

3.1. Metal concentrations in soil samples

Table 3 lists the nine heavy metal concentrations (As, Ba, Cd, Cu, Hg, Ni, Pb, Al, and Zn), OM, pH, and EC in the soil samples near an industrial phosphate plant. The concentrations of heavy metals (g/kg) were found to be between 22.544 and 39.22 for As, 308 to 682 for Ba, 13.58 to 25.22 for Cd, 76.25 and 110 for Cu, 142 to 190.21 for Ni, 41.53 to 78.88 for Pb, 3780 to 4900 for Al, and 172.35 to 188.22 for Zn.

In comparison to S1 and S2 (5.5-5.8) sites, the mean pH value was considerably low in S3 and S4 (8-8.4). The electrical conductivity, however, indicated much greater values at the S2 site (20.1 dSm-1), which is close to the main GCT plants, while the lowest value was found at Arram (S4), the site that is farthest from the TCG (1.8 dSm-1). The EC value at the control location is relatively close to S4's (2.6 dSm-1) value. In comparison to S3 and S4 (32.37-30.73 g/kg MS), S2 and S1 had a higher than average concentration of OM (75.03-66.75 g/kg MS). As, Ba, Cd, Cu, Hg, Ni, Pb, Al, and Zn concentrations for S1 exhibit rises in the spatial distribution of heavy metals, while most metal concentrations in S4 tend to reductions, reflecting both natural and anthropogenic source material inputs (Li & Zhang, 2010). The following, in decreasing order, are the mean concentrations of heavy metals found in soil samples: Zn, Cu, Pb, As, Al, Ba, Ni, Zn, and Cd. Each study site has relatively high mean heavy metal concentrations. Site-2 > Site-3 > Site-1 > Site-4 was the order in which total metal concentrations were measured in this investigation. However significant levels of these heavy metals in the soil samples point to anthropogenic sources that have been introduced

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
ST	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) to the area under study. The high presence of all elements in the soil samples from the research areas points to clay mineral management as well as industrial effluent.

According to Hossain et al., (2015), the Igeo is frequently used to assess the level of metal contamination in geologic samples. Table 4 displays the statistical results for Igeo in the soil samples. Zn and Pb have mean Igeo values of 1.21 and 1.24, respectively, indicating considerable metal contamination. As a result, the mean Igeo value for Al (-4.75) is < 0, which indicates that the analyzed soil samples are essentially uncontaminated. The sample soils are, nevertheless, moderately to strongly contaminated, as shown by the group-wise mean Igeo values for Cu (2.18) and Ni (2.6). Additionally, the area's significant industrial activity is supported by the mean Igeo values for As (3.23) and Cd (6.97), which indicate strongly and extremely contaminated soils, respectively, due to anthropogenic source material input.

According to Bhuiyan et al., (2010), the CF and PLI are frequently employed to assess the level of heavy metal pollution in soils. Table 5 contains a list of the calculated CF and PLI. All of Gabes' sites have CF values more than 3, which indicate at less a considerate contamination. As a matter of fact, the soils at sites 1 and 2 had CF values for Zn, Cu, Cd, Ni, and As that were > 6, indicating a "very high contamination" as well as a "considerable contamination" for Pb and a "low contamination" for Al. Pb CF measurements demonstrate low contamination by this metal at any of Gabes' sites. The silt at Site 4 that is most remote from the phosphate industries had values of CF> 6 for Cd, Ni, and As that suggest "very high contamination," while those for Zn and Cu show "considerable contamination." The metals in the Gabes Golf have mean CF values in the following 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).

The EF of heavy metals is most frequently used to assess contamination caused by humans. While EF values > 1.5 show non-crustal contributions and/or artificial weathering processes (such as anthropogenic impacts), EF values 0.5–1.5 disclose regional rock compositions (Zhang & Shan, 2008). Table 6 contains a list of the calculated EF and DC. The examined metals in this work have the following EF ranges: 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.

Table 4. Geo-accumulation index (Igeo) 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	
ST	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	488.7	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	6.9	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

In the phosphate industrial zone, 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) suggest that human activity has had an impact on the metal levels. All heavy metals' EF values indicate very extreme enrichment in the soils of all sampling sites. Site-1 came first, followed by Site-2, Site-4, and Site 3, in terms of total EF values.

