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# Evaluation by X-ray fluorescence (XRF) of major and trace elements accumulated in Xanthoria parietina (L.) Th. Fr. (1860) indicating levels of pollution in Blida area (Algeria)

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## ABSTRACT/RESUME

***Abstract:*** *The purpose of this study consists of the biomonitoring of air pollution in the Blida area in Algeria. Samples of the cosmopolitan lichen Xanthoria parietina were collected from trees situated in different sites through 14 surrounding districts. The observation of lichen under SEM improved our understanding that lichens have a porous structure that accumulates mineral elements more than plants, which have on their epidermis a protective cuticle. We used the XRF analysis technique to view the multi-element aspect in our project. A total of 14 elements were measured and approved by QA/QC procedures. The maximum and minimum values of the 5 major elements are: Al (4351-15616), Cl (119-701),Fe (2397-5493), K (2068-4437),and P (519-1486) µg/g. And the values for the nine trace elements are: Br (11-61), Cr (4-10), Cu (6-80), Mn (24-161), Pb (13-244), Rb (12-60), Sr (15-103), V (8-19) and Zn (26-416) µg/g. Mapping registers high values in some areas due to local emissions of industrial facilities, road traffic, waste, and urbanization regardless of the environment. Even theforest area, including the Chréa National Park, is affected due to repeated fires, high frequency of traffic, and due to the tracks management.*

## I. Introduction

Atmospheric pollution constitutes a public health hazard. The pollutants do not remain near their emission source but may be carried on long distances and create environmental issues. The study of the atmospheric pollution of Blida and its surroundings constitutes a good opportunity to understand this phenomenon. Blida is surrounded by urban and suburban areas and is located at the foot of the Blidian Atlas, which rises over 1500 meters above sea level. It is where the natural cedar (Cedrusatlantica) forest of Algeria is located, with its specific biodiversity represented by some rare and endemic species (Macacasylvanus, Taxusbaccata). The National Park of Chréa was created in 1926 and was registered officially by the Algerian area after independence in 1983, in order to protect the natural forest area. The Blida area spreads out over the best part of the most important plain of Metidja, which is marshy in winter and subjected to severe drought in the summer. It is located in an area devoted to agriculture but invaded by accelerated and uncontrolled urbanisation and industrialisation. The development and intensification of the means of communication and transport in particular require the thinking of tracking devices for the air quality. Environmental surveys are necessary to measure the emission of heavy metals into the atmosphere with special regard to the threat presented for the health of the population.

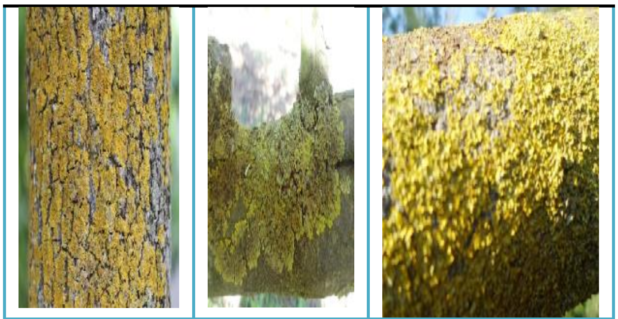
A number of studies [1, 2, 3] have shown the heterogeneity of the targets of the metallic trace element in the human organism, as well as their toxicity (neurological, cardiovascular, respiratory or renal impairments), and even their carcinogenicity [4, 5, 6, 7]. The environmental monitoring becomes a necessity to identify the potential danger to human health and present ecosystems, and would be at the basis of preventive or curative appropriate measures [3, 8]. In this scope, the use of living organisms in the monitoring of the air quality (biomonitoring) constitutes an important research field that develops into ambitious applications [9, 10, 11]. This method complements the other means of environmental monitoring [12]. The advantage is that it is fast and relatively simple to implement, and is less expensive compared to chemical methods or other physical measurements requiring technical installations and the involvement of qualified personnel. Bioaccumulation is a reliable method for estimating cumulative effects over time and synergy between pollutants [6, 13, 14]. Recently, a novel technique based on gold nanomaterial and biological molecules was developed for sensitive lead detection in environmental monitoring [15, 16]. Lichens are considered as bioindicators, and their advantage lies in using them as sensors for the long term. They will be able to retrace the historical reasons for human habits and to monitor current human actions in general, and the impact of industrial facilities in particular. Lichens are particularly suitable organisms for the study of atmospheric pollutants [9, 17, 18, 19, 20, 21, 22, 23]. With a very slow metabolism, lichens accumulate substances over a long period of time and are able to trap very fine particles [14, 21]. According to atmospheric modifications, they are therefore sensitive to the fallout of pollutants present in both dry and wet deposition. Lichens have been used for more than 40 years [14, 17, 20] to monitor the contamination of the environment by metallic trace elements and are able to accumulate large quantities of these elements [20,24]. They are good carriers for measuring metal elements using their fully atmospheric-dependent feed ways [20,25]. Lichens are relevant to diagnose the impact of atmospheric pollution and its spatial distribution. They constitute an approach and a complement that can be interesting to use in physicochemical measurements, statistical studies, and to establish mapping and modelling of air quality [17,18]. Several works have been published dealing with the topic of air pollution using various lichen species [26, 27, 28]. Xanthoria parietina (L.) Th. Fr. has a cosmopolitan distribution even at high altitudes and it is the most widely available lichen that is moderately tolerant to air pollution [19, 29]. This species is considered to have a moderate resistance to atmospheric metals pollution [30]. Xanthoria parietina persists inside and outside cities, where the pollution is accentuated but not at extreme degrees. It can be observed on house roofs and stuck on trees and even on road sides. Thus, this species of lichen constitutes a favourable choice to monitor the air quality before it arrives at extreme levels of pollution, damaging human health and leading to the collapse of the environment. On the basis of this principle, we must measure the quantities of heavy metals and trace elements accumulated within the thallus of the lichen to certify real levels reached in order to know with more certainty the reality of the quality of the air. Then, we can clarify how to stop the progression or to enhance an expected quality if sources of emission are detected and controlled.

In this study, our goal consist of analyzing lichen samples in order to determine how Xanthoria parietina accumulates detected concentrations of major and trace elements by XRF analysis in the location of the urban districts in the Blida area, in comparison with the forest area of the Chréa National Park. We also plan to compare data between districts and with other cases both in Algeria and throughout the world

## II. Materials and methods

### II.1. Presentation of the species *Xanthoria parietina* (L.) Th. Fr. (1860)

*Xanthoria parietina* or *Xanthorea* is foliose lichen, quite abundant in many parts of the world. Its toxic tolerance index is 7, which qualifies it as a moderately tolerant species for air pollution [31]. The advantage of this species is: easy identification, availability for sampling in various environments, and resistance to a certain degree of pollution. Its cosmopolitan trait reduces costs in biomonitoring, particularly in developing countries (see Figure.1).



| | | |
|---|---|---|
| *Xanthoria parietina* at Suomenlinna Island (Finland) in a non-polluted environment, September 1, 2016. | *Xanthoria parietina* in a slightly polluted environment in Chiffa (Blida), Algeria, October 24, 2016 | *Xanthoria parietina* in a moderately polluted environment in Oued Alleug (Blida), Algeria, October 24, 2016 |

***Figure1.****Presence of Xanthoria parietina in different environments.*

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### II.2. Presentation of the study area

Blida is located 50 km south of the capital, Algiers. The area of the study (Figure 2) includes the central and western part of the area. This area is located between the latitudes 36° 23.818' and 36° 37.137' north and longitudes 2° 36.360' and 3° 02.685 east. The altitude varies between 63 m from sea level and 1629 m (highest point) in the Chréa National Park. Administratively, the area of Blida is divided into 25 districts, of which 15 were prospected: Ain Romana, Benkhelil, BeniTamou, Blida, BouarfaBoufarik, Bouinan, Chebli, Chiffa, Chréa, El-Affroun, Guerrouaou, Mouzaia, Oued El Alleug, and Soumaa (Figure 2).

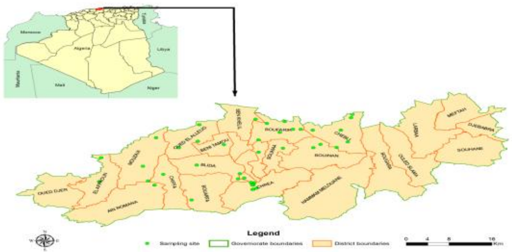


***Figure 2***. *Positioning of the sampling sites in Blida and its surroundings on the administrative districts map of the Blida area (National Institute of Cartography and Teledetection, 2016)*

#### II.2.1 Repartition of the industry and landfills

***Industries:***

Although the Blida area is devoted to agriculture, it has reached a significant industrial development, thus expanding its industrial network by the gradual establishment of several industrial units working in varied fields. The industrial infrastructure consists of 4,258 production units characterized by an agro-food industry followed by metallurgical, chemical and glass industries distributed as shown above in Table 1(see Figure 3).

***Table 1***: *The industrial network in the Blida area*

| Field of activity | The main activity | Number of production units | % |
|---|---|---|---|
| Food | • Cheese dairy-flour mill- beverage<br>• Bakeries- industrial confectionery<br>• Confectionary-cookie factories-dairies | 1 768 | 43 |
| Metallic and Electrical Industries | • Electrical appliances-manufacturing<br>• Industrial-metal frame and foundry | 383 | 9 |
| Textiles, Shoes and Leather | • Garment-socks making<br>• Fabric-leather-mattress bags | 356 | 8 |
| Chemistry and Plastic | • Chemicals and cosmetics<br>• Plastic packaging- plastic processing<br>• Cleaning products | 294 | 7 |
| Materials of Construction and the Glass Industry | • Concrete blocks, tiles, cement<br>• Mirror-Glazier-Ceramic-Sanitary Products | 182 | 4 |
| Printing Houses Stationery Wood and Tobacco | • Joinery-furniture manufacturing<br>• Wooden packaging and notebooks<br>• Paper transformation | 134 | 3 |
| Services | • Services provided to businesses<br>• Non-market services provided to the community<br>• Services and works tankers<br>• Market services provided to households | 1 141 | 27 |
| Total | | **4258** | **100** |

***Landfills:***

It appears from the comprehensive inventory of landfills in the various districts of the Blida area that the most dominant type of landfill remains the uncontrolled dumping site(see Figure 3). With the exception of the following districts that dump their household waste at the BeniMered composting plant: Blida, OuledYaich, BeniMered, Guerrouaou and Chréa.It is important to note that the majority of these uncontrolled landfills are located mostly in the Mitidja plain and along areas known as Oueds (riverbeds) including: Oued El-Harrach, OuedChiffa, OuedBou-Roumi, OuedDjemaa and Oued El-Had. Landfills have become a potential pollution source for rivers and streams in these areas, affecting population health.

