Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2018, 10(3): 1-8
(http://www.derpharmachemica.com/archive.html)

Bio-monitoring of Metal Trace Elements by Epiphytic Lichen in the Bordj Bou Arreridj Area, East of Algeria

Fatima Adjiri[1], Messaoud Ramdani[1*], Takia lograda[1], Pierre Chalard[2]

[1]Laboratory of Natural Resource Valorisation, SNV Faculty, Setif 1 University, 19000 Setif, Algeria
[2]SIGMA Clermont, Campus des Cezeaux, CS 20265, 63178 Aubière cedex, France

ABSTRACT

The objective of this study is to use a bio-sensor in order to assess environmental by metal trace elements (MTE) contamination in the Bourdj Bou Arreridj region, East of Algeria. The sampling of biological material from 32 locations was performed using a natural bioaccumulators represented by a lichenic species; Xanthoria parietina. Samples were taken and ten heavy metals (Fe, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb and Zn) were selected for analysis. The metal content recorded in various sampled sites were found greatly fluctuating and exceeded standard values with the exception of Pb at the Kseur and Ghilassa locations. The level of Fe was very high in all sampled locations with an average of (43184.4 ± 16373.7 mg/kg). This important accumulation of MTE in thalli was correlated to road and rail traffic as well as to industrial activities. These results show the tolerance of X. parietina to metallic stresses and therefore its effectiveness as a bio-sensor in the bio-monitoring programs assessing air quality.

Keywords: Metal trace elements, Bio-monitoring, Bio-accumulation, *Xanthoria parietina*, Bourdj Bou Arreridj, Algeria

INTRODUCTION

The level of urban air pollution is due to the intensive development of industry, road traffic, population density and urbanization, leading to the degradation of air quality [1,2]. Bio-monitoring of air quality is the use of responses, at all levels, of biological organisms to predict and reveal environmental alterations and to follow its evolution [3]. Bio-monitoring is a very effective operational tool [2,4-6]. It is a complementary method to the physico-chemical analyzes and highlights the impregnation of the environment by the Metallic Trace Elements (MTE) [7].

The MTE, known as heavy metals or toxic metals, are widely reputed pollutants emitted into the atmosphere by a large number of natural and anthropogenic sources [8-10]. Epiphytic cryptogams are gaining increasing importance in environmental bio-monitoring because they can absorb and accumulate elements in their systems [11,12].

Bio-indication studies involving lichens provide much information on the qualitative status of the environment and are useful for assessing the long-term effects of bio-monitoring programs [2]. Lichens are among the most commonly used cryptogamic organisms in the bio-monitoring of MTEs in air [2,13,14]. Foliaceous lichens are highly tolerant to metal trace elements and reflect the history of the environment [11,12,15]. *Xanthoria parietina* is the most widely used lichen in bio-monitoring studies [2,13,16-19].

The aim of this study is to assess MTE environmental contamination by drawing up a map of the distribution of pollution in the 32 municipalities of the Bordj Bou Arreridj province (BBA), East of Algeria, using the lichen *X. parietina.*

MATERIALS AND METHODS

Sample collection

The foliaceous lichen *X. parietina*, widespread in the studied areas and widely used in similar studies in several countries, has been selected as a bio-accumulator [16]. Samples were collected in 34 locations spread throughout the BBA province (Figure 1).

