

Heavy metals accumulation in *Hertia cheirifolia* along the highway in Setif region, Algeria

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Abstract. *Belguidoum A, Lograda T, Ramdani M. 2020. Heavy metals accumulation in Hertia cheirifolia along the highway in Setif region, Algeria. Biodiversitas 21: 2786-2793.* The aim of this work was to study the possibility of using *Hertia cheirifolia* spontaneous plant, generally present in uncultivated environments, as an indicator of pollution. The aerial parts of ten *H. cheirifolia* populations were collected along the East-West highway. Sampling is carried out in areas considered polluted or low contaminated in the region of Setif. Nine metallic trace elements concentrations (Pb, Zn, Cu, Fe, Mn, Cd, Ag, Bi, and Sb) were determined, for each population, by Atomic Absorption Spectrophotometry with Flame (AASF). Statistical analyzes were performed using mainly box and whisker diagrams, principal component analysis, and UPGMA. The concentrations detected for contaminants (MTE), in general, were very high, far exceeding international certified standards. The MTE concentrations in different populations were calculated for each metal and a positive correlation is observed. The order of MTE in the plant was found as follows: Fe > Zn > Mn > Pb > Sb > Cu > Bi > Ag > Cd. The Fe concentrations are very high in *H. cheirifolia* with an average of 3600 ± 1491.5 mg/kg. The populations of *H. cheirifolia* have shown a significant capacity to accumulate heavy metals. The presence of metal ions in the aerial parts of the plant designates that *H. cheirifolia* is a super accumulator of MTE and can be used as a bioindicator, which opens up prospects for its application to soils phytoremediation.

Keywords: Algeria, bioaccumulation, bioindication, heavy metal, *Hertia cheirifolia*, Setif

INTRODUCTION

The term metallic trace elements (MTE), is assimilated to the term “heavy metals”, designates metals and metalloids often reputed to be toxic, present in low dose environments (Connelly 2005; Rollin and Quiot 2006; Hasanuzzaman et al. 2018). The accumulation of heavy metals, natural components of the environment, is worrying. This occurrence is attributed to rapid population growth, urbanization, and the expansion of industrial activities (Aksoy et al. 2000; Simmons et al. 2003; Aslam et al. 2012; Tossapol et al. 2015).

The presence of MTE in the soil is not indicative of pollution (Baize 2000), because the rates of MTE in the soil depend on the rock of origin (Dung et al. 2013). Road transport contaminates the atmosphere, water, and soil near highways by atmospheric fallout. Traffic pollutants include potentially toxic metals (Caussy et al. 2003; Akbar et al. 2006; Olukanniand and Adebisi 2012). Many studies have shown contamination by these elements, near highways (Turer and Maynard 2003; Atayese et al. 2010). Plants are the basis of the food chain and can absorb MTE ground by biosorption or bioaccumulation (Atayese et al. 2010). The levels of heavy metals in roadside plants vary by species, so-called hyper-accumulating plants. These plants are able to accumulate high levels of MTE at concentrations 10 to 100 times the value tolerated by most plants (Krämer and Chardonnens 2001; Gratao et al. 2005; Gav et al. 2015).

Plants are used in bioindication; it is a low-cost process to assess the degree of pollution (Rucandio et al. 2011). *Hertia cheirifolia* species is considered a heavy metal accumulator and has a potential for phytoremediation of metallic trace elements (Lograda et al. 2016). The aims of the work are the study the bioaccumulation potential of MTE by *Hertia cheirifolia*, collected on the along a highway, and to identify its potential for phytoremediation.

MATERIALS AND METHODS

Study area

Ten stations, located at Setif region, Algeria (Table 1), were selected for the sampling of the species *Hertia cheirifolia* (Figure 1). The climate of the study area is semi-arid, cold in winter and hot in summer. The average annual rainfall is 322mm and rarely exceeds 500mm and the annual average temperature is 15°C.