Degree of contamination (Dc) values ranged from 377.07 at site 3 to 715.41 at site 1, with an average value of 524.68 (Table 6). All of the sites for study are located in the fourth class, which corresponds to a very high Dc value, according to Hakanson (1980).

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

Table 7 contains the calculated Er and Ri. According to Hakanson (1980), low Er values were found at all of the investigated sites 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, every site displays very high Cd levels (3993.90–7417.50, average = 5766). For Ni, all values range from 38.15 to 51.10, with an average value of 45.937, indicating a moderate ecological risk. Regarding the ecological risk factor, the Er value for As ranged from considerably contaminated (112.20) to very high contaminated (196.10). Ri was determined to determine the biota's sensitivity to harmful substances. According to Hakanson (1980), the Ri index assesses the environmental impact of all six risk variables (Zn, Cu, Cd, Ni, As, and Pb) on soil's heavy metal toxicity. All of Gabes' study sites exhibited extremely high Ri values (4186.48 - 7739.95, average = 6018.298), indicating that they are all at very high risk.

3.3. Cluster analysis

A group analysis (CA) was employed for spatial variability (clustering of similar research locations). This approach is frequently used in soil/sediment contamination results analysis investigations (Ghannem et al., 2018; Karbassi et al., 2016). Dendrogram analysis is crucial to understanding the degree of similarity between the environment and the source of different sample station components. However, a statistically significant cluster divides the four study locations into two groups at 97% similarity (Figure 3). Sites 1 and 2 (Cluster 1), which are characterized by a severe

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

Sample	Er						Ri
	Zn	Cu	Cd	Ni	As	Pb	
ST	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	45.94	144.95	18.48	6 018.30

metal rejection from industrial phosphate, stand in for the highly polluted area. Sites 3 and 4 in Cluster 2 depict a region that is moderately contaminated. The examined elements were also clustered using CA. Additionally, a dendrogram was used to organize the investigated data (Figure 4). A cluster, however, was found to group three statistically significant groups with 79% similarity. Cd and As (pollutants from anthropogenic sectors: trash from the industrial zone) were of Cluster 1. Cu, Pb, Zn, Ni, and Ba were also present in Cluster 2 and came from anthropogenic sources, including phosphate plant waste and domestic and industrial trash. Al was found in Cluster 3, which came from lithogenic sources.

3.4. Correlation matrix

Based on the results of the Pearson correlation coefficients, a significant positive correlation between the hazardous components was discovered (Table 8). According to Wang et al., (2012), heavy metals with significant correlations may have shared sources and exhibit comparable behavior during transformation or migration. Al doesn't show a significant correlation with any of the factors in this investigation. This demonstrates that it is also appropriate to use it as a reference element in EF calculations. 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) all have positive correlations with OM, indicating that this element is greatly influenced by soil OM. Cd (r = 0.99, p 0.05), Ni (r = 0.96, p 0.05), and Pb (r = 0.98, p 0.05) all had positive correlations with EC.

Ward's approach was used to perform hierarchical clustering on standardized data (Li et al., 2013), and the squared Euclidean distance was used as a measure of similarity (Bhuiyan et al., 2010; Li et al., 2013). In order to demonstrate an ecological sampling method, metal variables are frequently evaluated using CA (Li and Zhang, 2010; Li et al., 2013). The dendrogram generated from the CA was out at sampling sites, however, revealed three statistically significant groups, namely cluster 1 (S 1 and S 2) and cluster 2 (S 3 and S 4) (Figure 3). The clusters demonstrate a significant level of anthropogenic-derived pollution. The majority of the sampling locations in Ghannouch and Gabes belonged to clusters 1 and 2, respectively, which correlate to areas with extremely heavy pollution levels. The presence of relatively high levels of Pb, Al, As, Zn, Br, Cu, Ni, and Cd in clusters 1 and 2 indicates that these areas are heavily contaminated and that the heavy metals were likely sourced from industrial effluents.