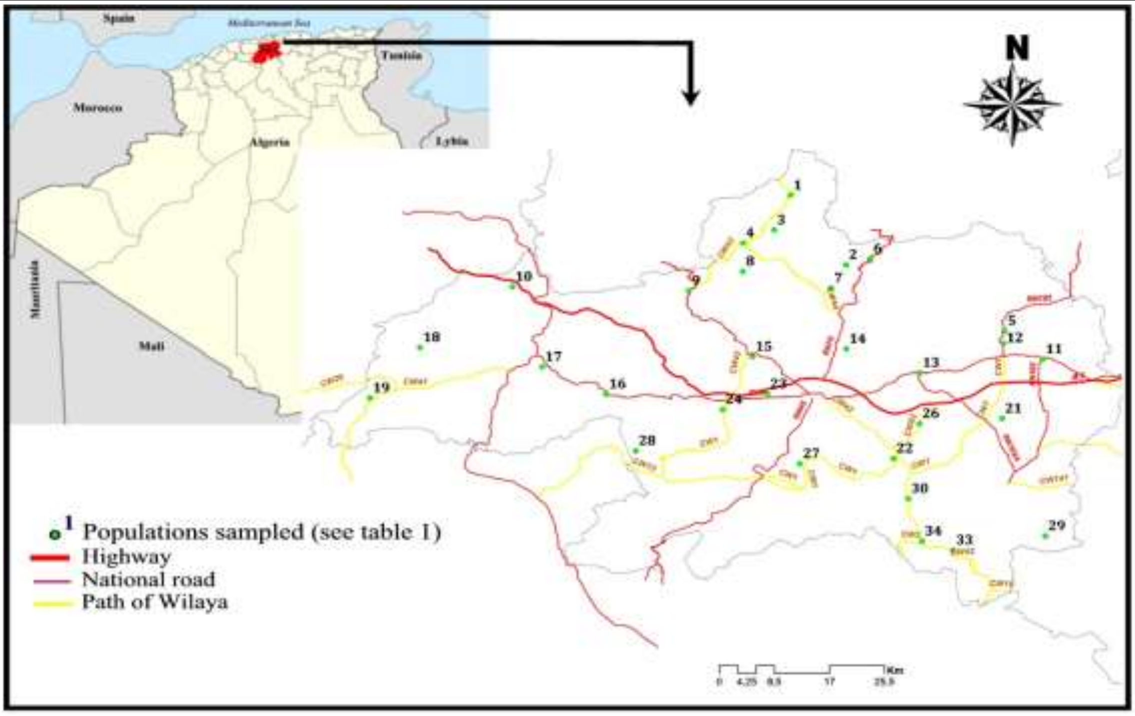

Figure 1: Sampled populations of *Xanthoria parietina*

Samples were collected avoiding the usage of tools or containers which may contaminate them (We avoided steel tools or stainless steel containers whose walls contain pigments based on trace elements such as PVC). Each sampled site consists of an area of a maximum 100 m^2, located near high traffic roads and secondary roads. The geographical coordinates of each sampled area were noted using a GPS (Table 1). The BBA province is characterized by a semi-arid continental climate, with hot dry summers and severe winters. Rainfall is inadequate and irregular both in time and space.

Samples treatment

Lichen samples were digested in the laboratory in aseptic conditions, using a mixture of $HNO_3/HF/H_2O$ in Teflon containers [20,21]. A solution of our samples is prepared using the grinded solid material to which 10 ml of 40% Hydrofluoric Acid (HF) and 3 ml of 70% Perchloric Acid ($HClO_4$) were added. Evaporation takes place on a hotplate at 160°C. After a quasi-total evaporation, 1 ml of 65% Nitric Acid (HNO_3) and 10 ml of distilled water were added. The samples are then left for 30 min at 4°C in the refrigerator.

The dissolution of the residue is performed by placing the samples on a hotplate at 60°C for 1 h. The resulting mixture is transferred to a 100 ml flask for filtration, adjusting the volume with distilled water.

Table 1: Geographic coordinates of the sampled areas

Code	Locations	Latitude North (N)	Longitude East (E)	Altitude (m)
1	El Main	36° 21' 59.907"	4° 43' 56.866"	983
2	Tassameurt	36° 15' 52.732"	4° 48' 11.329"	629
3	Tefreg	36° 18' 39.333"	4° 42' 30.243"	1131
4	Djaafra	36° 17' 33.561"	4° 39 42.894"	1335
5	Khelil	36° 10' 1.578"	5° 1' 25.946"	964
6	Bordj Zemoura	36° 15' 59.677"	4° 50' 21.156"	913
7	Ouled Dahmane	36° 13' 41.188"	4° 46' 50.138"	1250
8	Colla	36° 15' 32.299"	4° 39 43.326"	1250
9	Teniet En Nasr	36° 13' 34.759"	4° 35 21.930"	1250
10	Ouled Sidi Brahim	36° 13' 52.071"	4° 20 31.498"	580
11	Ain-Taghrout	36° 7' 31.180"	5° 4' 44.572"	907
12	Bir Kasdali	36° 9' 0.853"	5° 1' 16.698"	955
13	Sidi Embarek	36° 6' 13.896"	4° 54' 29.289"	1011
14	Hasnaoua	36° 8' 17.610"	4° 48' 13.622"	993
15	Medjana	36° 7' 55.621"	4° 40' 20.503"	1052
16	Mansoura	36° 4' 16.060"	4° 28 21.561"	807
17	El M'hir	36° 6' 57.042"	4° 23 2.713"	557
18	Haraza	36° 8' 20.085"	4° 12 52.610"	1201
19	Ben Daoud	36° 3' 59.274"	4° 8' 42.662"	1050
20	Tixter	36° 2' 49.300"	5° 5' 8.592"	947
21	Aïn Tesra	36° 2' 17.28"	5° 0' 75.81"	1039
22	El Ansseur	36° 1' 47.470"	4° 53' 80.124"	980
23	Bordj Bou Arreridj	36° 4' 22.548"	4° 41' 31.452"	901
24	El Achir	36°3' 10.771"	4° 37' 54.631"	967
25	Ras El Oued	35° 56' 58.912"	5° 2' 2.774"	1078
26	Belimour	35° 58' 40.738"	4° 52' 25.165"	937

27	El Hamadia	35° 58' 24.081"	4° 44' 29.356"	819
28	Ksour	36°59' 29.014"	4°30' 39.281"	1250
29	Ouled Brahem	35° 51' 53.737"	5° 4' 55.452"	1259
30	Bordj Ghédir	35° 55' 8.500"	4° 53' 22.47"	1387
31	Taglait	35° 50' 35.347"	4° 57' 10.404"	1434
32	Ghilassa	35° 51' 35.031"	4° 54' 39.110"	1171

Analytical methods for ETM concentration measurements in lichens

The concentrations of the following elements; Fe, Cd, Co, Cu, Cr, Mn, Ni, Pb, Sb and Zn, were determined by Atomic Absorption Spectro-photometry with Flame (AASF). There are no established standards of trace elements concentration in lichens [22]. To interpret the results of each element studied we used as a standard reference, values of the European Commission BCR information CRM-482 (Table 2) [23].