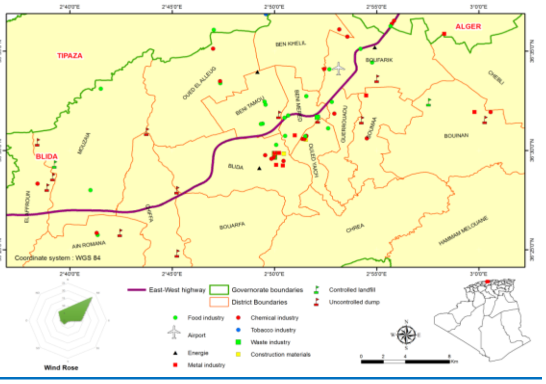
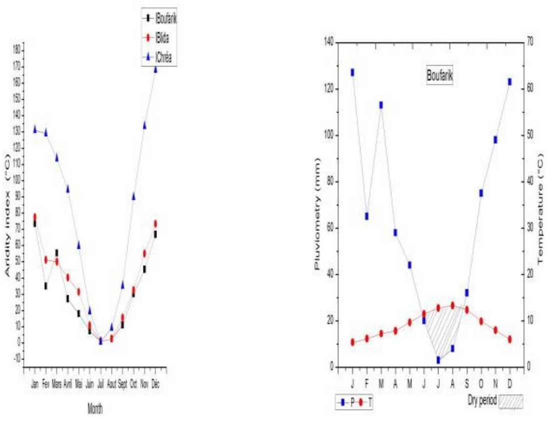


***Figure 3****. Geographical distribution of the types of industries and landfills in the study area (Blida and its surrounding districts)*

### *II.2.2.* The climat

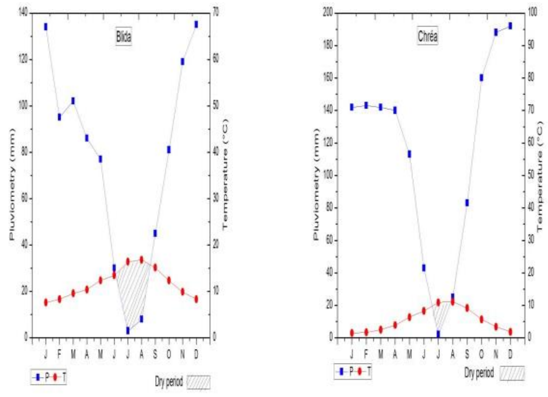
*The average annual rainfall is about 646 mm/year and more than 1500 mm/year at Chréa[32]. The areas of snow during the winter are particularly those of the Blidian Atlas chain, the mountains of Chréa, and Mouzaia. The monthly average temperatures range from M = 43.20°C in the hottest month (July 2015) to M=1.5°C in the coldest month (February 2015). The records are m'=-3.2°C and m'=44.6°C for the recorded period from the years 2000 to 2016. The prevailing winds during the sampling period of May, June and July 2015 were recorded as follows: calm wind 42.93%, NE: 22.37% (National Office of Metrology,2016). The most likely hypothesis concerning the direction of the fallout of the pollutants under the industrial atmospheric incidence must be oriented towards the direction of the north-east wind, without neglecting possible pollution towards the caps at 90° (8.68%) and 315° (8.53%).*



(a) Aridity index of the Blida Station

(b) Ombrothermic diagram and dry period in Boufarik

$$I = 12 * P/(T+10)$$



(c) Ombrothermic diagram and dry period in Blida

(d) Ombrothermic diagram and dry period in Chréa

***Figure 4****. (a) Aridity index, dry periods and ombrothermic diagrams of the stations in (b)Boufarik, (c) Blida, (d)Chréa*

**Aridity indices and calculation of dry periods***:* The ombrothermic diagrams of Boufarik, Blida and Chréa stations show two main periods (Figure 4).The first period is from November to May and consists of fresh *coolness*, brought about by the winter rains and during which temperatures are low. And the second is from May to October, consisting of rather dry conditions, with peak dryness seen in July and August, even for the station of Chréa, which has an altitude of over 1500 m.

This dry period coincided with the collection period of lichen samples for this study.

### II .2.3. Location of sampling sites

Samples were chosen only from trees and not from roofs of houses or other facilities. The sampling sites were from natural environments such as forests, cultivated fields, or roadside trees. The aim was to cover areas of different pollution levels. Samples were picked close to industrial activities and urban areas, while others were taken near roads that are exposed to different traffic intensities. Some samples were also picked in forest environments in the Chréa National Park.

Forty-two (42) samples were collected during the period from May to July in 2015, targeting locations near industries, roads and landfills (Figure 3). Lichen samples were taken separately, so as to limit contamination and loss. For each collected sample, we recorded the following aspects of the data: sampling time, date, name, GPS coordinates (longitude and latitude), and the altitude of the location. Lichen samples were codified and were stored in paper envelopes on the same day. Collecting of lichen Xanthoria parietina was from trees throughout the 15 districts during the period of three months: May, June and July. This period is characterized by hot and dry climatic conditions as shown in Figure 4.

**II.3. Sample preparation**

For drying the samples we used the protocol method developed by [33]. The samples were washed with distilled water thrice to remove any residue from the surface of the lichen. After that, the samples were thoroughly dried in an oven at 60°C for 2 hours, removing any existing moisture. They were ground with a ceramic mortar to obtain a more or less homogeneous powder with a particle size of less than 63µm. Powdered samples of lichen were transferred into plastic bottles and irradiated at the Nuclear Research Center of Algiers (CRNA) by a source of cobalt (Co60) with a dose of 25Gy in order to preserve them.

The treated samples and the IAEA-336 lichen standard underwent the same treatment and were placed in plastic capsules on a 4 µm-thick mylar support.

**II.4 XRF analysis device**

The device used consists mainly of a PANalytical X-ray tube delivering a voltage of 50 kV and a current of up to 3.0 mA, which makes it possible to define specific excitation conditions for an optimized application, with a silver primary target and a Peltier Silicon Detector (SDD) with a resolution of 132.6 KeV for K_α-Mn-Xray [Epsilon].

The deconvolution of the X spectra is carried out by the Epsilon3 XL spectrometer software.

**II.4.1. Measurement of concentrations of major and trace elements**

The measurements of the element concentrations of major elements (Al, Cl,Fe, K,and P) and trace elements (Br, Cr, Cu , Mn, Pb, Rb, Sr, V and Zn) were carried out with the help of X-ray fluorescence (XRF) with Peltier-based silicon drift detectors (SDD), at 132.6 keV resolution for Kα-Mn X-rays and X-ray tube excitation (PANalytical, Ag primary target, 50 kV).

The characteristic X-rays are identified thanks to the Epsilon 3XL software. The yields of characteristic X-ray peaks (Kα-Al, Kα-P, Kα-Cl, Kα-K, Kα-V, Kα-Cr, Kα-Mn, Kα-Fe, Kα-Cu, Kα-Zn, Kα -Br, Kα-Rb, Kα-Sr, Lα-Pb) are measured after the adjustment and the subtraction of the background interference.

The concentrations of the elements were determined with the use of the Omnian procedure with several filters (Ti, Al-50, Al-200 and Ag, Cu 300) in triplicate of the Lichen samples. The elements were analysed in an air environment with the exception of aluminium which was done in a helium atmosphere to reduce the absorption effects.

**II.4.2. Quality Assurance and Quality Control Procedures (QA/QC)**

In our analysis procedure and for the QA/QC ratio of the XRF technique, we used the Lichen epiphyte biological matrix IAEA-336 as a standard reference.

The objective is to assess the quality of the results obtained. Statistical assessment was performed to determine the performance of the analyses and the significance of the results. Three statistical parameters: Z-score, U-score and Relative Bias (RB,%) are the most commonly used [34]. The evaluation using U-score includes measurement uncertainties and the uncertainty of the value found.

In this study, the following equations were used in the calculations:

$$U_{score} = \frac{\left| X_{Lab} - X_{Ref} \right|}{\sqrt{\mu_{Lab}^2 + \mu_{Ref}^2}} \quad \textbf{(1)}$$

Where:

xLab, µLab, xRef and µRefare the results of laboratory measurements, overall/combined standard uncertainties, assigned values and standard uncertainties, respectively.

$$Z_{score} = \frac{\left| X_{Lab} - X_{Ref} \right|}{\mu_{Ref}} \quad \textbf{(2)}$$

Where the performance of the laboratory equipment is deemed satisfactory if zscore≤ 2,questionable for2•zscore• 3 and unsatisfactory for zscore≥ 3.

$$RB = \frac{X_{Lab} - X_{Ref}}{X_{Ref}}.100\% \quad \textbf{(3)}$$

The evaluation of the quality of our work was carried out through the results of the relative bias, Z-score and U-score.

The comparison of our measured data with the recommended value is shown in Table 2.

***Table 2.*** *Concentrations (µg/g) of the 14 elements in the reference samples (Epiphytic lichen IAEA-336)*

| Element | Measured value ± s* (**) | Value Certified | RB (%) | Z-score | U-score |
|---|---|---|---|---|---|
| Al | 580,82±18.16 (5) | 680±126.12(15) | -14.59 | 0.79 | 0.77 |
| Cl | 2026,85±11.89 (14) | 1900±377.41(13) | 6.68 | 0.34 | 0,34 |
| Fe | 407,71±1.91 (14) | 430±35.02(35) | -5.18 | 0.64 | 0.64 |
| K | 1949,84±4.8 (14) | 1840±172.57(24) | 5.97 | 0,64 | 0.64 |
| P | 516,48±27.95 (12) | 610±159.27(12) | -15.33 | 0.59 | 0.58 |
| Br | 11,89±0.21 (14) | 12.9±1.74(18) | -7.86 | 0.58 | 0.58 |
| Cr | 1,09±0.19 (14) | 1.06±0.15(22) | 3.10 | 0.22 | 0.18 |
| Cu | 4,10±0.08 (7) | 3.6±0.47(21) | 13.89 | 1.06 | 1.05 |
| Mn | 60,31±0.37 (14) | 63±5.42 (29) | -4.27 | 0.50 | 0.5 |
| Pb | 4,37±0.20 (6) | 4.9±0.53(23) | -10.88 | 1.01 | 0.93 |
| Rb | 1,55±0.19 (13) | 1.76±0.24(16) | -11.71 | 0.86 | 0.77 |
| Sr | 8,59±0.23 (14) | 9.3±1.09(19) | -7.60 | 0.65 | 0.64 |
| V | 1,49±0.25 (10) | 1.47±0.39 (8) | 1.36 | 0.05 | 0.05 |
| Zn | 27,97±0.31 (5) | 30.4±2.26(38) | -8.88 | 1.18 | 1.18 |

* s: Standard deviation (SD) ** (number of analysis test)

The results of the analyzed elements were in agreement with the recommended value of lichen epiphyte IAEA-336. The results of relative bias (%), Z-score and U-score were satisfactory.

We discuss the results through the statistical evaluation where the RB, Z-score and U-score are accepted or rejected according to the previous conditions. This evaluation shows excellent quality of the results obtained in this study.

## II.5. Mapping techniques

In our study, the Kriging modelling method [35, 36] was used to trace the mapping of major and trace elements in the Blida area and to highlight the spatial distribution in the concentration of these metals. They are averaged with ArcGIS 10.4.

software based on the Kriging method and carried on location maps for each measured element.