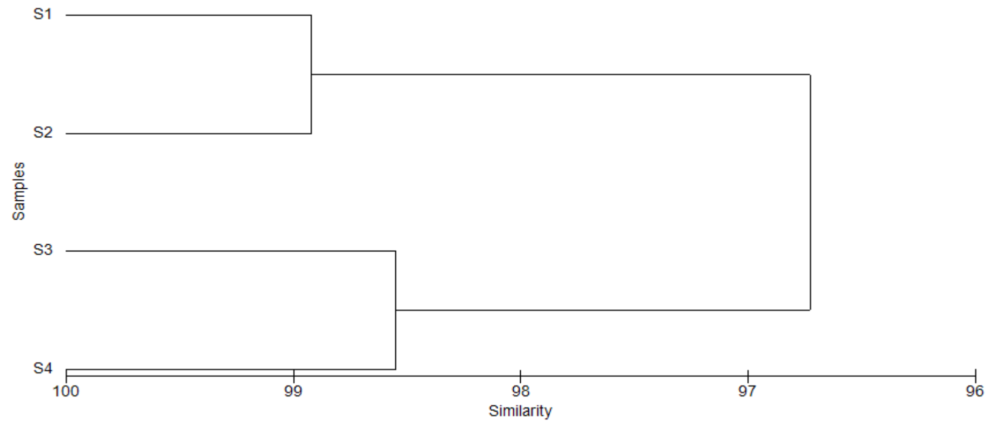

Figure 3. Dendrogram showing clustering of sampling sites in the vicinity of the phosphate industrial zone and control site

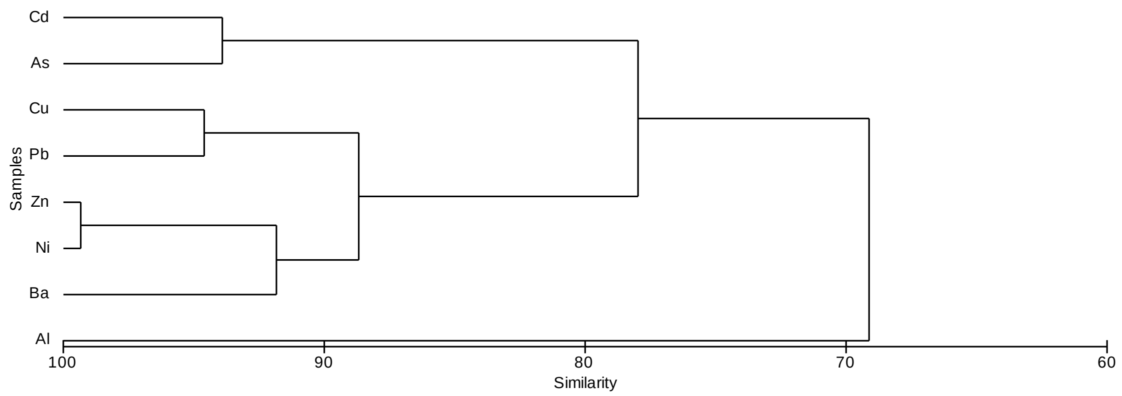

Figure 4. Dendrogram showing clustering of the analyzed parameters

Table 8. 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	0934	**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

A correlation matrix for harmful elements in soils was created in attempt to establish links among metals and identify the common source of metals near the industrial phosphate of Gabes. The information indicates that one factor, coming from the waste discharges of industrial phosphate and also migrating simultaneously, affected the distributions of the components. It is also obvious that at the most polluted site, the correlation pattern is highest. Al and As had a significant correlation ($r = 0.573$, $p < 0.05$) proving they were both produced from lithogenic sources. All toxic elements have positive correlations with OM, indicating that soil OM plays a significant role in controlling these elements (Zhang et al., 2009; Hossain et al., 2015). According to Tume et al. (2011), soil OM has a high adsorption capacity for Cr, Ni, Pb, and Zn, indicating that OM has a positive correlation with these heavy metals (Yin et al., 2002; Quenea et al., 2009). According to Dragovic et al. (2008), heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) have a positive correlation with OM, indicating that they share a preference for clay minerals. A significant amount of soluble salts in the soil's aqueous solution is suggested by the positive correlation of EC with Cd, Ni, and Pb.