Table 2: Certified CRM-482 values of trace elements (mg/kg) using AASF

MTE	Symbols	Certified values	Uncertainty
Lead	Pb	40.9	1.40
Copper	Cu	7.03	0.19
Cadmium	Cd	0.56	0.02
Zinc	Zn	100.6	2.20
Nickel	Ni	2.47	0.07
Chrome	Cr	4.12	0.15
Cobalt	Co	0.32	0.03
Iron	Fe	804	160
Manganese	Mn	33.0	0.50
Antimony	Sb	0.35	0.09

Statistical analysis

Data were first subjected to Principal Components Analysis (PCA) to examine the relationship among the trace elements and the bio-accumulation by lichens, and also the relation between the presence of these elements and the pollution. Cluster analysis (UPGMA) was carried out on the original variables and on the Manhattan Distance Matrix to look for hierarchical associations among the elements and the locations. Statistical analyses were carried out using STATISTICA 10 software.

RESULTS

The concentrations of metal elements (Fe, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb and Zn) accumulated in the *X. parietina* were determined by Atomic Absorption Spectro-photometry with Flame (Table 3).

Table 3: ETM concentrations in *Xanthoria parietina* (mg/kg dry weight)

Stations		Pb	Mn	Fe	Cu	Sb	Cd	Co	Zn	Ni	Cr
1	El Main	110	800	65900	78	158	3	638.04	611.37	99.93	380.95
2	Tassameurt	120	1300	68500	80	194	3	658.15	348.55	77.16	321.09
3	Tefreg	96	800	46400	56	203	4	605.36	376.47	101.32	376.87
4	Djaafra	89	1300	72800	63	187	3	692.5	614.25	93.89	406.8
5	Khelil	133	500	36600	35	219	3	347.3	437.36	3.72	202.72
6	Bordj Zemoura	105	400	29000	51	163	3	416.84	323.88	42.3	274.83
7	Ouled Dahmane	111	400	45100	36	253	4	668.2	484.19	52.99	334.69
8	Colla	60	700	32900	33	185	3	674.91	433.4	98.07	387.76
9	Teniet En Nasr	81	500	47800	55	145	2	673.23	482.75	95.75	406.8
10	Ouled Sidi Brahim	110	1300	71400	68	167	3	714.29	514.28	105.51	395.92
11	Aïn Taghrout	206	500	40700	28	212	5	254.29	916.87	30.68	127.89
12	Bir Kasdali	114	300	36000	36	210	4	389.19	372.87	26.96	201.36
13	Sidi Embarek	115	1300	73000	67	162	3	579.39	497.7	46.01	293.88
14	Hasnaoua	136	800	48900	65	238	3	527.44	408.72	90.17	359.18
15	Medjana	173	700	46400	87	226	4	600.34	429.97	95.28	390.48
16	Mansoura	90	600	43800	52	183	3	581.06	469.96	123.63	434.01
17	El M'hir	96	500	46000	67	178	3	811.48	438.8	100.4	472.11
18	Haraza	93	400	50200	66	170	3	772.1	360.8	118.52	443.54

19	Ben Daoud	71	900	58000	33	186	3	814.83	570.66	133.4	428.57
20	Tixter	169	400	32800	24	243	5	283.62	983.52	16.27	144.22
21	Aïn Tesra	86	400	30100	43	164	3	434.44	471.04	7.44	229.93
22	El Ansseur	99	1100	63200	76	190	3	488.06	539.67	43.69	292.52
23	Bordj Bou Arreridj	68	400	17000	23	93	3	601.17	549.4	38.58	303.4
24	El Achir	120	600	40800	39	194	3	711.77	390.34	107.83	378.23
25	Ras El Oued	93	400	29500	23	175	4	297.86	431.96	3.3	161.9
26	Belimour	66	500	23500	38	182	3	633.01	347.65	54.38	303.4
27	El Hamadia	58	900	42100	37	174	3	572.69	480.41	88.31	348.3
28	Ksour	6	900	24200	27	226	3	591.12	451.23	95.75	386.39
29	Ouled Brahem	95	700	45100	51	190	3	380.81	364.77	4.65	165.99
30	Bordj Ghédir	91	500	37100	62	233	3	457.06	364.77	32.07	227.21
31	Taglait	67	400	30100	23	171	3	426.06	406.92	19.99	239.46
32	Ghilassa	23	300	7000	72	102	3	510.68	377.56	30.68	209.52
Average		98,4	671.9	43184.4	49.8	186.8	3.3	556.5	476.6	65	313.4
SD		39,5	312.4	16373.7	19.3	35.7	0.6	152.6	145.9	40.3	97.3
CV%		40,1	46,5	37,9	38,8	19,1	18,2	27,4	30,6	62,0	31,1
Min		6	300	7000	23	93	2	254.3	323.9	3.3	127.9
Max		206	1300	73000	87	253	5	814.8	983.52	133.4	472.1
Certified standard		40.9	33	804	7.03	0.35	0.6	0.32	100.6	2.47	4.12

The MTE concentrations in the 32 sampled sites are found highly variable. It is noted that the (Fe) concentrations are too high in the thalli. The high Fe rate hid the variability of the rest of the elements in the analysis (Figure 2a), this element was removed and a second analysis was performed to reveal the variability of the MTE in *X. parietina* (Figure 2b).