Selection of the plant

Hertia cheirifolia, synonymous with *Othonnopsis cheirifolia*, is a species with very original leaves, persistent, gray, thick, forming a dense ground cover. In spring, the flowering is bright yellow. This species is native to Algeria and Tunisia. The selection of *H. cheirifolia* is based on a previous study on the bioaccumulation of heavy metals in this species (Lograda et al. 2016). It is a very popular plant in the region. The samples were transported to the laboratory in paper bags.

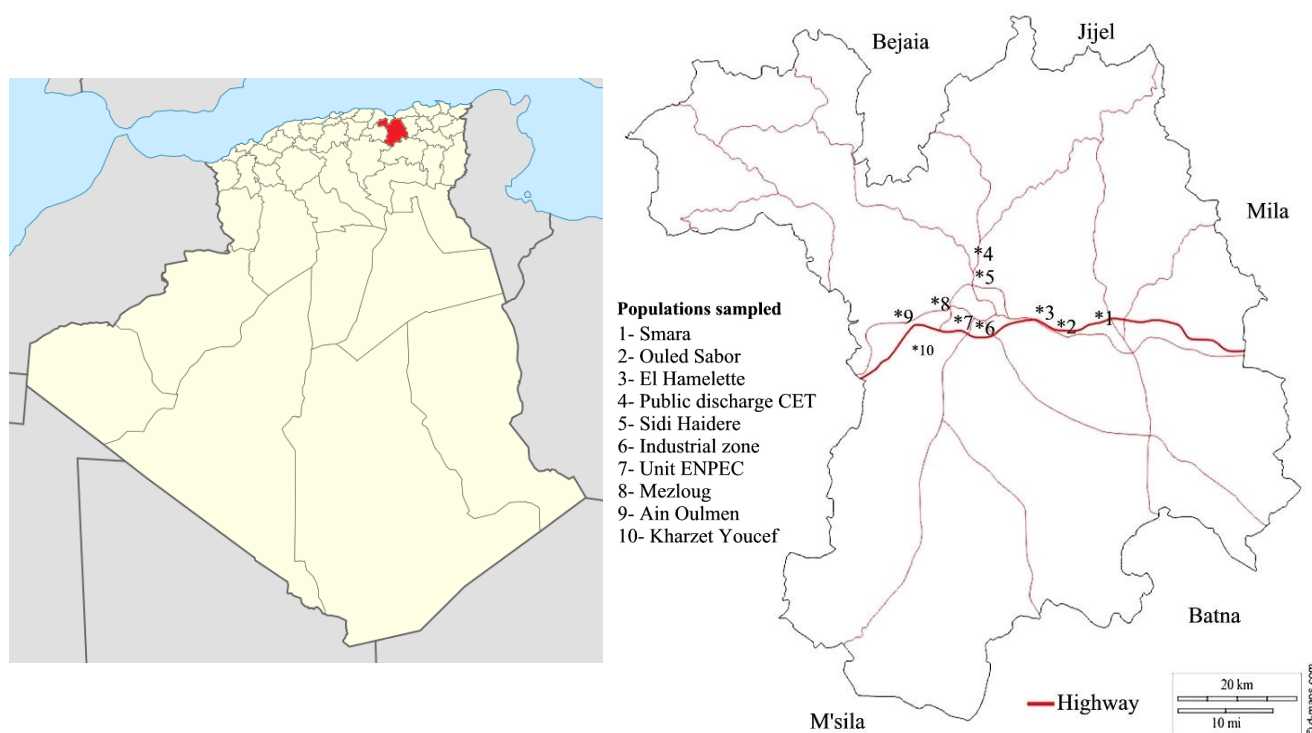


Figure 1. *Hertia cheirifolia* populations sampled along the highway in Setif region, Algeria