# III. Results and discussion

## III.1. Anatomical structure of *Xanthoria parietina*

In order to clarify how the structure of Xanthoria parietina is made and to know how it accumulates aerosols, we proceeded to do anatomical checking using the Scanning Electron Microscope (SEM).
The presence of the foliose thallus with lobes and rich in apothecia was noticed.

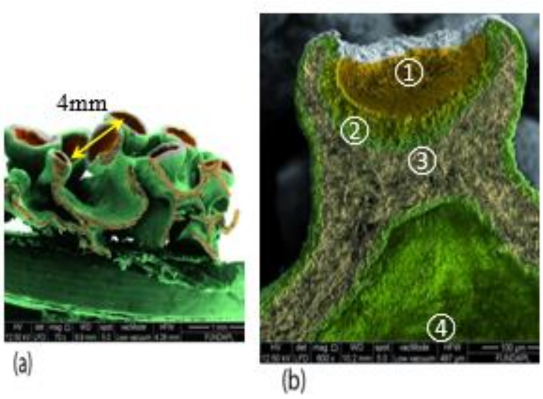



***Figure 5***. *Cross-section of the lichen Xanthoria parietina observed with the SEM QUANTA 650 FUNDAPL microscopes.*
*(a): Thallus and apothecium on the surface of Xanthoria parietina (scale 1mm);*
*(b): Vertical section of apothecium of Xanthoria parietina (scale 100 µm) : ①Epithecium , ②Thecium (paraphyse + spores), ③ Medulla , ④ Upper Layer*

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Through the detailed SEM examination (Figure 5a), we can observe the anatomy of the upper and lower layers of the thallus and also the appearance of the apothecia (Apothecium sing) (Apothecia and thalli); the shape and the size of the asci, the spores, the shape of the hyphae and their compartmentalized arrangement (Figure 5b). It is noted that the epithecium has a fissured structure on which particles of telluric origin or airborne particles can be deposited and which can, through moisture or rain, enter the cavities of the thecium and the remains in the thallus, and then pass into the cavities of the medulla. The porous structure makes it possible to trap soluble and even solid particles that are in suspension in the atmosphere. The lichen is different from the leaves of plants, which are usually covered with a cuticle. It is possible to distinguish the existence of solid particles suspended in the atmosphere, clumped on the surface of the thallus or in its cavities.

**III.2. Distribution of major elements and trace elements concentrations.**

The average values of the concentrations obtained for the major elements (Al, Cl, Fe, K and P) and the trace elements (Br, Cr, Cu, Mn, Pb, Rb, Sr, V and Zn) analyzed by the XRF technique are given, respectively, in

Table 3 and Table 4 for the forty-two (42) sampling sites picked in the 15 districts of Blida. The maximum, minimum and the mean values are reported.

***Table 3**. Concentration values of major elements (Al, Cl., Fe, K., P.) in µg/g in the lichen Xanthoria parietina in Blida and its surroundings.*

| Sites | **District** | **Al** | **Cl** | **Fe** | **K** | **P** |
|---|---|---|---|---|---|---|
| B1 | El-Afroun | 5905 | 231 | 2397 | 2068 | 681 |
| B28 | El-Afroun | 10977 | 243 | 4162 | 3567 | 794 |
| B4 | OuedAlleug | 5324 | 380 | 2579 | 3837 | 984 |
| B5 | OuedAlleug | 11644 | 233 | 5100 | 2877 | 607 |
| B6 | OuedAlleug | 10145 | 319 | 4048 | 2658 | 697 |
| B3 | Benkhelil | 8777 | 613 | 3672 | 2990 | 935 |
| B24 | BeniTamou | 6718 | 287 | 3534 | 3126 | 853 |
| B7 | Mouzaia | 12136 | 316 | 4594 | 2886 | 754 |
| B8 | Mouzaia | 12318 | 563 | 4155 | 4188 | 897 |
| B29 | Mouzaia | 8885 | 264 | 3244 | 3252 | 694 |
| B30 | Ain Romana | 10989 | 271 | 3787 | 3822 | 1126 |
| B9 | Chiffa | 10351 | 353 | 4556 | 3736 | 690 |
| B26 | Bouarfa | 7353 | 437 | 3439 | 4049 | 768 |
| B27 | Blida | 11868 | 296 | 4340 | 3159 | 712 |
| B33 | Blida | 8915 | 226 | 3779 | 3786 | 762 |
| B34 | Blida | 9772 | 162 | 4176 | 3634 | 827 |
| B35 | Blida | 5685 | 315 | 2677 | 4437 | 815 |
| B18 | Guerrouaou | 15616 | 227 | 5188 | 3022 | 581 |
| B19 | Boufarik | 11807 | 317 | 4982 | 3236 | 741 |
| B21 | Boufarik | 8900 | 416 | 2756 | 2528 | 615 |
| B22 | Boufarik | 7942 | 398 | 2895 | 3120 | 771 |
| B23 | Boufarik | 7870 | 415 | 3781 | 3259 | 798 |
| B2 | Boufarik | 4351 | 701 | 2586 | 3795 | 1192 |
| B25 | Boufarik | 10354 | 318 | 3808 | 2994 | 658 |
| B17 | Soumaa | 12411 | 460 | 4422 | 3781 | 1486 |
| B15 | Bouinan | 14514 | 228 | 5493 | 2902 | 692 |
| B16 | Bouinan | 5795 | 556 | 2813 | 2874 | 885 |
| B10 | Chebli | 10632 | 331 | 4843 | 3842 | 1017 |
| B11 | Chebli | 5744 | 491 | 3556 | 3483 | 884 |
| B12 | Chebli | 10356 | 256 | 4001 | 3136 | 1059 |
| B13 | Chebli | 10883 | 389 | 5471 | 3008 | 751 |
| B14 | Chebli | 9079 | 363 | 4742 | 3158 | 744 |
| B20 | Chebli | 11288 | 324 | 4556 | 3123 | 658 |
| B31 | Chréa | 10935 | 119 | 5225 | 2679 | 709 |
| B32 | Chréa | 11440 | 198 | 4090 | 3385 | 647 |

| | | | | | | |
|---|---|---|---|---|---|---|
| B36 | Chréa | 9186 | 221 | 4053 | 2893 | 602 |
| B37 | Chréa | 9716 | 299 | 3684 | 3672 | 720 |
| B38 | Chréa | 9850 | 285 | 4193 | 3921 | 716 |
| B39 | Chréa | 12399 | 217 | 4461 | 2984 | 519 |
| B40 | Chréa | 9633 | 376 | 3710 | 3475 | 682 |
| B41 | Chréa | 8177 | 236 | 2935 | 3567 | 714 |
| B42 | Chréa | 11195 | 294 | 3526 | 2202 | 658 |
| Min | | 4351 | 119 | 2397 | 2068 | 519 |
| Mean | | 9710 | 332 | 3953 | 3288 | 788 |
| Max | | 15616 | 701 | 5493 | 4437 | 1486 |

***Table 4**. Concentrations of trace elements (Br, Cr, Cu, Mn, Pb, Rb, Sr, V and Zn) in µg/g in the lichen Xanthoria parietina in Blida and its surroundings*

| Station | Districts | Br | Cr | Cu | Mn | Pb | Rb | Sr | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **B1** | El-Afroun | 17 | 4 | 6 | 24 | 13 | 12 | 16 | 8 | 31 |
| **B28** | Al-Afroun | 32 | 8 | 28 | 47 | 25 | 33 | 87 | 14 | 57 |
| **B4** | OuedAlleug | 16 | 5 | 8 | 33 | 51 | 23 | 53 | 9 | 37 |
| **B5** | OuedAlleug | 49 | 9 | 18 | 76 | 244 | 43 | 103 | 13 | 63 |
| **B6** | OuedAlleug | 25 | 7 | 10 | 41 | 40 | 31 | 54 | 14 | 45 |
| **B2** | Boufarik | 22 | 5 | 10 | 34 | 88 | 13 | 28 | 8 | 53 |
| **B3** | Benkhelil | 57 | 6 | 13 | 43 | 52 | 29 | 51 | 13 | 56 |
| **B24** | BeniTamou | 11 | 6 | 10 | 46 | 26 | 14 | 46 | 10 | 289 |
| **B7** | Mouzaia | 31 | 8 | 11 | 58 | 61 | 33 | 45 | 15 | 49 |
| **B8** | Mouzaia | 22 | 7 | 80 | 56 | 55 | 31 | 30 | 14 | 91 |
| **B29** | Mouzaia | 17 | 6 | 30 | 47 | 24 | 31 | 41 | 12 | 42 |
| **B30** | Ain Romana | 43 | 7 | 10 | 48 | 64 | 40 | 43 | 14 | 49 |
| **B9** | Chiffa | 29 | 8 | 13 | 50 | 69 | 28 | 30 | 15 | 48 |
| **B26** | Bouarfa | 61 | 6 | 15 | 36 | 70 | 39 | 53 | 14 | 55 |
| **B27** | Blida | 34 | 8 | 16 | 54 | 74 | 29 | 43 | 15 | 64 |
| **B33** | Blida | 43 | 7 | 8 | 49 | 80 | 42 | 33 | 14 | 41 |
| **B34** | Blida | 29 | 7 | 8 | 51 | 30 | 35 | 32 | 15 | 41 |
| **B35** | Blida | 22 | 5 | 8 | 161 | 33 | 26 | 15 | 9 | 30 |
| **B18** | Guerrouaou | 34 | 10 | 13 | 59 | 82 | 46 | 59 | 18 | 78 |
| **B19** | Boufarik | 36 | 9 | 16 | 63 | 108 | 43 | 61 | 15 | 79 |
| **B21** | Boufarik | 20 | 5 | 21 | 32 | 32 | 21 | 39 | 10 | 416 |
| **B22** | Boufarik | 31 | 5 | 9 | 29 | 30 | 22 | 56 | 9 | 101 |
| **B23** | Boufarik | 35 | 9 | 31 | 52 | 228 | 30 | 74 | 10 | 90 |
| **B25** | Boufarik | 25 | 7 | 12 | 42 | 47 | 31 | 79 | 13 | 91 |
| **B17** | Soumaa | 21 | 9 | 11 | 44 | 65 | 48 | 51 | 16 | 57 |
| **B15** | Bouinan | 34 | 10 | 61 | 78 | 56 | 60 | 44 | 19 | 68 |
| **B16** | Bouinan | 12 | 5 | 20 | 39 | 27 | 24 | 41 | 9 | 152 |
| **B10** | Chebli | 29 | 9 | 10 | 50 | 34 | 31 | 42 | 16 | 60 |
| **B11** | Chebli | 19 | 6 | 10 | 42 | 21 | 16 | 32 | 12 | 51 |
| **B12** | Chebli | 22 | 7 | 8 | 55 | 23 | 27 | 40 | 14 | 53 |
| **B13** | Chebli | 32 | 9 | 18 | 65 | 47 | 38 | 101 | 16 | 64 |
| **B14** | Chebli | 16 | 9 | 10 | 76 | 75 | 31 | 73 | 15 | 48 |
| **B20** | Chebli | 33 | 8 | 11 | 54 | 60 | 34 | 41 | 16 | 56 |
| **B31** | Chréa | 29 | 8 | 8 | 140 | 21 | 44 | 32 | 17 | 33 |
| **B32** | Chréa | 33 | 7 | 8 | 50 | 24 | 37 | 32 | 15 | 45 |
| **B36** | Chréa | 44 | 7 | 7 | 55 | 40 | 35 | 30 | 14 | 32 |
| **B37** | Chréa | 31 | 6 | 7 | 47 | 20 | 32 | 26 | 12 | 51 |
| **B38** | Chréa | 38 | 8 | 8 | 59 | 29 | 33 | 34 | 14 | 55 |
| **B39** | Chréa | 39 | 8 | 12 | 81 | 32 | 35 | 40 | 17 | 255 |
| **B40** | Chréa | 45 | 6 | 7 | 65 | 35 | 39 | 25 | 13 | 34 |
| **B41** | Chréa | 31 | 5 | 6 | 51 | 16 | 31 | 18 | 9 | 26 |

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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **B42** | Chréa | 47 | 6 | 7 | 52 | 34 | 30 | 38 | 13 | 35 |
| **Min** | | 11 | 4 | 6 | 24 | 13 | 12 | 15 | 8 | 26 |
| **Mean** | | 31 | 7 | 15 | 56 | 54 | 32 | 46 | 13 | 76 |
| **Max** | | 61 | 10 | 80 | 161 | 244 | 60 | 103 | 19 | 416 |

The distribution maps of major and trace elements are shown in figure 6 to 19.