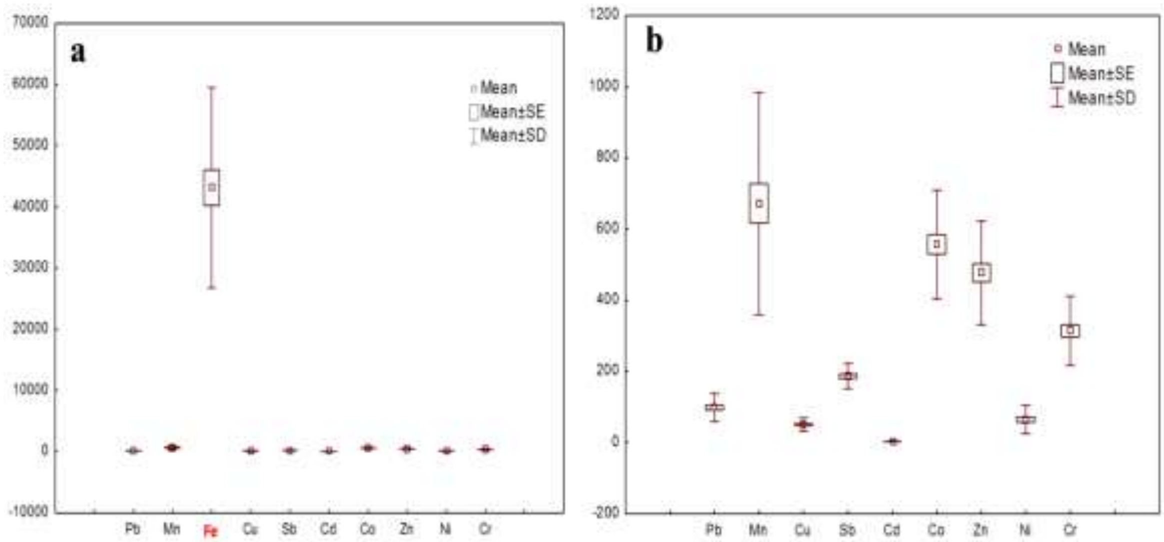

Figure 2: Variability of MTE concentrations in *X. parietina* thalli

The Fe element exhibits the highest mean concentration in *X. parietina* samples with (43184.4 ± 16373.7 mg/kg), while Cd is the least abundant in the thalli (3.3 ± 0.6 mg/kg). The metals concentrations analyzed are distributed in the following order: Fe > Mn > Co > Zn > Cr > Sb > Pb > Ni > Cu > Cd. Fe showed the greatest variation followed by Mn (671.9 ± 312.4 mg/kg). Concentration levels of Co, Zn and Cr are relatively close and exceed standard values. The mean concentrations of Sb and Pb found in rural and urban communes are relatively similar (186.8 ± 35.7 mg/kg) and (98.4 ± 39.5 mg/kg), while concentrations of Ni and Cu are the lowest in order of appearance after the Cd.

The three-dimensional spatial projection of the stations, based on the first three axes resulting from the ACP, shows the separation of populations into two more-or-less distinct groups, thus isolating three Ghilassa, Ain Taghroute and Tixter areas (Figure 3). The concentrations of ETMs found in the thalli at Ain Taghrout and Tixter are high and similar, especially Cd and Zn, exceeding standard values. On the other hand, at the Ghilassa station, the thalli accumulate low concentrations of MTE, while the Pb concentration is below the standard values (40.6 mg/kg).

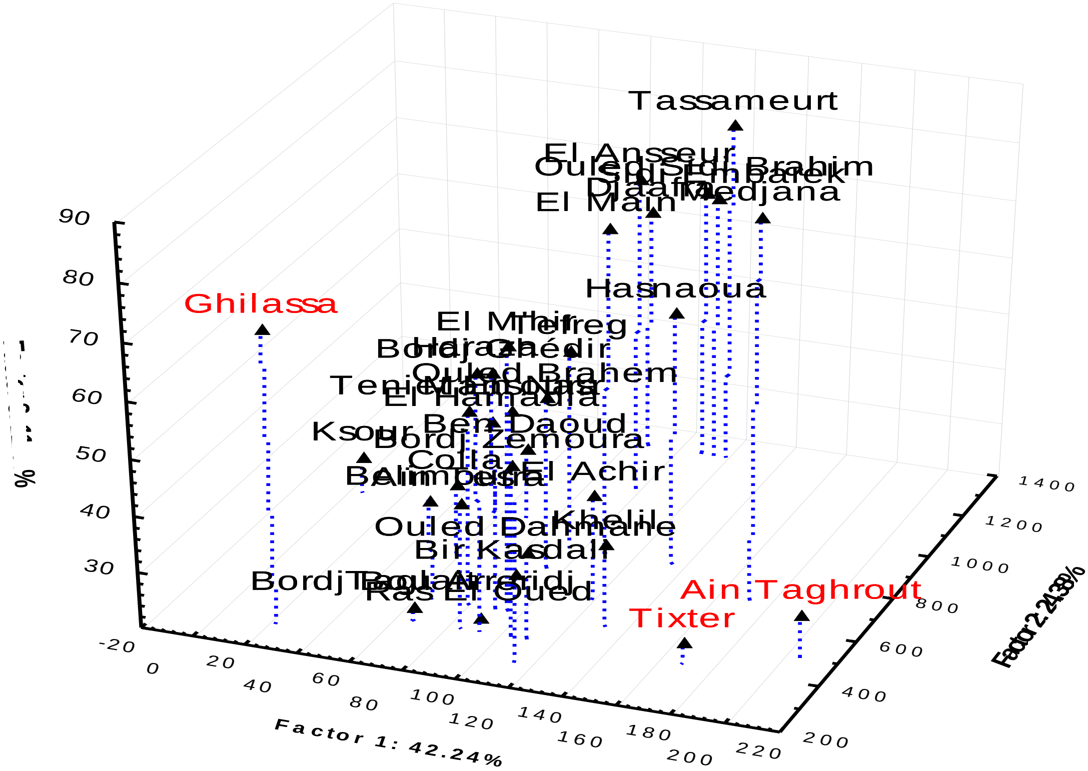

Figure 3: Spatial projection of stations based on the first three axes from the ACP

The use of UPGMA, a statistical method based on the un-weighted pair average and the distance from city-block (Manhattan), reflects heterogeneity in metal accumulation in *X. parietina* thalli and confirms disaggregation of the studied sites into several clades (Figure 4).