Table 1. Geographical coordinates of sampled stations

No.	Stations	Geographic coordinates	Altitude (m asl)
1	Smara	36°09'47.2"N 5°36'54.1"E	1000
2	Ouled Sabor	36°10'30.3"N 5°30'45.3"E	1100
3	El Hamelette	36°09'32.2"N 5°33'24.5"E	1150
4	Public Discharge CET	36°14'13.3"N 5°28'58.9"E	1130
5	Sidi Haider	36°13'23.1"N 5°27'44.1"E	1150
6	Industrial zone	36°09'35.3"N 5°25'08.4"E	1000
7	Unit ENPEC	36°09'54.5"N 5°25'10.6"E	1000
8	Mezloug	36°05'41.7"N 5°20'23.4"E	1050
9	Ain Oulmen	35°56'40.0"N 5°17'48.3"E	950
10	Kharzet Youcef	35°50'28.2"N 5°27'45.5"E	900

Samples preparation

Cleaning and grinding

It consists of eliminating any atmospheric deposit. After measuring the fresh weight, samples of 400g of plants were dried at 80 °C for 48 h, and then the dry weight was measured, crushed, and sieved through a nylon sieve to obtain a fine powder.

Mineralization

The method of Tauzin and Just (Adjiri et al. 2018) was used. It consists in calcining 1 to 2g (stems, leaves, and roots crushed) in a muffle furnace at 450°C for four hours. The ash thus obtained are mineralized by aqua regia (25% HNO₃ and 75% HCl), then reduced to dry until discoloration of the mineral deposit occurs, on a sand bath. The residue is dissolved in 10ml HCl 5%. Then filtered on Whatman, paper with 0,45µm of diameter, and completed to 20 ml with HCl 5%. Heavy metals were assayed by Atomic Absorption Spectrophotometer with Flame

(AASF) in the laboratory of Valorization of Natural Biological Resources, Setif University.

Analytical procedures for MTE concentrations

The concentrations of the following elements (Pb, Zn, Cu, Fe, Mn, Cd, Ag, Bi, and Sb), were determined by Atomic Absorption Spectrophotometry, with Flame (AASF). There are no established standards of trace elements concentration in ppm. To interpret the results of each element studied, we use as standard reference values, the unit's concentration ranges. The obtained results in (g/l) are transformed into mg/kg using the following relationship:

$$T \left(\frac{mg}{kg} \right) = C \frac{V}{S}$$

Where; T: element concentration in mg/kg; C: concentration of the element in mg/l determined by the calibration curve; V: extraction volume in ml and S: sample weight in grams

Statistical analysis

Data were first subjected to Principal Components Analysis (PCA) to examine the relationships among the trace elements and the bioaccumulation by this plant and the relationships between the presence of these elements and the vehicle circulations. Cluster analysis, Un-weighted pair group method with arithmetic mean (UPGMA), was carried out on the original variables and on the Manhattan distance matrix to seek for hierarchical associations among the elements and stations. The statistical analyses were carried out using STATISTICA 10 software.

RESULTS AND DISCUSSION

Results

After selecting the sites of studies; the aerial parts of *Hertia cheirifolia* were collected and subjected to analysis of heavy metals by AASF. This analysis revealed the presence of high rates of MTE in this species (Table 2).

All elements quantified in *Hertia cheirifolia* populations far exceed the standard values. The concentrations detected for contaminants (MTE), in general, were very high, far exceeding international certified standards values (Figure 2). The concentration of MTE in the different populations was calculated for each metal and a positive correlation is observed. The order of MTE in the plant was found as follows: Fe > Zn > Mn > Pb > Sb > Cu > Bi > Ag > Cd.

The cluster analysis clearly shows the presence of two clades (Figure 3). The element Fe, present in populations with very high concentrations with an average of (3600 ± 1491.5 mg/kg), forms the first clade. In the second clade, Zn forms a subgroup and isolates itself from the rest of the elements with an average concentration of (1000 ± 434.6 mg/kg), followed by Mn and Pb. The UPGMA confirms the correlation that exists between the concentrations of MTE in the different populations.