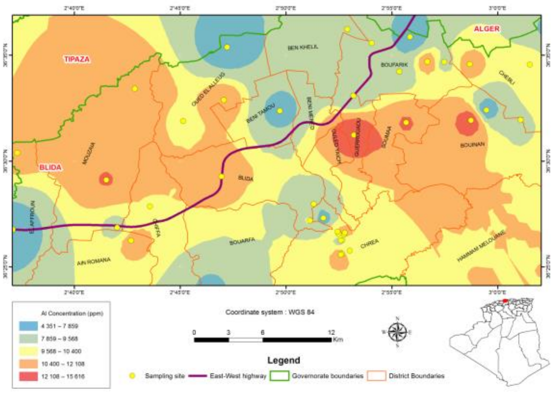

***Figure 6**. Geographical Distribution of the Aluminium Concentrations*

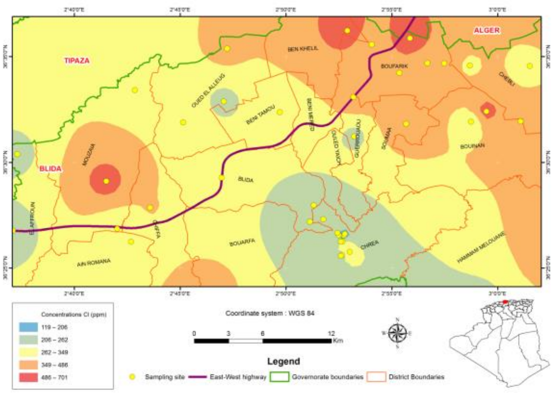

***Figure 7**.Geographical Distribution of Chlorine Concentrations*

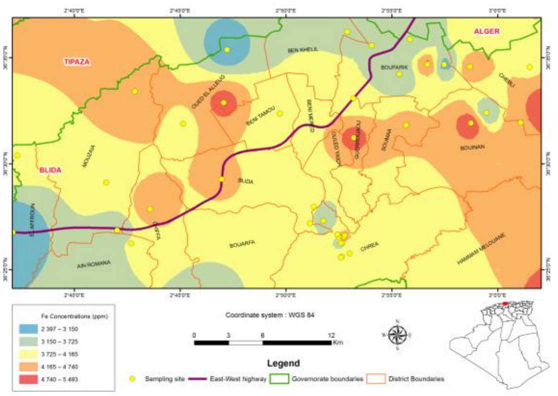

***Figure8**.Geographical Distribution of Iron Concentrations*

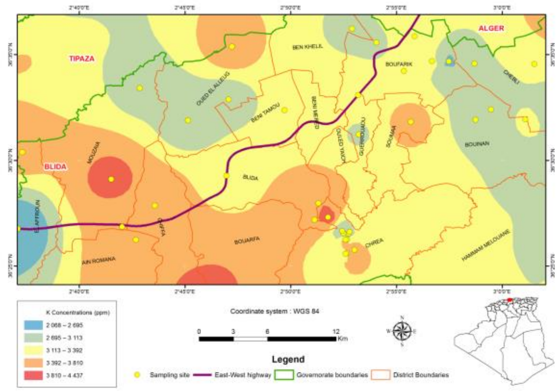

***Figure 9**. Geographical Distribution of Potassium Concentrations*

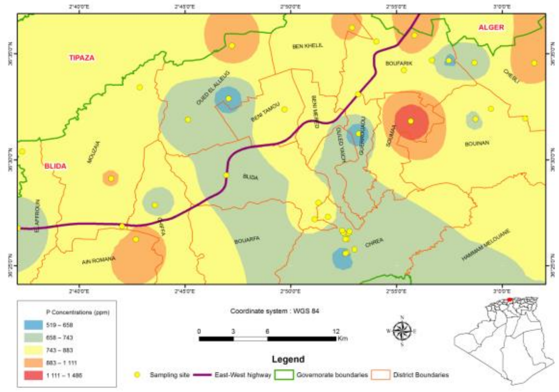

***Figure10** .Geographical Distribution of Phosphorus Concentrations.*

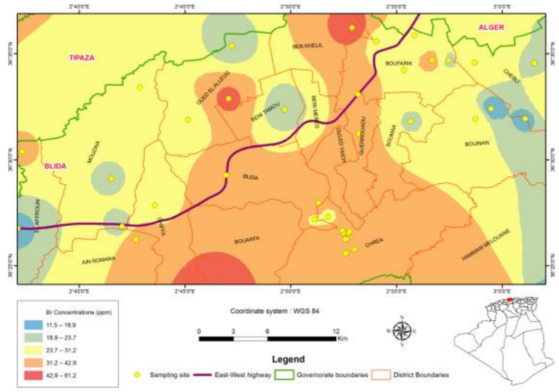

***Figure11**. Geographical Distribution of Bromine Concentrations*

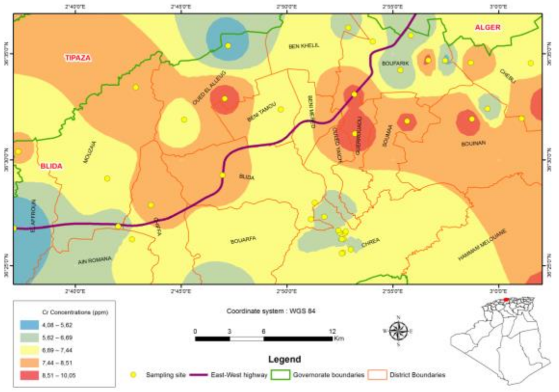

***Figure12***.*Geographical Distribution of Chromium Concentrations*

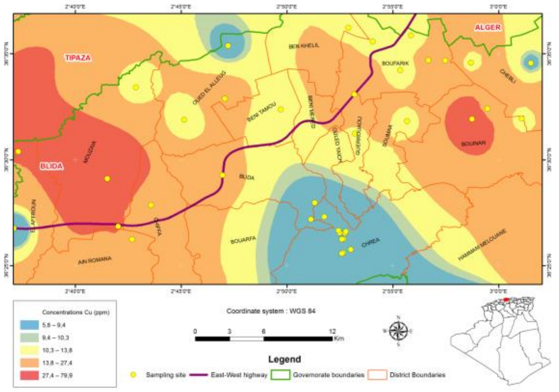

***Figure 13***.*Geographical Distribution of Copper Concentrations*

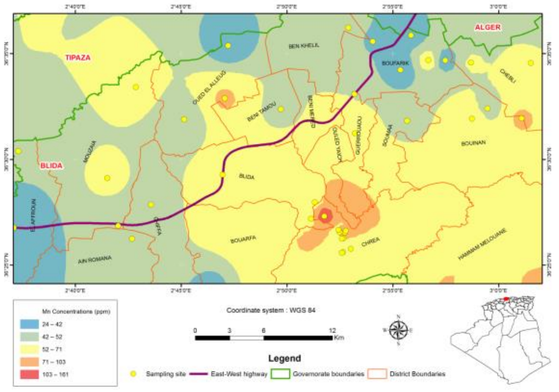

***Figure14***.*Geographical Distribution of Manganese Concentrations*

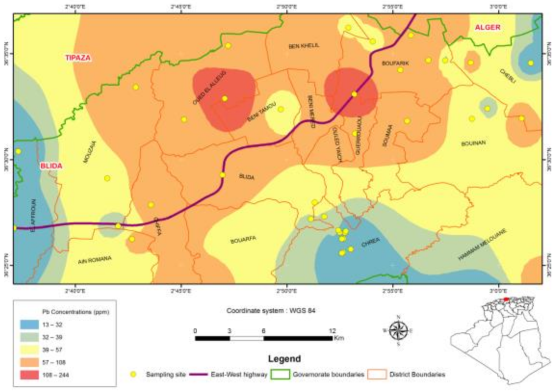

***Figure 15***.*Geographical Distribution of Lead Concentrations.*

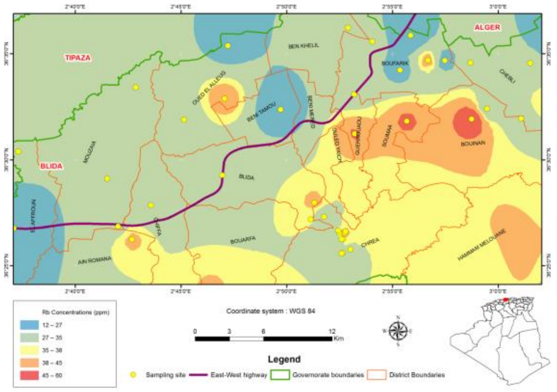

***Figure 16***.*Geographical Distribution of Rubidium Concentrations*

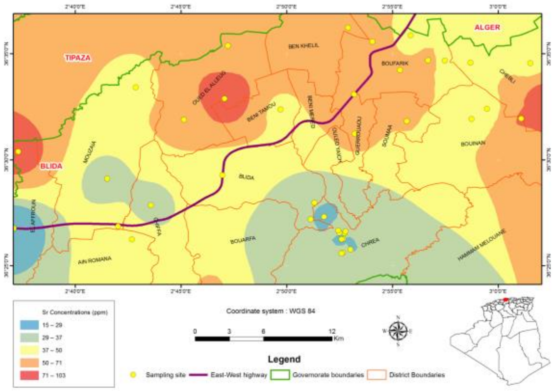

***Figure 17***. *Geographical Distribution of Strontium Concentrations*

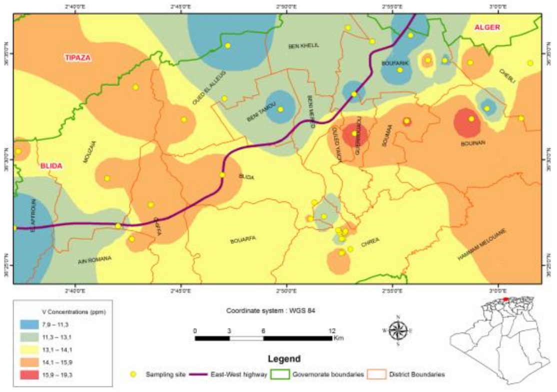

***Figure 18***.*Geographical Distribution of Vanadium Concentrations*

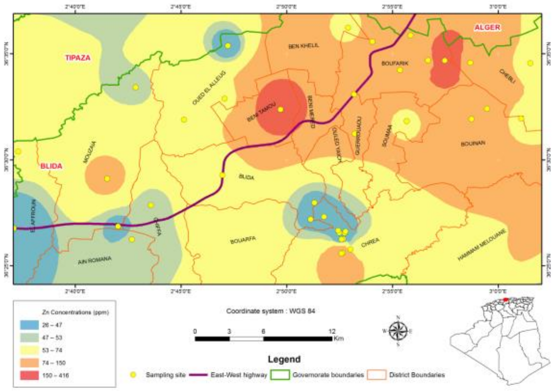

***Figure 19***. *Geographical Distribution of Zinc Concentrations*

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**Iron and Aluminum:**
According to [37], the high concentration of iron and aluminium in the lichen Xanthoria parietina may be related to several local factors. The telluric origin and the proximity of the wastes generated by industrial activities are the most likely causes. In addition, forest fires and roadtraffic [38,39] are also an emission source of the iron, mainly from transport exhaust fumes from diesel fuel vehicles. Catalytic converters [29, 40, 41] are also registered as important sources of iron emission. Building materials can also affect iron concentrations in the air [42].
Aluminium concentrations are the highest in all districts, followed by iron concentrations. This is most likely due to these elements' origin from the surrounding rocks and soil. The iron concentration values accumulated by Xanthoria parietina are between 2397 µg /g and 5493 µg /g with an average value of 3953 µg/g. The aluminium concentration values accumulated by Xanthoria parietina are between 4351 µg/g and 15616 µg/g with an average value of 9710 µg/g. According to [37], the high concentration of iron and aluminium in lichen Xanthoria parietina may be related to local factors. The telluric origin and the proximity of the wastes generated by the industrial activities are the most likely causes concerning this study case.

**Chlorine:**
The chlorine concentrations accumulated by the lichen Xanthoria parietina record values between 119 µg/g and 701µg/g with an average value of 332µg/g. The origin can be accounted for from the species itself or from the sea. Xanthones derived from lichexanthone and norlichexanthone are very often chlorinated [43].

**Potassium:**
In our case, the concentration content of potassium is in third position after that of aluminium and iron. The potassium concentration values accumulated by Xanthoria parietina ranges from 2068 µg/g and 4437µg/g with an average value of 3288 µg/g. which is comparable to the background values for potassium in lichens (500 to 5000 ppm), whereas enriched levels in lichens are 5,000 to 9,500 ppm [44]. This rate is explained by the proximity of the sampling points of agricultural areas containing a fertilization activity, and intense road traffic; as well as the proximity of this region to the sea. [38, 39, 42] give forest fires and road traffic as the emission sources.

**Phosphorus:**
The phosphorus concentration values accumulated by Xanthoria parietina are between 519 µg/g and 1486 µg/g with an average value of 788µg/g. The terrigenous aerosols and their use in agriculture and industry constitute the main source [45].

**Bromine:**
The bromine concentration values accumulated by lichen Xanthoria parietina are between 11µg/g and 61 µg/g with an average value of 31 µg/g. [46] demonstrated that a bromoperoxidase is present in this lichen. Purified enzymes from this lichen contain vanadium, which is essential for its activity. The elevation of bromine concentration can be related to the use of pesticide.

**Chromium:**
[29]gives volcanic activities and aerosol as the natural origin of chromium in the air, and the iron and steel industries (glass, cement and paper), as well as transport, agriculture, energy, and waste as the anthropogenic sources. Chromium is often higher in soils of ultramafic regions [47]. The values for lichen are between 0 and 10 ppm [44]. Although, [44] indicate that improved levels of as low as 4 ppm have been observed near industrial areas. According to [26], an average chromium concentration level is 7 (5-10) ppm, and may be higher near urban/industrial areas with levels of 25 to 130 ppm.

**Copper:**
In our study, the copper concentration values accumulated by lichen Xanthoria parietina are between 6 µg/g and 80µg/g with an average value of 15 µg/g.
The natural origin of copper in the air is possible from terrigenous aerosols, marine, volcanic activities, and also vegetation. Anthropogenic activities which enhance those values are transport, industry, metallurgy, waste, agriculture[29, 48, 49], vehicular exhaust fumes, and wear of vehicles brakes [40, 50, 51].