The first group is represented by the station of Ghilassa with a low ETM accumulation in the thalli, while the second group splits into two branches; The Sidi Embarek, Djaafra, Ouled Sidi Brahim, Tassameurt, El Anasseur, El Main and Ben Daoud stations with a very high Fe accumulation, exceeding standard values (804 mg/kg). The remaining sites form an amalgam representing the same groups as those coming from the ACP. Sites with high concentrations of Pb and Zn in the thalli are located close to high traffic road axes such as Ain Taghrout and Tixter and then decrease in low traffic stations.

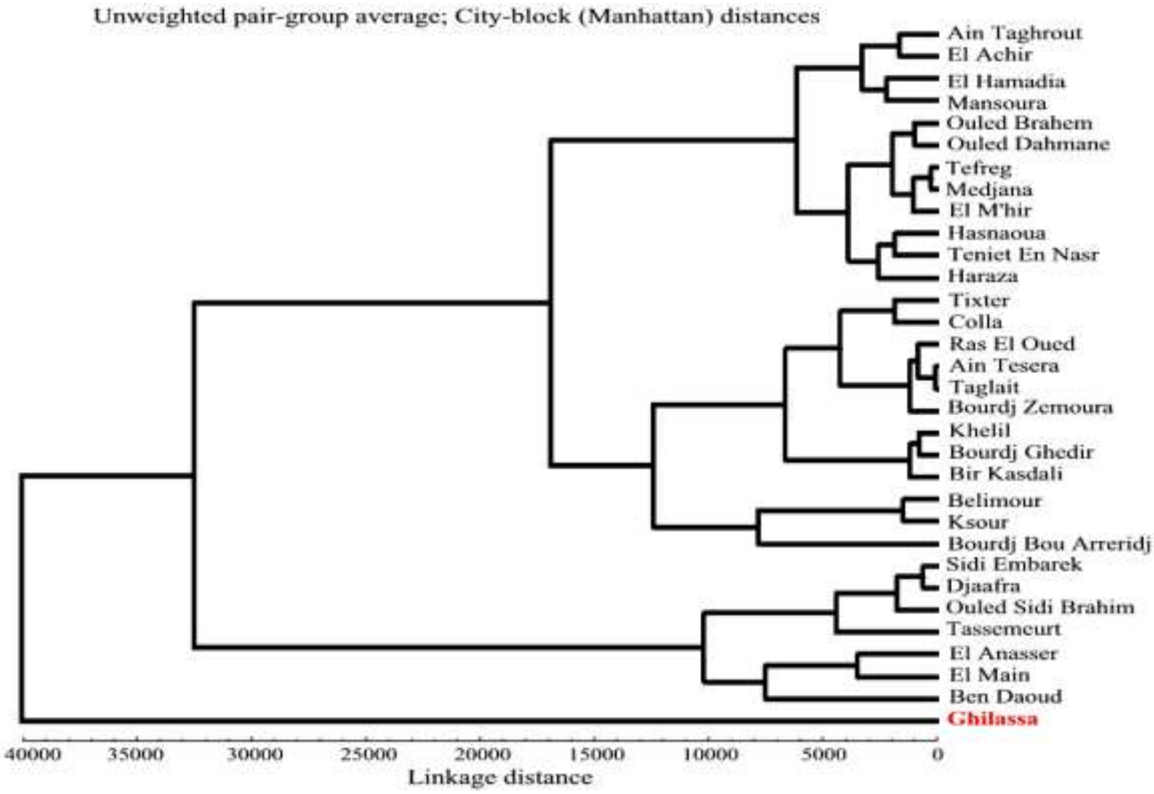

Figure 4: UPGMA based on the concentration of heavy metals

DISCUSSION

Assessment of levels of contamination in the BBA province for ten different metals showed Pb contamination values similar to those previously found in lichen thalli *X. parietina* in Italy [16], France [8,24], Turkey [25], and Poland [10]. Generally, high concentrations of Pb measured in thalli near roads are closely related to vehicle emissions and fuel combustion [18,25-32]. In addition, in the studied areas the observed high concentrations of Pb may be related to the increase in industrial activities [8-9,32], and the incineration of waste [24].

A low Pb accumulation in the southern mountainous sites (Kseur and Ghilassa) was observed with values between (6 and 23 mg/kg). However the concentration of Pb in northern mountainous sites was high due to a higher air humidity level as suggested by some authors [14,33].

The values of Zn in the thalli of *X. parietina* exceeded standard values. These high rates are due to traffic [18,29] and industrial activities [25,34]. The same Zn concentrations were observed in France [8,9,24] and Turkey [25]; In contrast, low concentrations were found in Italy [16], Turkey [29] and Poland [10].