The concentrations of Zn, Pb, Fe, and Mn, in *H. cheirifolia*, are highly variable (Figure 4). Iron is very high in all stations with rates exceeding the standard value. The samples of Kharzet Youcef (pushing on the floor of the mine) and the Public discharge CET reveal a presence of high levels of Zn and Mn elements, far exceeding international standards.

Cd and Ag although their concentrations exceed the standard values, their concentrations in *H. cheirifolia* are low compared to the other elements like Sb, Cu, and Bi (Figure 5).

Hertia cheirifolia populations show very high differences in the concentrations of the MTE. To compare profiles with Elements trace metallic we considered each

MTE as a quantitative variable. The spatial three-dimensional projection of the 10 populations based on the three main axes from the PCA (Figure 6), shows that the populations of Kharzet Youcef, Unit ENPEC and Public discharge CET are distinctly separated, but the others populations studied are not clearly distinguished and their separation into homogeneous groups is less clear.

The UPGMA clusters analysis based on the linkage distance confirms the results of the PCA and separates *H. cheirifolia* populations in two distinct clades (Figure 7). These populations' clustration in small groups indicates differences in the MTE concentrations. The first cluster regroups Ain Oulmen and Kharzet Youcef populations, who are characterized by a high content of Fe, Zn, and Mn, these two stations are located near a Zinc mine.

The second cluster is composed of three subgroups: The unit of ENPEC and the Public discharge CET are characterized by a high level of Fe, Pb, Zn, Mn, Sb, and Bi. The second subgroup includes the populations of Ouled Sabor, Sidi Haidere, Industrial Zone, Elhamelette, Smara, and Mezloud; those populations are characterized by a high level of Fe, Zn, Sb, and Bi.

Discussion

The populations of *Hertia cheirifolia* analyzed showed variable MTE accumulation responses in the different stations. For most elements, studied concentrations are high, in particular for Fe, Zn, Mn, Pb, and Sb. These elements are, generally considered to be mainly of anthropogenic origin (Adimalla and Wang 2018; Djeddi et al. 2018; Adimalla et al. 2019; Saljnikov et al. 2019; Sun et al. 2019). The high sample contamination has many origins, including, the mining activity of Kharzet Youcef, Industrial Zone, Unit ENPEC (manufacture of Batteries), Technical landfill center, Sidi Haidere (Scrap depot) and the vehicle traffic, which can transmit this contamination to the food chain (Ben Ghaya et al. 2013).

Table 2. Accumulation of metallic trace elements by *Hertia cheirifolia*

Stations	Pb	Zn	Cu	Fe	Mn	Cd	Ag	Bi	Sb
Ouled Sabor	68	800	70	3800	230	7	8	71	170
El Hamelette	21	800	89	2700	200	6	6	60	120
Smara	90	700	100	2400	530	7	7	62	160
Sidi Haidere	45	900	150	3100	310	11	9	62	170
Public discharge CET	175	1800	124	3300	260	11	9	64	190
Industrial zone	71	800	92	3300	460	9	11	66	70
Unit ENPEC	1100	1000	111	2300	420	8	10	65	170
Mezloug	27	600	96	2700	580	6	10	50	150
Ain Oulmen	26	800	73	5400	380	5	8	52	100
Kharzet Youcef	44	1800	62	7000	300	15	10	37	90
Average	166.7	1000	96.7	3600	367	8.5	8.8	58.9	139
Min.	21	600	62	2300	200	5	6	37	70
Max.	1100	1800	150	7000	580	15	11	71	190
SD	331	434.6	26.6	1491.5	128.9	3.1	1.6	9.9	41
RSD	198.56	43.46	27.5	41.43	35.12	36.47	18.18	16.8	29.49
Standard value	1	50	10	150	200	0.05	0.2	0.06	0.1