According to [44], the average copper concentration is 20.5 (8-31) ppm and the values for lichens are 1 to 50 ppm. More ranges of 15 to 1100 ppm and levels as low as 13.5 ppm can be observed in bryophytes [52]. The high copper concentration is due to the proximity of the sampling points to industrial activity areas, which include the metallurgical and chemical industries, to the presence of CET, and to intense road traffic releasing copper from the exhaust fumes of the vehicles and the wearing of the vehicular brakes.

**Manganese:**
The manganese concentrations accumulated in the lichen Xanthoria parietina samples are in the order of 24 µg/g and 161 µg/g with an average of 56 µg/g. The principal sources of manganese areterrigenous aerosols, vegetation and forest fires [29]. However non-natural sources are metallurgy, energy (coal), exhaust fumes from gasoline-powered vehicles, vehicle brake wear and road traffic [48, 40, 39, 53, 38]. Background values for lichens are between 10

to 130 ppm [26], which proves that our values are within acceptable limits.

**Lead:**

The principal source of lead is due to industry, metallurgy, intensity of road traffic, and waste and energy processing[29, 54, 55].The lead concentrations accumulated by lichen Xanthoria parietina are between 13 µg/g and 244 µg/g with an average value of 54 µg/g.

**Rubidium:**

The main known source of rubidium is waste incineration[45]. The rubidium values registered in this study are between 12 µg/g and 60 µg/g with an average value of 32 µg/g. Our values are similar to those recorded in Slovenia but higher than those in Brazil.

**Strontium:**

[29]gives two sources of emission for this metal. The natural source is from terrigenous aerosols and the non natural sources are from the energy of oil, fuel of vehicles, and coal as well as waste. In our study, the strontium concentrations accumulated by lichen Xanthoria parietina range between 15 µg/g and 103 µg/g with an average value of 46 µg/g. The average value in our findings is three times higher than the values recorded in France.

**Vanadium:**

The origin of vanadium can be natural from volcanic activities and also terrigenous and marine aerosols. The non-natural sources are energy processing and oil, transport, waste as well as particular extraction of copper and zinc [29] and from the exhaust fumes from diesel vehicles [48].

The Vanadium concentration values accumulated by lichen Xanthoria parietina range from 8 µg/g and 19 µg/g with an average value of 13µg/g. The vanadium is associated with the enzyme bromoperoxidase in Xanthoria parietina[46].

**Zinc:**

The natural origin of zinc can be terrigenous aerosols, volcanic activities, vegetation and forest fires. And the non-natural sources are from the metallurgical industry, energy (coal), wastes, transport, and agriculture [29, 38], as well as vehicular exhaust, and engine and tire wear [48, 50, 56, 57].

The zinc concentration values accumulated by lichen Xanthoria parietina are between 26 µg/g and 416 µg/g with an average value of 76 µg/g.

### III.3. Statistical analysis

#### III.3.1. Inter-element correlation

The study of inter-element linear correlations by the use of the Pearson coefficient with a risk α = 0.01, reveals two correlation groups. The first has correlation coefficients that are higher than 0.3932, more exactly corresponding to a ddl = 41, unlike the second group, where they are lower than 0.3932. The values of correlation coefficients for major and trace element respectively are shown in Table 5 and Table 6.

***Table 5***. *Inter-element correlation matrix for major elements (R)*

| **Variables** | **Al** | **Cl** | **Fe** | **K** | **P** |
|---|---|---|---|---|---|
| **Al** | **1** | -0,4211 | **0,8117** | -0,1719 | -0,2356 |
| **Cl** | -0,4211 | **1** | -0,3558 | 0,2320 | **0,4985** |
| **Fe** | **0,8117** | -0,3558 | **1** | -0,1027 | -0,1828 |
| **K** | -0,1719 | 0,2320 | -0,1027 | **1** | **0,4502** |
| **P** | -0,2356 | **0,4985** | -0,1828 | **0,4502** | **1** |

A strong correlation is observed for the elements Al-Fe (r = 0.8117), P-Cl (r =0.4985) and K-P(r =0.4502). The presence of a linear correlation between iron and aluminium is due to their sharing the same origin of air enrichment, which can be strongly related to the soil. The second correlation between chlorine and phosphorus may be explained by coastal upwellings containing chlorine[58].The third correlation registered between phosphorus and potassium is due probably to their addition to agricultural soil and from industries

***Table 6***. *Inter-element correlation matrix for trace elements (R).*

| Variables | Br | Cr | Cu | Mn | Pb | Rb | Sr | V | Zn |
|---|---|---|---|---|---|---|---|---|---|
| Br | **1** | 0,2269 | -0,0829 | 0,0490 | 0,3147 | 0,4975 | 0,1493 | 0,3482 | -0,2444 |
| Cr | 0,2269 | **1** | 0,2569 | 0,2700 | 0,4525 | **0,7065** | 0,5171 | **0,8243** | -0,1230 |
| Cu | -0,0829 | 0,2569 | **1** | 0,0253 | 0,1869 | 0,2503 | 0,1396 | 0,1855 | 0,1317 |
| Mn | 0,0490 | 0,2700 | 0,0253 | **1** | 0,0472 | 0,3498 | -0,0793 | 0,2775 | -0,1451 |
| Pb | 0,3147 | 0,4525 | 0,1869 | 0,0472 | **1** | 0,2543 | 0,5415 | 0,0325 | -0,0585 |

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| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Rb | **0,4975** | **0,7065** | 0,2503 | 0,3498 | 0,2543 | 1 | 0,2585 | **0,7712** | -0,2618 |
| Sr | 0,1493 | **0,5171** | 0,1396 | -0,0793 | 0,5415 | 0,2585 | 1 | 0,2180 | 0,0635 |
| V | 0,3482 | **0,8243** | 0,1855 | 0,2775 | 0,0325 | **0,7712** | 0,2180 | 1 | -0,1571 |
| Zn | -0,2444 | -0,1230 | 0,1317 | -0,1451 | -0,0585 | -0,2618 | 0,0635 | -0,1571 | 1 |

Significantly, Pearson's coefficient is shown between the couples Cr-V (r=0.82), Cr-Rb (r=0.71) and Cr-Sr (r=0.52), and remarkably, the strontium is moderately linked with lead (r=0,54).