Cd concentrations are high in thalli and similar to the results observed in France [8,9,24], Turkey [25] and in Algeria [35]. Road traffic and anthropogenic activities [25,36] contribute to the increase in Cd concentrations in the thalli of *X. parietina* [18,29,37]. The concentrations below standard values were observed in Italy [16] and Morocco [37].

The levels of Sb concentrations measured in the thalli of *X. parietina* are above standard values, whereas earlier studies in France [9,31] and Spain [38] showed that Sb concentrations in the thalli are below standard values (0.35 mg/kg). According to the authors of these studies, high Sb levels were attributed mainly to road traffic, waste incineration and the production of batteries [9,39]. Sb contamination spreads to rural areas where the maximum concentration is recorded in Ouled-Dahmane (253 mg/kg), and this high rate comes probably from sources outside the studied area, as reported by [31].

The levels of iron (Fe) in lichenic thalli are very high. The results obtained are similar to those recorded in other countries such as France [24], Turkey [25], and Poland [10]. On the other hand, the concentrations recorded in Portugal by [40] are lower than the standard values. The high rate of Fe in the studied sites has been linked to geographical factors [10,13,25,37]. The other explanation for the high level of Fe in the thalli is the accumulation of dust from anthropological activities [15,25,32,37,39,40-42].

The results of the Cu analysis show that the levels accumulated in the thalli are high and exceed standard values. The same remarks were observed in *X. parietina,* in France [9,24] and in Poland [10]. The highest Cu contamination was observed especially in rural communities, while the lowest contamination levels were observed in high industrial stations. The high level of Cu in rural communes is probably due to the usage of pesticides and fertilizers that can be sources of copper emission [2,9,16,25]. The presence of Cu in the thalli sampled in urban sites is due to road and rail traffic, as well as to metallurgical activity [9,10].

The concentrations of Mn recorded in the thalli of *X. parietina* are almost identical to those reported in France [9,24] and Turkey [25]. Approximately 50% of Mn in the air is of natural origin [10,24,37] and to this natural source can be added an anthropic source such as the usage of fertilizers due to agricultural activities [39].

Ni levels are high and there is a gradient of concentration of this element from west to east. The same observations are cited in literature in Italy [16], Turkey [25], France [9,24] and Poland [10]. Nickel pollution is linked to emissions from the metallurgical industry and combustion processes [10,18].

Chromium concentrations in the studied areas are above standard values (4.12 mg/kg) and the same results were observed in other regions such as France [9] and Italy [18,43].

The highest accumulation of Cr was observed in western sites; which then drops in eastern sites with a minimal concentration recorded at Ain Taghrout (127.89 mg/kg). Vehicle emissions and industrial activities can be important sources of air pollution by Ni and Cr [38].

High concentrations of Co in the thalli of *X. parietina* were observed at all studied locations. Dust from quarrying and building materials can be the main reason for these high concentrations [31] however, the metal industry may be an important source of cobalt [25] as lichenic thalli may accumulate more atmospheric elements when exposed for longer periods of time [29,33].

The classification of the elements by cluster analysis revealed two main clusters of elements with similar affinities or characteristics (Figure 5). Cluster 1, included Pb, Cd, Zn and Sb, three out of the four elements of this group (Pb, Cd and Sb) showed constant or decreased alteration loads in the present study, while Zn showed a high percentage contamination it the studied areas.

A relationship between Cd and Zn is rather common in lichens [16,44-45]. It may be due to anthropogenic sources or metabolic interactions, since these two elements are essential for lichen metabolism [46]. The correlation between Pb and Zn indicates some affinity with atmospheric particles [31,47].

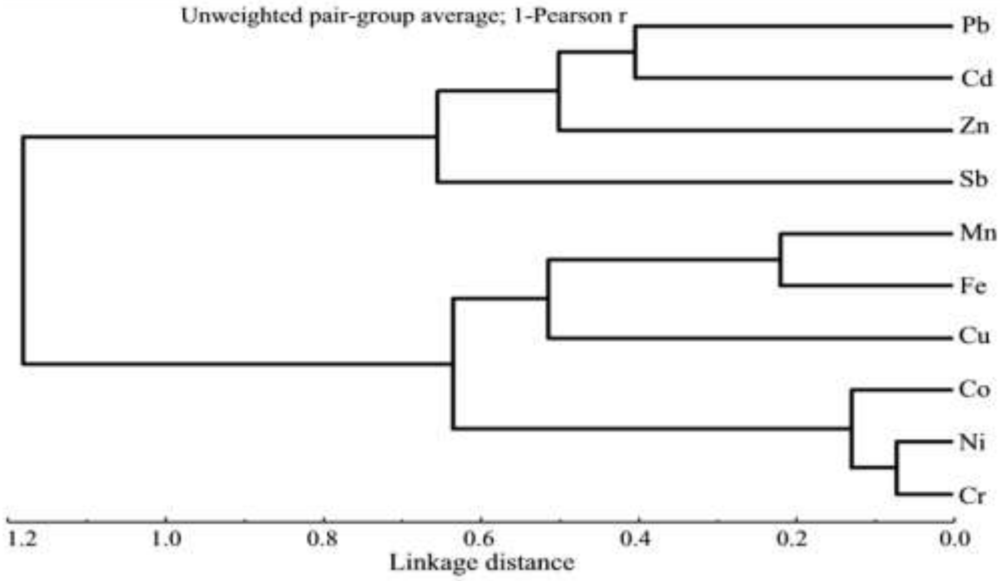

Figure 5: Cluster dendrogram of the elements in *X. parietina*

A common feature between Cd and Zn, including the fact that they accumulate in lichen cells [48] and plant emissions are the results of indirect sources of Cd and Zn [25,29]. According to [18], the found concentrations of Zn, Pb and Cd in sites which are far from sources of pollution are related to the usage of fertilizers and pesticides that are characteristic of the region.