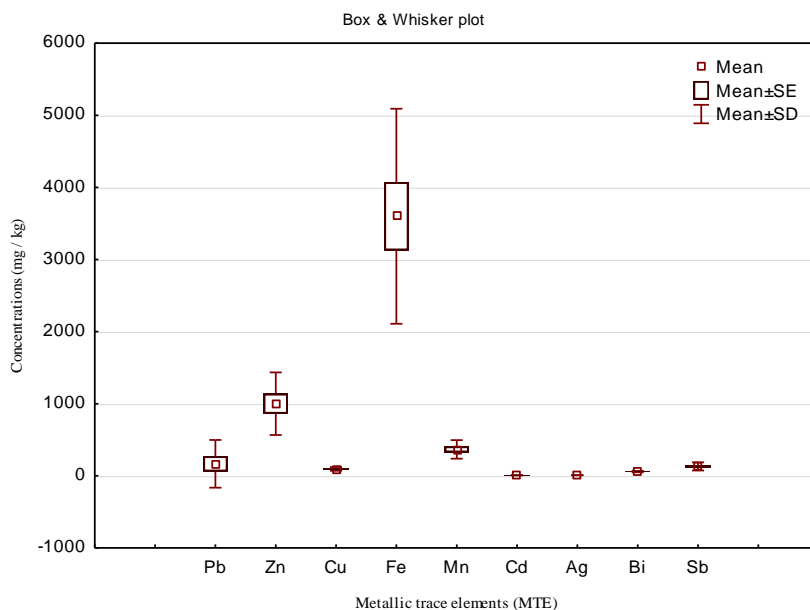


Figure 2. Variation in MTE concentrations in *Hertia cheirifolia*

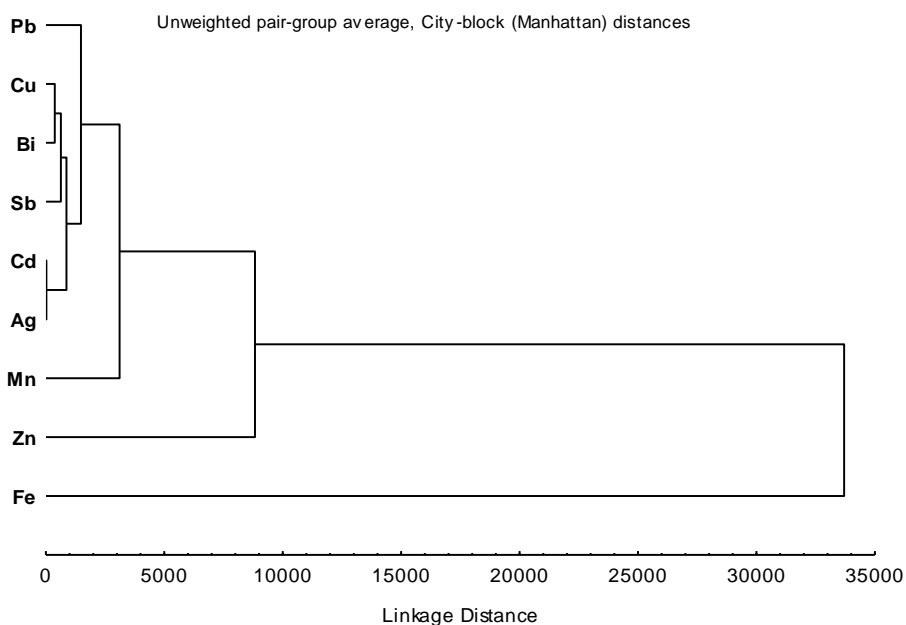


Figure 3. Correlation of concentration heavy metals in *Hertia cheirifolia*

The concentrations of Pb, Cu, Zn, Mn, Cd, and Fe are very high in most samples of *H. cheirifolia* and exceed the standards values, according to Cheng (2003) species with this characteristic can be used in bioindication to monitor soil and area contamination. *H. cheirifolia* can be used in the phytoextraction of MTE, based on the use of potential hyper-accumulation to extract the MTE from the soil and transfer them to the aerial parts (Kambhampati et al. 2003; Gardea-Torresdey et al. 2005; Mnasri et al. 2015).