### III.3.2. Statistical concentration analysis for Blida area

The relationship dendrogram based on the major elements is presented in Figure 20and constitutes of the two main groups. The first group (GM1), which includes B15 (Bouinan) and B18 (Guerouaou), is characterized by the highest values in aluminium and iron concentrations.
The second group (GM2) consists of two subgroups:
The subgroup (GM2a), consisting of B1 (El-Affroun), B2 (Boufarik), B3 (Benkhelil), B11 (Chebli), B16 (Bouinan), B24 (BeniTamou) and B35 (Blida), is characterized by lower values in aluminium and iron. The site B35 (Blida), situated at only 8m from the road leading to the center of Blida, is distinguished by the high concentration of potassium compared to other sites of the subgroup. On the contrary, the lowest concentrations of the major elements are found in the western and northern parts near B1 (El-Affroun). Other factors such as the congested weekend traffic, the landfills, and the frequent forest fires can be potential causes of the increased potassium concentrations
The highest chlorine values are located in the north of the study area at Benkhelil (B3) and Boufarik (B2), and are explained by the proximity of the sampling points to a chemical industrial plant. These points are also located about fifteen kilometres from the sea, increasing their chances of chlorine exposure. The highest chlorine concentration is recorded at the B26 (Bouarfa) site, which is linked to its proximity to the East-West

Highway (about 8m) and an agricultural area. These two elements are strongly correlated ($R2 = 0.81$). The tendency in this occurrence is related to the nature of the soil present in this area.
The subgroup (GM2b), consists of two populations. The first has the points B31, B32, B39 and B42 (Chréa), B8 (Mouzaia), B17 (Soumaa), B9 (Chiffa), B10, B13, B20 (Chebli), B30 (Ain Romana), B28 (El-Affroun), B5 (OuedAlleug), B19 (Boufarik), B27 (Blida), and B7 (Mouzaia). It is also characterized by high values of aluminium and iron but a low concentration of chlorine. These areas are probably less exposed to marine influence. The increased concentration of potassium in B8 (Mouzaia) is due to the fact that it is located in the middle of an agricultural area famous for its intensive use of chemical fertilizers and its nearness to forests and potential fires. The highest phosphorus concentrations are in Soumaa (B17). This explains the influence of local activities. The B17 sampling point at Soumaa is in the middle of agricultural fields and the high phosphorus concentration could be due to fertilizers.

The second population consists on the one hand of the sampling points B21, B23 (Boufarik), B26 (Bouarfa),and B41 (Chrea), all of which have moderate values in the elements aluminium, chlorine, iron and phosphorus. On the other hand, the sampling stations consist of points at B12 (Chebli), B6 (OuedAlleug), B25 (Boufarik), which have moderate levels in aluminium; and B37, B38 and B40 (Chréa), and B34 (Blida), which are rich in iron, potassium and phosphorus, and B14 (Chebli), B36 (Chréa), B33 (Blida), B29 (Mouzaia), and B3 (Benkhelif), which have moderate values in aluminium and iron due to the nature of the surrounding soil, but with a high cumulative concentration of iron and potassium. The increased concentrations of potassium and phosphorus in the area are influenced by the agriculture activities and the chlorine effect from the sea, which contributes to the segregation of the two groups.

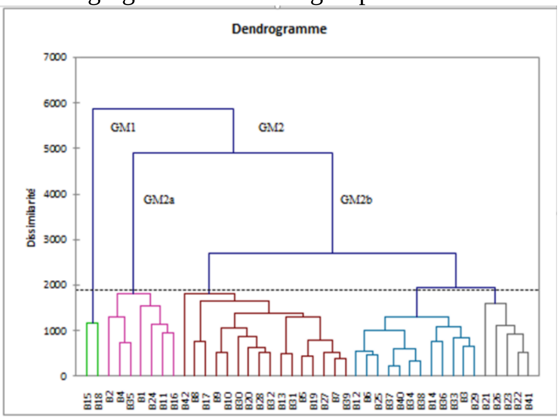


***Figure20****.Dendrogram relationships of districts based on major elements in the districts of Blida*

The dendrogram relationships based on the trace elements is presented in Figure 21.

The first group (GT1), constituted by B21 (Boufarik), B24 (BeniTamou) and B39 (Chréa), and is characterized by a high concentration in zinc. This high concentration of zinc originates due to the proximity of the sampling point located 300 m from the road leading to the agglomerations, and 250 m from the East-West Highway, which experiences significant traffic. The concentration is also affected by the existence of a metallurgical industry nearby and emission released by the residual sector (domestic heating) without neglecting the presence of landfills and coinciding with the predominant direction of the north-east wind. Those more polluted sites are probably affected by local emission.

The second group (GT2) constituted by two subgroups:

The subgroup (GT2a): The lead with a high concentration individualizes two sites; B5 (Oued El-Alleug) and B23 (Boufarik). Those two most polluted sites by lead also exhibit high values in strontium. For the B23 site's values, the situation can be explained by the very large road traffic on the East-West Highway and the soot discharged by jet engines at the military airport, as well as the fuel from vehicles coming from a station, in addition to the metallurgical and chemical industries along the highway south of the sampling site and coinciding with the predominant direction of the north-east wind.

For the B5 site, the high concentration of lead seems to come from the traffic of the RN 4 Highway connecting the agglomerations to the west (distance of 250 m), to the east (from 140 m), and to the north (from 310 m), in addition to the two service stations and the existence of an incinerator south of this sampling point.

The subgroup (GT2b): B31 (Chrea) and B35 (Blida) in the high altitude part of Blida stand out from the other subgroups bythe high level concentrations of manganese, probably influenced by forest fire. B16 (Bouinan) is also isolated from the rest because of its elevated concentration of zinc. Being near an industrial activity zone housing chemical and metallic industries and an uncontrolled landfill, B8 (Mouzaia) and B15 (Bouinan) are the two sites most affected by a high concentration level of copper.

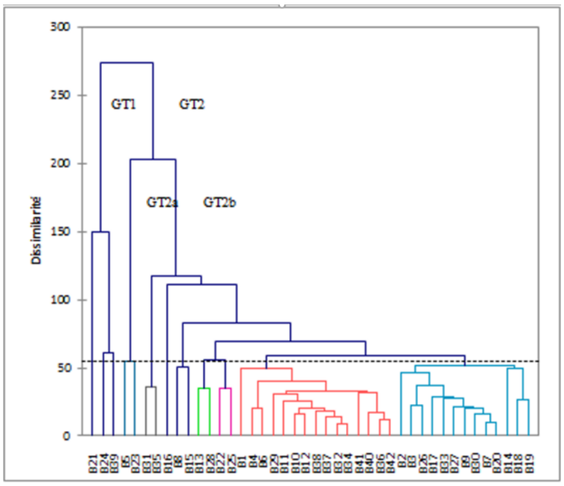


***Figure21****.Dendrogram relationships of districts based on trace elements*

The presence of high manganese concentrations characterized B31 (Chréa) and B35 in the high altitude part of Blida which are not so far from each other and are probably affected by forest fires. B16 (Bouinan) is also isolated from the rest because of its elevated concentration of zinc. B8 (Mouzaia) and B15 (Bouinan) are the two sites most affected by high levels of copper.

Strontium is found with the highest values at B13 (Chebli), B25 (Boufarik), B28 (El-Afroun) and it can be attributed to car fuel, coal burning, and waste mismanagement in these areas.

What remains is divided in two populations. The first part constitutes sites with moderate values of lead, with a concentration of more than 50 µg/g due to the high traffic in the area and and probably more waste. Related sites are B2, B19 (Boufarik), B3 (Benkhelil), B26 (Bouarfa), B17 (Soumaa), B27, B33 (Blida), B9 (Chiffa), B30 (Ain Romana), B7 (Mouzaia), B20 (Chebli), B14 (Chebli), B18 (Gueroaou). Between them, B3 (Benkhelil) and B26 (Bouarfa) are the two sites most affected by bromine. The second part constitutes 15 sites: B1 (Al-Afroun), B4, B6 (OuedAlleug), B10, B11, B12 (Chebli), B29 (Mouzaia), B34 (Blida), B32, B36, B37, B38, B40 B41, B42 (Chréa). They have the lowest concentrations of lead, which do not exceed 50 µg/g. These are the areas least affected by trace elements.

The sites B15 (Bouinan) and B18 (Gueroaou) have the highest values in chromium, rubidium and vanadium, like in location B39 (Chrea). These elements are strongly correlated but do not show formulation of the same group in the dendrogram, which is dominated by high values' isolation effect of zinc, lead, manganese, and strontium.

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### III.4. Statistical concentration analysis for Chrea natural Park

The average values, min, max and SD of concentrations obtained for the major elements (Al, Cl, Fe, K and P) and from trace elements (Al, P, Cl, K, V, Cr, Mn, Fe, Cu, Zn, Br, Rb, Sr et Pb) are given in Table 7 for the thirty-three (33) sites sampled in the urban zones surrounding the Blida district and the nine sites from the natural forest areas, including the Chréa National Park, for reference. The ANOVA One-Way technique was applied for the two populations of urban and reference zones for each analyzed element and it indicates that Cl, P, Sr, are significant. The chlorine ratio shows the proximity of urban sampled sites to the sea. The phosphorus and strontium ratios are probably influenced by the coal waste in this urban area.

***Table 7****.Min, average, max, SD, and ANOVA One-way test on concentrations values of major elements (Al, Cl, Fe, K and P) and trace elements (Al, P, Cl, K, V, Cr, Mn, Fe, Cu, Zn, Br, Rb, Sr et Pb) in µg/g obtained from the lichen Xanthoria parietina in the urban districts of Blida compared with the forest area represented by the Chréa National Park*

| Region | Al | Cl | Fe | K | P | Br | Cr | Cu | Mn | Pb | Rb | Sr | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Blida (33 sites) | | | | | | | | | | | | | | |
| Min | 4351 | 162 | 2397 | 2068 | 581 | 11 | 4 | 6 | 24 | 13 | 12 | 15 | 8 | 30 |
| Average | 9554,7 | 354,5 | 3943,4 | 3313,1 | 822,1 | 29,1 | 7,2 | 17,1 | 52,5 | 61,6 | 31,3 | 49,6 | 13,2 | 78,9 |
| Max | 15616 | 701 | 5493 | 4437 | 1486 | 61 | 10 | 80 | 161 | 244 | 60 | 103 | 19 | 416 |
| SD | 2700 | 124 | 877 | 511 | 190 | 12 | 2 | 15 | 23 | 50 | 11 | 21 | 3 | 76 |
| Median | 10145 | 319 | 4001 | 3159 | 768 | 29 | 7 | 11 | 49 | 52 | 31 | 44 | 14 | 56 |
| Chréa (9 Sites) | | | | | | | | | | | | | | |
| Min | 8177 | 119 | 2935 | 2202 | 519 | 29 | 5 | 6 | 47 | 16 | 30 | 18 | 9 | 26 |
| Average | 10281,2 | 249,4 | 3986,3 | 3197,6 | 663,0 | 37,4 | 6,8 | 7,8 | 66,7 | 27,9 | 35,1 | 30,6 | 13,8 | 62,9 |
| Max | 12399 | 376 | 5225 | 3921 | 720 | 47 | 8 | 12 | 140 | 40 | 44 | 40 | 17 | 255 |
| SD | 1305,9 | 73,7 | 642,5 | 547,2 | 67,0 | 6,8 | 1,1 | 1,7 | 29,4 | 8,1 | 4,4 | 6,8 | 2,5 | 72,7 |
| Median | 9850,0 | 236,0 | 4053,0 | 3385,0 | 682,0 | 38,0 | 7,0 | 7,0 | 55,0 | 29,0 | 35,0 | 32,0 | 14,0 | 35,0 |
| Urban Sites/Natural sites | 0,9 | 1,4 | 1,0 | 1,0 | 1,2 | 0,8 | 1,1 | 2,2 | 0,8 | 2,2 | 0,9 | 1,6 | 1,0 | 1,3 |
| ANOVA Test | NS | S | NS | NS | S | NS | NS | NS | NS | NS | NS | S | NS | NS |

NS: Non-significative S: Significative

The ratio for both copper (Cu) and lead (Pb) is more than two (2). This difference of concentration between the urban and the natural populations may be explained by the negative shift between median and average values in the urban area.