4. HEAVY METAL CONCENTRATIONS IN *ZYGOPHYLLUM ALBUM*

Eight ETMs were investigated in this study at four sites (S1, S2, S3, and S4) associated with the industrial activities of the Gabes region, primarily the TCG units. Being far from any industrial activity, especially that of the phosphate sector, the control site is the Cs site. The sampling site and the area of the *zygophyllum album* that was subjected to this analysis both had an impact on the samples' metal concentrations. According to Kabata-Pendias & Pendias (1992), all the ETM concentrations evaluated in the control site are either insufficient or much lower than the usual amounts (Table 9).

Total Zn values in *Z. album* tissues at Gabes locations range from 99 to 136,221 ppm. The highest Zn contents, regardless of the sampling location, are found in the shoots rather than the roots (Figure 5). S4 and S3 have the lowest and highest concentrations of the root portion, respectively (99 and 111.38 ppm). Similar to the shots, S4 and S3 both record the lowest and highest values (120.08 and 136.221 ppm, respectively). Zn levels in the *zygophyllum album* are hazardous to plants. In fact, Zn levels in the tissues of Z. album are within the range of amounts harmful to plant tissues, according to Kabata-Pendias & Pendias (1992) (Table 9).

Table 9. Normal, deficiency, excessive and phytotoxic values ($mg \cdot kg^{-1}$) 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

S1 in the roots has the lowest Cu level (29.66 ppm), and S3 has the highest (45.46 ppm). S1 has the highest quantity in the shoots (85.45 ppm), and S4 has the lowest (78.05 ppm). The Cu contents are within the range of hazardous amounts for plant tissues in both the roots and the shoots (Table 10).

The Cd levels at each of the Gabes sites fall within the range of concentrations that are harmful to plant tissues. The roots at S1 had the highest amount (17,957 ppm), whereas the shoots at S3 have the lowest (6,237 ppm).

For Ni, all values are within the acceptable range for toxicity. The lowest concentration of *zygophyllum* is found in the roots from S4 (12.2 ppm), and the maximum concentration is found in the shoots from S2 (27.8 ppm).

Site 4 has the lowest Pb concentrations (respectively 20,731 and 21,864 ppm) for both roots and shoots. These numbers fall beneath the toxicity thresholds. At S1 and S2, where the metal appears to be concentrated in the roots, the Pb content reaches dangerous levels. In fact, we measured a concentration of 38,098 ppm at S2, and a greater value of 46,647 ppm at S1. Except in shoots at S2, where it marginally exceeds the lower limit of the toxicity range (5.2 ppm), and concentrations are within limits.

With a pH decrease, the quantity of aluminum ions in the soil solution rises fast and starts to become hazardous at 5.5 (Hasni, 2015). This is the situation at sites S1 and S2, where the pH levels are 5.5 and 5.8, respectively.

Ba is not very hazardous to plants, according to various researches (Host et al., 2005). The dangerous concentration, according to Kabata-Pendias (2001), would start at 500 ppm. In our research, the roots and shoots of *zygophyllum* at S4 (respectively, 527.4 and 798.1 ppm) marginally exceed this value. However, in S2 (in roots: 1120 ppm) and S1 (in shoots: 1654.26 ppm), this hazardous concentration is significantly exceeded. Probably due to the fact that these two locations are close to phosphate industry and that these sectors have an adverse environmental impact. The Gabes region's groundwater may be contaminated with Ba, posing a threat to public health, as these relatively high values may conceal (Dridi, 2009).

5. BIOCONCENTRATION AND TRANSLOCATION FACTORS (BCF and TF)

The following order determines the ranking of the BCF values for heavy metals: Ba is followed by Cu > Zn > Cd > Pb > Al > Ni > As in Table 10. For Ni, As, and Al, *Zygophyllum album* was deemed an excluder (BCF < 1) (Table 10). The removal potential for Zn, Cu, Cd, Pb, and Ba was also good (BCF > 1).