The average Iron concentration exceeds the standard value in the *H. cheirifolia* plant; this high rate is due to the genetic and physiological capacity of the plant to accumulate this element. Fe is an element of the soil that undergoes significant bioaccumulation in plants that produce chelators (Marrassini et al. 2018). The high values for Zn and Pb in *H. cheirifolia* exceed certified standards. These concentrations are closely linked to emissions from heavy traffic (Francová et al. 2017; Bentum et al. 2018; Hassan 2018; Adimalla et al. 2019; Kumar et al. 2019).

The Unit ENPEC Station, which is well known by this electrochemical product and waste of heavy metals, recorded very high value of Pb, this element, can pollute the surrounding soil through releases and atmospheric deposits (Zhang et al. 2015; Dron et al. 2016). Similar studies were carried out in the mining regions, and the

same conclusions were issued (Wu et al. 2020). The concentrations of Zn, Fe, and Cd exceed regulatory levels in the region of Kharzet Youcef, which is associated with mining. Similar contamination has been reported in similar areas (Lograda et al. 2016; Drahota et al. 2018; Hesami et al. 2018).

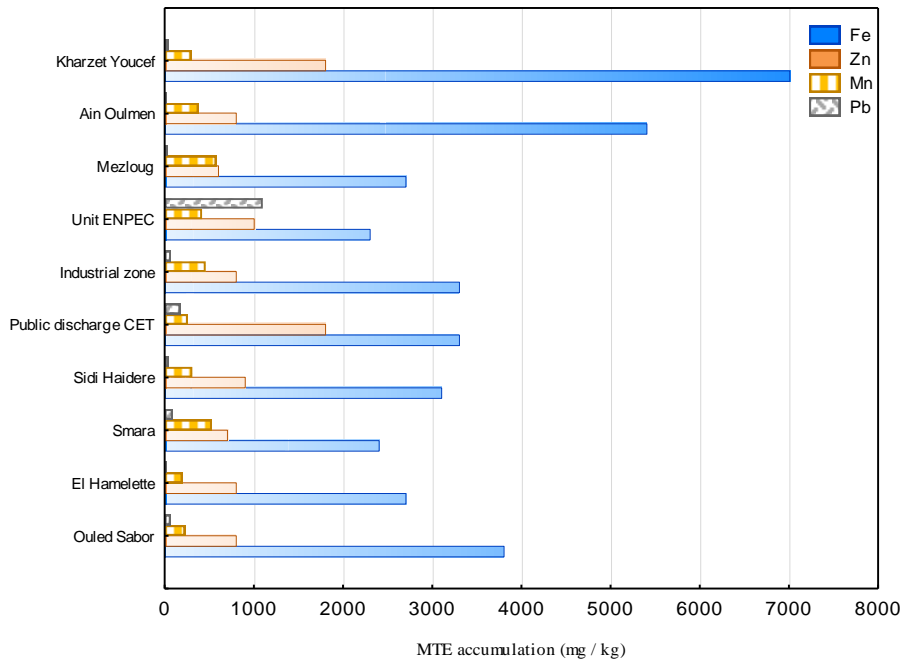


Figure 4. Concentration of Fe, Zn, Mn, and Pb in *Hertia cheirifolia*

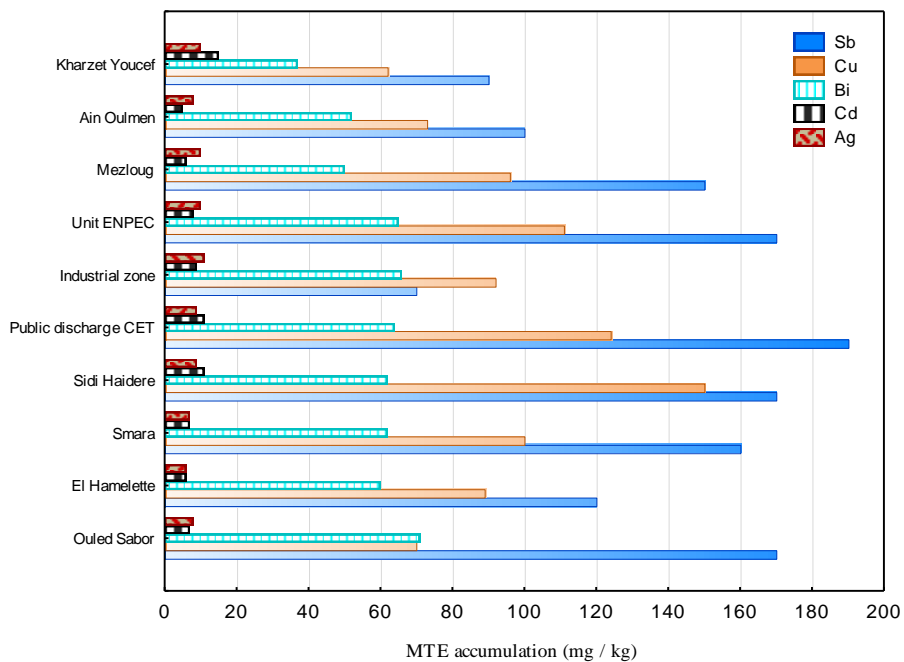


Figure 5. Concentration of Sb, Cu, Bi, Cd, and Ag in *Hertia cheirifolia*

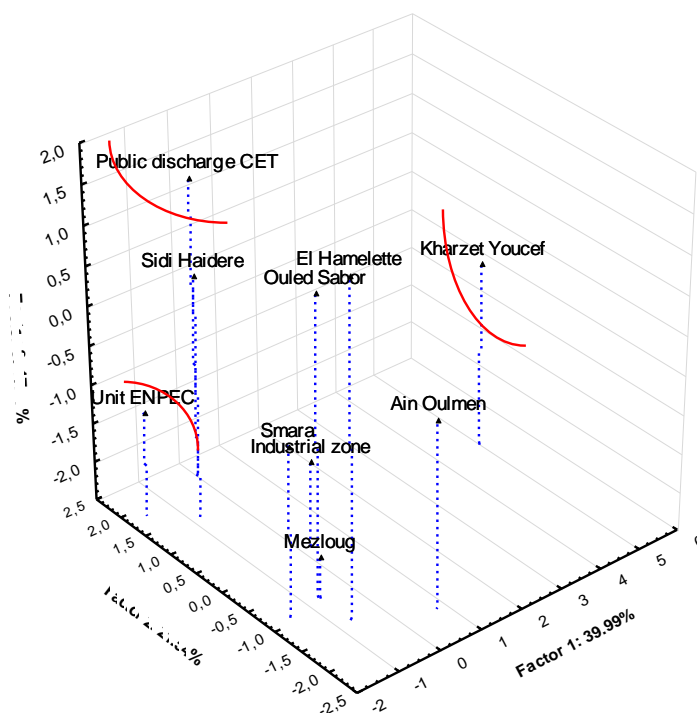


Figure 6. Three-dimensional spatial projection of *Hertia cheirifolia* populations