Zn is generally related to the association of Pb and Cd elements. This phenomenon is ubiquitous in nature and its distribution in the atmosphere does not locate the source of the contamination [18]. More than 2% of Zn derives from vehicular traffic and of road dust; it is a component found in leaded and lead-free gasoline [10,37,49], confirming the significant accumulation of Zinc in thalli of lichen collected near the roads of the BBA region. 95% of Pb in plants is of atmospheric origin [10] and combustion of fuels remains the main sources of this toxic element in the environment even in mountainous areas [30].

The Sb is an element highly related to Pb in several industrial uses, because it increases the hardness of this element [9,18]. The high coupling of Cd, Zn and Pb and their correlation with Sb also indicate their common sources in traffic activities along road axes [25]. These elements appear in vehicle components and lubricants [39], confirming that the contamination of the BBA region by these elements is of anthropogenic source.

The cluster 2 included Mn, Fe, Cu, Co, Ni and Cr, these relationships are in line with the results of other similar studies [16,50]. All these elements substantially accumulate by particulate entrapment [32,33,51]. Further, the relationship of the two terrigenous macro-elements (Mn and Fe) with Ni and Cr confirmed the presence of anthropogenic influence on their distribution in lichen material. This suggested that trapped soil particulate in lichen thalli was a highly variable contribution which did not closely reflect the element concentrations in the atmosphere, but depended rather on environmental sources [15,51].

CONCLUSION

The results of the present survey showed that the mean concentration of all ten elements in *X. parietina* thalli, with the exception of Cd, are included between middle to high naturality classes. Multivariate analyses allowed us to find the main correlations among the groups of element taken into account in the present study. The changes in the concentrations of the MTE, contained in the thalli, can provide useful information on the long-term assessment of air pollution and to monitor the progress of the contamination phenomenon in the time. It is important to focus on the possibility of monitoring a large study area completely lacking an instrumental network for detecting this kind of anthropogenic impact. This confirms that lichen bio-monitoring can be useful in risk assessment for human health and it can be a powerful tool for administrators involved in environmental planning.

REFERENCES

[1] P. Pinho, A. Bergamini, P. Carvalho, C. Branquinho, S. Stofer, C. Scheidegger, C. Mâgiias, *Ecological Indicators*., **2012**, 15, 36-42.
[2] A. Parzych, A. Zduńczyk, A. Astel, *J. Elementol*., **2016**, 21(3), 781-795.
[3] J.P. Garrec, C.H. Van-Haluwyn, Plant Bio surveillance of Air Quality, Concepts, Methods and Applications, Paris, Editions Tec et doc, Lavoisier, **2002**, 118..
[4] M.A. Rzepka, D. Cuny, *Air Pur*., **2008**, 75, 66-79.
[5] C.H. Van-Haluwyn. *Air Pur*., **2009**, 77, 5-10.
[6] C.H. Van-Haluwyn, D. Cuny, J.P. Garrec, *Pollution Atmosphérique*., **2011**, 7-12.
[7] D. Cuny, M.A. Rzepka, C. Van Halwyn, *Spectra Analyse*., **2008**, 264, 31-35.
[8] D. Cuny, S. Quarre, I. Devred, B. Jeanne, A. Reynaert, M.A. Rzepka, M.A. Cuny, *Air Pur*., **2009**, 77, 43-49.
[9] F. Occelli, M.A. Cuny, I. Devred, A. Deram, S. Quarré, D. Cuny, *Pollution Atmosphérique.*, **2013**, 220, 1-10.
[10] A. Parzych,, A. Astel, A. Zdunczyk, T. Surowiec, *J. Environ. Sci. Health*., **2016**, 51(4), 297-308.
[11] L. Paoli, A. Corsini, V. Bigagli, J. Vannini, C. Bruscoli, S. Loppi, *Environ. Pollution.*, **2012**, 161, 70-75.
[12] C.D. Ezeonyejiaku, M.O. Obiakor, *Am. J. Life Sci. Res*., **2013**, 1(2), 67-73.
[13] P.L. Nimis, S. Andreussi, E. Pittao, *Sci. Total Environ*., **2001**, 275, 43-51.
[14] S. Kar, A.C. Samal, J.P. Maity, S.C. Santra, *Int. J. Environ. Sci. Technol*., **2014**, 11, 899-908.
[15] C. Branquinho, F. Catarino, D.H. Brown, School of Biological Sciences, University of Bristol, United Kingdom, Portugal, **1997**, 5-16.