Following are some indications of a probable decline in trace element mobilization (TF): Cu follows Al > Zn > Ba > Ni > Pb > As > Cd. When choosing plant species to be candidates for phytoremediation, the translocation factor is an important consideration. We can assess the capacity of various plants to uptake metals from soils and transfer them to the shoots by comparing BCF and TF (Fitz & Wenzel, 2002). According to Yoon et al., (2006), species with BCF and TF values larger than 1 may be employed for phytoextraction. It should be emphasized that Z. album can be regarded as a phytoremediator in the cases of Zn, Cu, Pb, and Ba since the BAF is larger than 1 and TF is greater than 1. For Cd, the plant can be thought of as a phytostabiliser because the TF is more than 1 and the BAF is less than 1.

With the exception of Al at S2, all of the examined metals had TF values in the Gabes sites that are larger than 1. All of the examined metals, with the exception of Cd, are more concentrated in the shoots than the roots (Figure 5). Thus, it can be inferred that the *zygophyllum album* plant serves as a likely coherent transport medium for these heavy metals and that it has a significant impact on reducing the negative effects of MTEs. This finding is in accordance with those of Jalali et al., (2019), who claimed that this species is effective in soil phytoextraction contaminated, and Morsy et al., (2012), who demonstrated that this plant has the ability to increase antioxidant enzyme activities and alter the lipid composition of the root plasma membrane when exposed to heavy metal pollution.

6. CONCLUSION

Various tools, methods, assessment indices, and recommendations have been used to study soil

Table 10. Variation of Bio-Concentration Factors (BCF) and Translocation Factors (TF) in *Zygophyllum album* from different stations.

	Zn		Cu		Cd		Ni		As		Pb		Al		Ba	
Sites	BCF	TF	BCF	TF	BCF	TF	BCF	TF	BCF	TF	BCF	TF	BCF	TF	BCF	TF
ST	1.054	2.922	1.044	5.523	1.025	0.743	0.0356	0.209	0.002	0.875	1.14	1.155	0.065	1.567	5.608	1.98
S1	1.235	1.279	1.048	2.881	1.041	0.412	0.195	1.297	0.238	1.3	1.03	1.371	0.076	1.158	3.921	1.622
S2	1.354	1.141	1.087	2.006	1.07	0.546	0.267	1.209	0.232	1.333	1.013	1.1	0.019	0.783	5.002	1.291
S3	1.437	1.223	1.296	1.804	1.033	0.653	0.208	1.576	0.25	1.177	1.012	1.32	0.0377	3.047	4.676	1.384
S4	1.2478	1.208	1.503	2.136	1.087	0.984	0.194	1.262	0.2	0.701	1.026	1.055	0.051	5.273	3.777	1.513