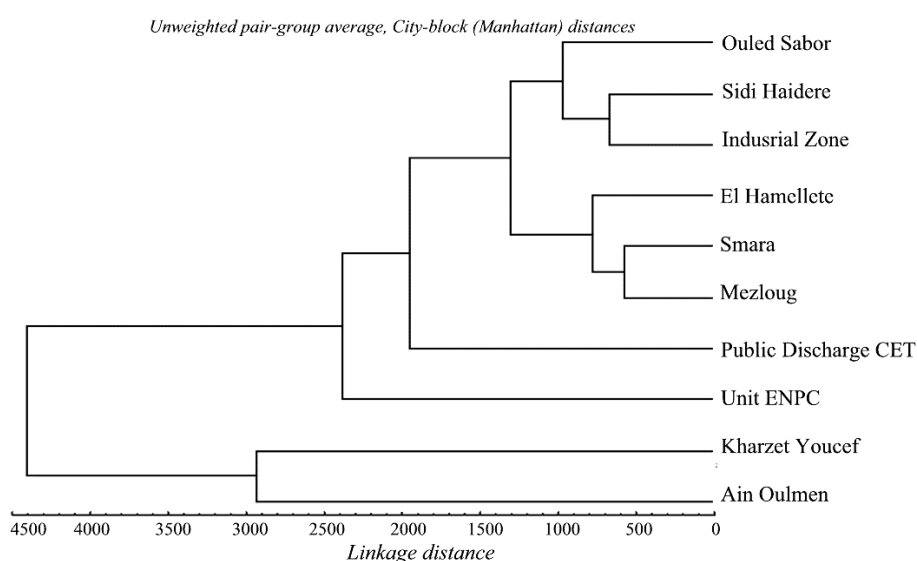


Figure 7. UPGMA, based on the concentration of heavy metals

The bismuth concentrations are very high, if we compare them with the Pb distribution rate, we notice similar values between the stations most contaminated by the two elements (Unit ENPEC, Public discharge CET and Industrial zone). Bi is often a sub-product of lead mining, so most industrial releases containing Pb imply the presence of traces of bismuth (Tighe et al. 2019). However, the highest concentration of Bi is recorded in the Ouled Saber station, this concentration is probably due to the agricultural activity that characterizes the region; the

application of fertilizers produces relatively high concentrations of Bismuth (Kabata-Pendias et al. 2007). The concentration of Sb is high in most of the stations studied; this is mainly due to road traffic, ash from the waste, which burns especially in summer (Bisson et al. 2007), industrial activity, and road traffic (Negral et al. 2020).

The high concentrations of MTE found in the uncontrolled open landfill site have several origins. The high levels of Zn, Sb, and Pb are the consequence of the

presence of leachate, which contains many mineral contaminants (Baziene et al. 2020). Authors made the same observations confirming that the leachate is highly polluted by MTE, with major contamination by Zn and Pb (Koné et al. 2007; Mehdi et al. 2007; Sangaré et al. 2016). A very significant accumulation of MTE was noted in the station of Sidi Haider (station that shelters an automobile breakage), this accumulation is the consequence of contamination by the products of decomposition of this waste materials. Several studies have reported this type of contamination of soil and vegetation by the deposition of particles from automobile wear (Lange et al. 2017; Zanello et al. 2018; Bernardino et al. 2019; Mihankhah et al. 2020).

The high Cu level in the Sidi Haider station of up to 150 mg/kg is due to the presence of this auto box; Several studies have proven the relationship between Cu levels and certain polluting sources (paint, brake pads, tires, and car wiring) (Winther and Slento 2010; Hsu et al. 2018; Barbosa et al. 2020).

Another fact that arises is that the plants having more accumulation properties can be used for removing the heavy metal toxicity in the roadside environment. Therefore, *H. cheirifolia* offers prospects of application of phytoremediation, and can be identified as tolerant to the presence of high concentrations of ETM, may be subject to further studies, particularly to effect elections of bio-accumulating populations.

In conclusion, this study gives evidence for the accumulation of Pb, Zn, Cu, Fe, Mn, Cd, Ag, Bi, and Sb in *H. cheirifolia* aerial parts sampled in the Setif area. It has shown that the sampled stations are heavily polluted by the presence of high levels of MTE. Overall, the results report that *H. cheirifolia* is good bioindicator and can be used in soil pollution-monitoring studies. The most frequent throughout the site, which offers prospects of application of phytoremediation. The results showed that both plants were able to uptake a considerable amount of MTE, indicating that *H. cheirifolia* has potential for elements phytoremediation.

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