### III.5. Comparison with other cases in the world

The average (min and max) concentrations of the major and trace elements (Al, P, Cl, K, V, Cr, Mn, Fe, Cu, Zn, Br, Rb, Sr and Pb) in µg/g obtained in the lichen Xanthoria parietina in Blida compared to other cases in the world is given in Table 8.

According to [5], there are no established standards for trace element concentrations in lichens to interpret the results. The values used to compare results obtained in this study with reference values defined from the works of the literature.

The comparison values max with other cases in Algeria and elsewhere in the world is presented in Table 8

●**Chromium (Cr):** The max value in Blida (Algeria) is comparable to the max value of Val Sambre (France), but it is 14x less than the max value in Sétif (Algeria), 6x lower than the max value of Romania, 117x less than the max value of Dunkerque (France), and 120x less than the max value of Northeast Morocco. The average value and also max are not so far from the standard values given in literature. However, this low relative value is more than the value of Cr in Biel and Nabel Switzerland.

●**Manganese (Mn)**: Max value in Blida (Algeria) is similar with the Setubal peninsula (Portugal), but is 4x more than in Lille (France), 6x less than in Kocaeli (Turkey), 10x less than in Luxembourg, and 8x less than BordjBouArreridj (Algeria). The average value in the forest area is relatively less than what is measured in the urban sites in Blida and its surrounding districts.

●**Iron (Fe)**: Max value in Blida (Algeria) is 5x less than Fos-sur-Mer (France) and Luxembourg, but 1.5x more than in Northeast Morocco, 2x more than in Biel and Nabel (Switzerland), and 3x more than in the Aegean (Turkey).

●**Copper (Cu)**: the value max in Blida (Algeria) is 6x more than in Setif (Algeria), 3x more than in Northeast Morocco, 2x more than in Biel and Nabel (Switzerland), but 3x less than the registered max values in the Setubal peninsula (Portugal), in Lille (France), and 9x less than in Kocaeli (Turkey).

●**Zinc (Zn)**: The max value in Blida (Algeria) is 2x more than in Sétif and Algiers (Algeria), 3x more than in Northeast Morocco, 3x more than in Romania, 3x more than in Kosovo (Slovenia) and 4x more in the forest areas of France, 7x more than in CollineMetallifere (Italy), 5x more than in Singapore, 9x more than in Canada, 11x more than in Greenland, 14x more than in Norilsk (Russia), but 1.5 less than in Fos-sur-Mer (France), 6x less than in Dunkerque (France) and 4x less than in Lille (France).

●**Lead (Pb)**: the max value concentration of lead in Blida (Algeria) is 56x more than in Greenland, 42x more than in Russia, 21x more than in CollineMetallifere (Italy), 21x more than in Canada, 7x more than in Veneto (Italy), 14x more than in Singapore, 8x more than in the Setubal peninsula (Portugal), 3-4x more than in Fos-sur-er and the forest areas of France, 2x more than in Romania, and 2x more than in Luxembourg. Max values are similar to Tiaret(Algeria) and Kosovo. However, Blida is 3.5x less than the critical cases of Lille (France), Dunkerque (France), Morocco, and 4x less than BordjBouArreridj (Algeria), 2x less than Rabat (Morocco), 1.5x less than Dunkerque (France),and than the Kocaeli province (Turkey).

●**Vanadium (V)**: The max value concentration in Blida (Blida) is similar to the Kocaeliprovince (Turkey) and 5x more than in Tuscany (Italy), 4-5x less than DunkequeHarbore in France, 2x more than in Val de Sambre in France

●**Bromine (Br)**: The concentration registered in Blida is 3x more than in São Paulo (Brazil) and Slovenia.

●**Rubidium (Rb)**: The max values found in Blida (Algeria) are similar with those found in Slovenia but 2x more than the max value registered in Sao Paulo (Brazil).

●**Stronsium (Sr)**: The max value concentration in Blida (Algeria) is 2x more than in the forest areas of France the unique value having been obtained in the literature.

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***Table 8***. *The average (min and max) concentrations of the major elements (Al, P, Cl, K, Fe) and trace elements in µg/g obtained in the lichen Xanthoria parietinainBlida compared to other cases in the world*

| Country (region) | Al | Cl | Fe | K | P | Br | Cr | Cu | Mn | Pb | Rb | Sr | V | Zn | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Romania | | | (412-6071) | | | | (5,08-64,47) | (2,66-34,08) | | (5-75) | | | | (5-156) | [33] |
| Kosovo | | | | | | | | | | 8,67(9,1-282,1) | | | | 149,5(8-272) | [59] |
| Russia-Norilsk | | | | | | | | | | 1,26(0,78-5,79) | | | | 20,05(9,73-29,6) | [60] |
| Italy (CollineMetallifere) | | | | | | | | | | 3,88(0,68-11,20) | | | | 25,9-57,7 | [61] |
| Canada (Barrenbdlands,Nunavut) | | | | | | | | | | 6,44(0,76-19,70) | | | | 22(15-44) | [62] |
| Greenland | | | | | | | | | | 1,72(0,32-4,29) | | | | 17,65(6,48-36,9) | [63] |
| Italy (Vaneto) | | | | | | | | | | 7,66(0,8-34,1) | | | | 33,56(20-99) | [27] |
| Singapore | | | | | | | | | | 11,86(2,83-16,59) | | | | 65,58(44,17-83,16) | [64] |
| Italy (Tuscany) | | | | | | | 2,235(0,36-10,70) | | | 3,44(0,9-27,66) | | | 1,13(0,32-4,02) | 30,15(5,5-80,5) | [65] |
| Turkey (Aegean) | | | 1170(270-18930) | 3490(220-13930) | | | | | 25(8,8-350) | 4,2(0,28-170) | | | | | [42] |
| Turkey (Kocaeli-Province) | 1500(700-5300) | | 3075(1280-13550) | 4550(2000-6200) | | | | 15,9(7,74-694) | 90(40-1022) | 40(8,15-394) | | | 9,5(3-23) | 166(64,8-1678) | [66] |
| France (forest areas) | 1058,4(225,8-3605,5) | | 616,1(127,6-2226,50) | | | | 1,8(0,4-6,1) | 5,2(2,1-12,4) | 61,4(16,8-626,8) | 3,1(0,7-58,1) | | 15,2(2,9-63,6) | 2(0,4-6,8) | 30,9(9,7-114,3) | [67] |
| France (Fos-sur-Mer) | 3807(934-12861) | | 7334(1844-25399) | | | | 18(4-61) | 21(9,3-49) | 221(47-1019) | 24(3,4-75) | | | 15(2,8-40) | 178(36-625) | [68] |
| France (Dunkerque) | 1504(349-6681,7) | | | | | | 38,3(2,6-1172,4) | 19(5,1-95,5) | 556,9(45,4-6305) | 32,7(3-371,9) | | | 13,2(2,6-102) | 178,9(40,4-2407,9) | [5] |
| France (Lille) | 1092,9(221-8745,7) | | | | | | 4,6(1-45,1) | 19,1(4,7-259,2) | 54(16-309) | 31,1(1,3-873) | | | 3,6(0,3-18) | 112,8(27,9-1582,7) | [5] |
| France (Val de Sambre) | 730,7(161-1933) | | | | | | 3,8(0,9-11) | 9,5(3,9-22,1) | 57,3(20-165) | 11,5(2,4-55) | | | 3(0,7-8,2) | 74,4(23,3-267,4) | [5] |
| Portugal (Setubal peninsula) | | | 2739,5(427,6-8358,4) | 3973,08(1358,13-6970,41) | | | 107,09(2,82-345,99) | 34,9(6,9-213,2) | 50,7(22,22-174,15) | 7,73(0,83-29,82) | | | | 132,58(23,83-1045,14) | [69] |
| Slovenia | | | | 3878(2304-6188) | | 10,92(4,62-22,35) | 3,67(1,11-35,85) | | | | 16,54(3,12-57,10) | | | 95,33(45,63-182,52) | [70] |
| Brazil (São Paulo) | | 529-1052 | | 3195-5712 | | 5,52-19,89 | | | | | 9,2-27 | | | 31,9-765,5 | [71] |
| France (Z. PortaireDunkerque 2002) | | | | | | | | | | 41,05(1,5-190) | | | 14,98(1-79) | 185,93(7,2-590) | [72] |
| France (Z. PortaireDunkerque2009) | | | | | | | | | | 32,32(7,3-110) | | | 18,83(3,3-110) | 164,56(27-490) | [72] |
| Luxembourg | 769-3258 | | 1239-27816 | | | | | | 31-1613 | 4-107 | | | | | [73] |
| Switzerland (Biel and Nabel) | 387-696 | 1143-1159 | 590-2208 | 3216-4908 | 1043-3296 | | 2,68-8,22 | 9,67-34,31 | | 31-178 | | | | 85-179 | [74] |
| Morocco (Rabat – Salé) | | | | | | | | | | 29,3-415,45 | | | | 42,5-129,3 | [75] |
| Morocco (Northeast) | | | 479,976-8422,018 | | | | 21,589-1242,326 | 4,065-22,524 | | 4,065-42,05 | | | | 22,027-218,994 | [76] |
| Algeria (Algiers) | | | | | | | | | | 31,67-254,06 | | | | 60,97-260,87 | [77] |
| Algeria (Tiaret) | | | | | | | | | | 76,31-208,30 | | | | | [78] |
| Algeria (SidiBelAbbès) | | | | | | | | | | 1,3 - 10,66 | | | | | [79] |
| Algeria (Setif) | | | | | | | 87,74(26,4-143,08) | 2,9(0,6-13,6) | | | | | | 91,7(38,98-184,70) | [80] |
| Algeria(Tlemcen) | | | | | | | | | | 378.96-1192,13 | | | | | [81] |
| Algeria (Bordj Bou Arreridj) | | | 43184(7000-73000) | | | | 313(127,9-472,1) | 49,8(23-87) | 671,9(300 – 1300) | 98,4 (6-208) | | | | 476,6(323,9 – 983,5) | [82 ] |
| Algeria (Blida)**This study** | 9710(4351-15616) | 332,1(118,7-701,3) | 3953(2397-5493) | 3288(2068-4437) | 788(518,9-1486) | 30,94(11,47-61,22) | 7,11(4,08-10,05) | 15,05(5,83-79,86) | 55,62(24,3-161,3) | 54,31(12,8-243,51) | 32,16(12,02-60,35) | 45,53(15,44-103,40) | 13,33(7,85-19,29) | 75,51(25,53-415,91) | **This study** |

**IV. CONCLUSION**

This study is the first of its kind carried out in Algeria in the Blida area, the second largest city near the capital, with over a million inhabitants and which has basic, natural and agricultural vocations. For the biomonitoring of air quality, samples of the lichen Xanthoria parietina were collected from trees in 42 sites situated in Blida and its surrounding districts. Five (5) major elements: Al, P, Cl, Fe, K., and nine (9) trace elements: V, Cr, Mn, Fe, Cu, Zn, Br, Rb, Sr, Pb were analyzed by X-ray fluorescence and have been validated.