[16] P.L. Nimis, G. Lazzarin, A. Lazzarin, N. Skert *Sci. Total Environ.*, **2000**, 255, 97-111.
[17] P.L. Nimis, Ch. Scheidegger, P.A. Wolsely, *Earth Environ. Sci*., **2002**, 7, 408.
[18] R. Scerbo, T. Ristori, L. Possenti, L. Lampuganini, R. Barale, C. Barghgiani, *Sci. Total Environ*., **2002**, 286, 27-40.
[19] C.H. Douibi, M. Ramdani, A. Khelfi, R. Benharket, T. Lograda, P. Chalard, *Unified J Environmental Sci and Toxicology*., **2015**, 1(1), 1-13.
[20] A.M. Rusu, In: P.L. Nimis, C.H. Scheidegger, P.A. Wolsely (Ed.), Sample Preparation of Lichens for Elemental Analysis: Monitoring with Lichens-Monitoring Lichens, Nato Science Series, Vol. 7, Springer, Netherlands, **2002**, 305-309.
[21] C.N. Picardie, Comparison of methods of analysis of metallic trace elements (ETM) and Polycyclic Aromatic Hydrocarbons (PAH) on soils and plants, Lyon, France, **2004**, 120.
[22] M. Bettinelli, S. Spezia, G. Bizzarri, *Atomic Spectroscopy*., **1996**, 17(3), 133-141.
[23] P.H. Quevauviller, R. Herzig, H. Muntau, *Sci. Total Environ*., **1996**, 187(2), 143-152.
[24] J. Dron, A. Austruy, Y. Agnan, P. Giraudeau, P. Chamaret, *Pollution Atmosphérique*., **2016**, 228, 1-14.
[25] A.D. Demiray, I. Yolcubal, N.H. Akyol, G. Çobanğlu, *Ecological Indicators.*, **2012**, 18, 632-643.
[26] M. Rahali, *Pollution Atmosphérique*., **2002**, 175, 421-432.
[27] S. Loppi, L. Frati, L. Paoli, V. Bigagli, C. Rossetti, C. Bruscoli, A. Corsini, *Sci. Total Environ.*, **2004**, 326, 113-122.
[28] B.A. Maher, C. Moore, J. Matzka, *Atmospheric Environment*., **2008**, 42, 364-373.
[29] K. Kinalioglu, T.B. Ozbucak, H.G. Kutbay, R. Huseyinova, A. Bilgin, A. Demirayak, *Ekoloji*., **2010**, 19(75), 64-70.
[30] M. Maatoug, K. Medkour, M. Ait-Hammou, N. Ayad, *Pollution Atmosphérique.*, **2010**, 205, 93-101.
[31] A. Agnan, N. Séjalon-Delmas, A. Probst, *Environ. Pollution*., **2013**, 172, 139-148.
[32] A. Francovà, V. Chrastný, H. Sillerovà, M. Vitkovà, J. Kocourkovà, M. Komàrek, *Environ. Pollution*, **2017**, 220, 286-297.
[33] B. Klimek, A. Tarasek, J. Hajduk, *Bull Environ. Contam. Toxicol*., **2015**, 94, 532-536.
[34] Y.P. Lin, T.K. Chang, C.W. Chiung-Wen Shih, C.H. Tseng, *Environ. Geol.*, **2002**, 42, 900-909.
[35] M. Sarmoum, R. Djebbar, K. Latreche, *Rev. Ecol. Environ.*, **2014**, 10, 25-29.
[36] F.Z. Ouali-Alami, A. Elabidi, L. Mouhir, M. Fekhaoui, A. Serghini, *Afrique Science.*, **2014**, 10(3), 89-106.
[37] A. Aslan, A. Cicek, K. Yazici, Y. Karagoz, M. Turan, F. Akkus, O.S. Yildirim, *African J. Agric. Res.*, **2011**, 6(7), 1698-1706.
[38] A. Achotegui-Castells, J. Sardans, A. Ribas, J. Peñuelas, *Environ. Monit. Assess*., **2013**, 185, 615-629.
[39] S. Azimi, V. Rocher, M. Muller, R. Moilleron, D.R. Thevenot, *Sci. Total Environ*., **2005**, 337, 223-239.
[40] C. Branquinho, G. Gaio-Oliveira, S. Augusto, P. Pinho, C. Maguas, O. Correia, *Environ. Pollution.*, **2008**, 151, 292-299.
[41] E. Nieboer, H.S. Richardson, F.D. Tomassini, *Bryologist*., **1978**, 81(2), 226-246.
[42] R. Bargagli, *Sci. Total Environ.*, **1995**, 176(1-3), 121-128.
[43] R. Scerbo, L. Possenti, L. Lampugnani, T. Ristori, R. Barale, C. Barghigiani, *Sci. Total Environ.*, **1999**, 241, 91-106.
[44] S. Loppi, S.A. Pirintsos, *Environ. Pollution*., **2003**, 121(3), 327-332.
[45] G. Brunialti, L. Frati, *Sci. Total Environ.*, **2007**, 387, 289-300.
[46] DP. Ormrod. In: M. Treshow (Ed.), Impact of trace element pollution on plants: Air pollution and plant life, John Wiley and Sons Ltd, Chichester, United Kingdom, **1984**, 291-314.
[47] L. Gandois, A. Probst, *Chemosphere*, **2012**, 87(2), 204-210.
[48] S. Loppi, *Biologia Ambientale*., **2006**, 20(2), 69-78.
[49] Z. Jeran, T. Mrak, R. Jaćimović, F. Batić, D. Kastelec, R. Mavsar, P. Simonćić, *Environ. Pollution.*, **2007**, 146, 324-331.
[50] J.P. Bennett, C.M. Wetmore, *Environ. Exp. Bot*., **1999**, 41, 75-82.
[51] S. Loppi, S.A. Pirintsos, D.E.V. Dominicis, *Environ. Monit. Assess*., **1999**, 58, 121-131.