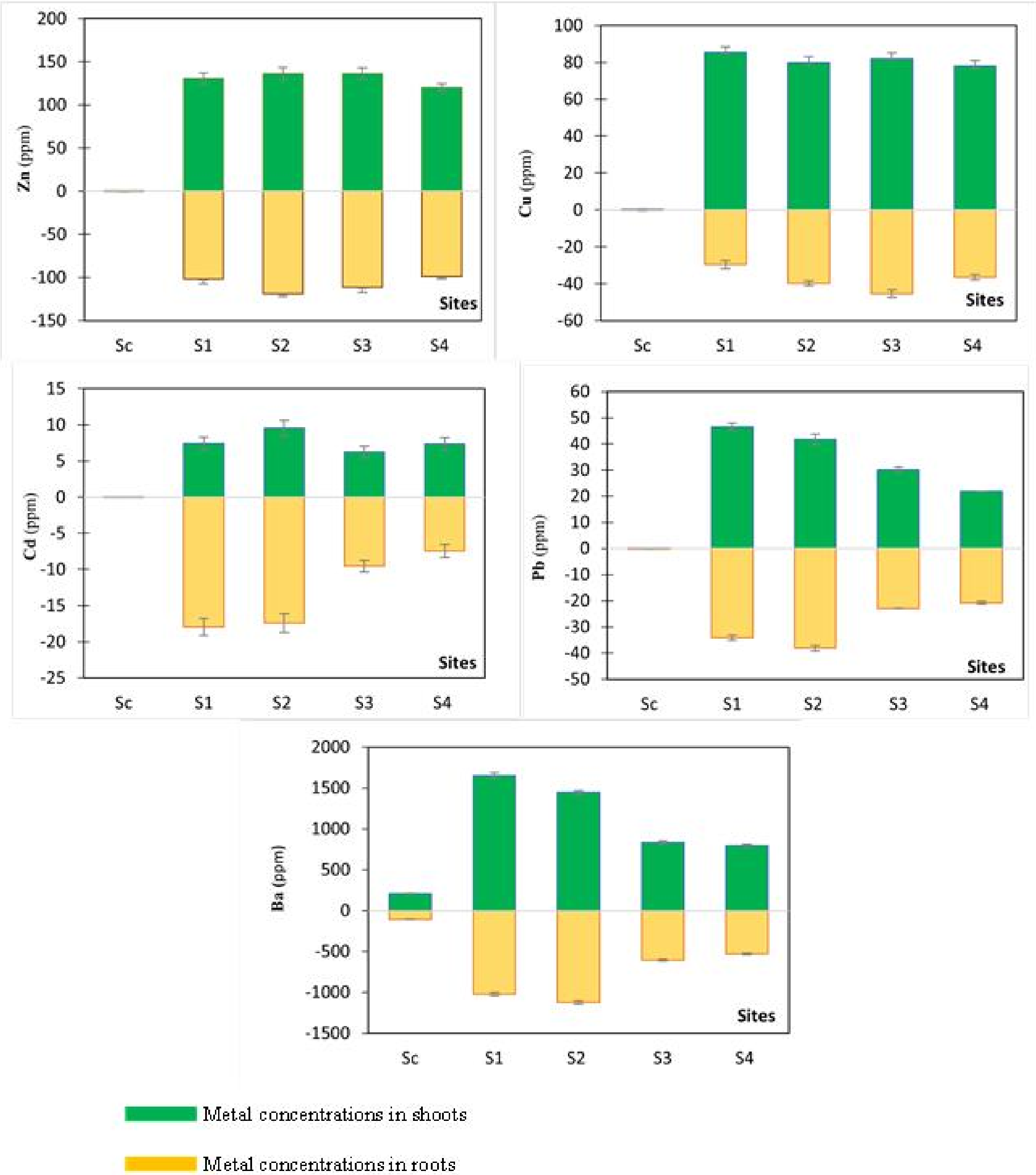

Figure 5. Concentration of heavy metals (Zn (a), Cu (b), Cd (c), Pb (d) and Ba (e)) in shoots and roots of *zygophyllum album.*

contamination in the Gabes, Tunisia, industrial phosphate area. The chemical group province's industrial sectors, which primarily discharge metallic wastewater at site 2, recorded the highest amounts of the harmful components. Strong metal concentrations are present at Site 1 (Ghannouch Province), Site 3 (Zarat), and Site 4 (Arram), which are all receiving sites for industrial and domestic effluent. The total ranking of the concentration of metals is: Al> Ba> Ni> Zn> Cu> Pb> As> Cd.

Indicating inputs from anthropogenic sources, the Gabes soils are distinguished by high mean relative concentrations of As, Ba, Cd, Cu, Ni, Pb, Al, and Zn at all studied sites. All of the study sites are highly polluted, according to the Igeo and PLI of the heavy metals. According to PCA, CA, and the correlation matrix, As, Ba, Cd, Cu, Ni, Pb, Al, and Zn are the main pollutants in the soils. High concentrations of these heavy metals in the examined soil samples, however, indicate an input from anthropogenic sources.

BCF values for heavy metals are ranked on the following sequence: Ba > Cu > Zn > Cd > Pb > Al > Ni > As. Cu and Zn, Cu, Cd, Pb, and Ba showed elimination potential in *Zygophyllum album* (BCF > 1). As a result, in a forthcoming study, we will look into how Z. album reacts physiologically to ETMs in the Gabes region that has been damaged by industrial phosphate pollution.

Conflict of interests

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

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