The 42 prospected sites can be classified as below: five (5) sites are affected by high level of Zn with a concentration of more than 100µg/g, 200µg/g, and 400µg/g in various areas. Even the forest area is affected, with more than 200 µg/g of Zn. Two other sites are affected by high levels of copper with a concentration of more than 60µg/g. Two other sites have concentration values > 100µg/g in strontium and three others are affected by both strontium and lead. Two sites in the forest area are affected by manganese, with a concentration level of more than 100µg/g. There are two (2) sites affected strongly by a concentration of more than 200µg/g in lead, and thirteen other sites that have lead concentration levels exceeding 50 µg/g. Only fifteen (15) sites have lower than 50µg/g concentration values of lead. All prospected districts are actually affected by at least of one or two element ratios at higher than normal concentrations due to the effervescence of industrial activities and the intensification of traffic on roads. Poor waste disposal systems are, in general, suspected of contributing factors, hence the situation should be improved in the future if proper waste collecting and incineration procedures are adopted and generalized. Even the forest area, including the Chréa National Park, is affected due to recurring fires and high traffic frequency. This situation requires more efforts and facilities to manage the flux of visitors to the park throughout the year.

Mapping elements shows that propagation is under dominant wind influence. While chlorine is under maritime influence, others elements are clearly affected by local emission and require more attention. The vocation should be respected because only 43% of the industry is devoted to agriculture and food transformation. New tendencies are registered in other industrial fields. If not controlled, the environmental quality will regress under the effect of urbanisation and roads intensification. Lichens constitute a nature-offered sensor to enhance air quality. Obtained values of heavy metals and trace elements should be considered as a basic data and quantifying their levels in soils and water remains an urgent matter.If not controlled, the environmental quality will regress under the effects of urbanisation and roads intensification.

Lichens constitute a nature-offered sensor to monitor air quality. Obtained values of heavy metals and trace elements should be considered as a first step in measuring our air quality; and quantifying their levels in soils and water should remain an urgent task because lichen are absent in highly populated urban sites.

The use of Xanthoria parietina confirms moderate air pollution. It will be interesting to explore sites where these lichen despair, indicating extreme degrees of environmental alteration, as well as the impact of pollution emission on soil and in aquatic ecosystems (rivers and irrigation systems). The intensification of measurement sites and adoption of new techniques are necessary to help management programs. The urbanization plan, the location of industrial zones, and the public landfills must be reconsidered urgently to stop the regression of the quality of the area.

The results of this study show that Blida and its surroundings are experiencing increasingly strong urbanization and industrialization. And even if the district of Chréa is set apart because of the national park headquarters, all other districts are not spared the excessive use of fertilizers and pesticides. Another major problem remains that of waste and fire management. Also, the hypothesis that the park of Chréa is a reference zone of weak human and industrial activity is questioned, in particular for the lead. Other elements such as aluminum and iron are certainly related to the nature of the earth's substrate. As for zinc and manganese, forest fires are probably the main cause.

However, the practical value of biomonitoring lies in the ease of its being realized quickly and cheaply compared to a city or even to the scale of a region. In suburban or industrial areas, where sensors are lacking, as is the case in Blida, biomonitoring remains an opportunity to measure atmospheric pollution caused by major and trace elements. The mapping of the 14 elements shows a general trend that proves their displacement away from their sources of emission. At the level of the districts surveyed, and whatever their vocation, the sources of emission are of various origins. Agricultural activity is also not to be neglected. The industrial network, the installation of equipment, and road access are one part of the equation; and the management of the waste generated both industrially and domestically is another, and affects almost all the townships. It is appropriate to review the need to respect the communal vocations and revise its industrial policy. The question becomes: Should we continue to provide all districts with zones of industrial activities without prescribing rules and restrictions? It is imperative to relocate polluting industries, monitor their emissions, and eradicate landfills located on the edge of the townships and close to agglomerations, to reduce the risk of air pollution as well as that of surface

water and groundwater, thus protecting water resources, the health of the general population and animals, and the sustainable state of ecosystems in general.
Finally, it should be noted that this study concerns only the points where Xanthoria parietina were taken. There is no doubt that heavy metal concentrations are higher in downtown Blida where there are no more lichens that can withstand pollution. The listing (of sampling sites codifying the districts) is here as a proof of the need to direct the environmental management towards the classification of the districts prospected and to widen the samples to the other non-prospected districts.On the local level, we recommend,in order to stop the ill-effects of urbanization, the administrative borders of districts should be revised to take into consideration the impact of pollution. On a global level, the cosmopolitan nature of the species makes it an indicator of economic pollution worldwide compared to other aerosol collection modes. The QC/QA procedure has shown that the XRF technique is suitable for use ingeneral pollution monitoring.

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## V.References

1. Nriagu, J.O. A silent epidemic of environmental metal poisoning. *Environement.Pollution* 50 (1988)139-161.
2. Burnol, A. ; Duro, L. ; Grive, M. Eléments traces métalliques: Guide méthodologique, Rapport d'étude 28/06/2006 INERIS-DRC n°06-66246\ DESP-Rola-p53.
3. Rzepka, M.A.; Cuny, D. Plant and fungal biosurveillance of atmospheric ETMs. Clean Air N ° 75 2nd half of (2008)66.67.
4. OMS. Burden of disease from the joint effects of household and ambient air pollution for 2012.Geneva. p4.
5. Occelli, F. ; Cuny, M.A. ; Devred, I. ; Deran, A. ; Quarré, S. ; Cuny, D. Etude de l'imprégnation de l'environnement de trois bassins de vie de la région Nord-Pas-de-Calais par les éléments traces métalliques vers une nouvelle utilisation des données de bio surveillance lichénique. Pollution Atmosphérique N°220 Octobre-Décembre (2013)10.
6. Occelli, F. Systèmes d'Information Géographique et Lien Environnement – Santé SIGLES Contribution au développement d'outils cartographiques d'aide à décision face aux risques sanitaires liés à l'environnement. Thèse de Doctorat Université de droit et Santé de Lille 2, (2014) . 19-20-40.
7. Catinon, M. La détermination de la Pollution Atmosphérique Métallique : Etude critique de l'utilisation des écorces d'arbres. Thèse de doctorat, Université Grenoble 1, (2011). 36.
8. Brunialti, G.; Frati, L. Biomonitoring of nine elements by the lichen Xanthoria parietina in Adriatic Italy: A retrospective study over a 7 year time span. Science of Total Environment 387 (2007) 289-300.
9. Garrec, J. P.; Van Haluwyn, C. Bio surveillance végétale de la qualité de l'air : Concepts, Méthodes et Applications. Editions Tec et Doc, Lavoisier, Paris (2002) 118.
10. Benard, A. ; Durif, M. ; Van Damme, L.Utilisation d'une technique de bio surveillance pour évaluer les retombées de métaux lourds. INERIS-DRC (2004) -04-55891-AIRE-n°0565-MDu/LVa, Paris, 61p.
11. Van Haluwyn, C. ; Cuny, D. ; Garrec, J.P.Introduction générale Définitions, concepts et enjeux généraux de la biosurveillance de la qualité de l'air. Pollution Atmosphérique, Numéro Spécial (2001) 7-13.
12. Cuny, D.; Rzepka, M. A.; Van Haluwyn, C. Introduction to plant and fungal biomonitoring of air quality, concept and interest - Spectra Analyze (2008) n ° 264: 31-35.
13. Chakhparonian, M. Développement d'un système biologique de surveillance de la pollution atmosphérique: étude sur des populations d'Arabidopsisthaliana sous conditions contrôlées. Diplôme de biologiste, Université de Lausanne(1995) 48.
14. Conti, M.E. ; Cecchetti, G. Biological monitoring: lichens as bioindicators of air pollution assessment - a review. *Environmental Pollution* 114(2001) 471-492.
15. Zhu, Y.; Zeng, G.; Zhang, Y.; Tang, L.; Chen, Y.; Cheng, M.,;Zhang, L.; He.L.;Guo, Y., He.X.; Yi-bin Heab, M . Highly sensitive electrochemical sensor using a MWCNTs/GNPs-modified electrode for lead (II) detection based on Pb2+-induced G-rich DNA conformation, Analyst (2014) 139, 5014-5020.
16. Zeng, G.; Zhu, Y.; Zhang, Y.; Zhang, C.; Tang, L.; Guo, P.; Zhang, L.; Yuan, Y.; Chenab, M.; Yangab, C. Electrochemical DNA sensing strategy based on strengthening electronic conduction and a signal amplifier carrier of nano Au/MCN composited nanomaterials for sensitive lead detection, *Environement Science Nano* 3(2016) 1504-1509.
17. Bargagli, R. Trace elements in terrestrial plants. An eco-physiological approach to biomonitoring and biorecovery. Berlin-Verlag Berlin Heidelberg,. New York, (1998) 179–206.
18. Bari, A.; Rosso, A.; Minciardi, M. R.; Troiani , F.; Piervittori, R. Analysis of heavy metals in atmospheric particulates in relation to their bioaccumulation in explanted Pseudeverniafurfuraceathalli. *Environmental Monitoring and Assessment*, 69(2001)205–220. doi:10.1023/A:1010757924363.
19. Van Haluwyn, C. ; Lerond, M. La lichenosociologie dans l'évaluation de la qualité du milieu, Colloques phytosociologique XV : Phytosociologie et conservation de la nature (1987) 233-250.
20. Garty, J. Biomonitoring atmospheric heavy metals with lichens: theory and application. Critical Review. *Plant Science*. 4 (2001) 309–371.
21. Adamo, P.; Giordano, S.; Vingiani, S.; Castaldo, R.; Cobianchi, Violante, P. Trace element accumulation by moss and lichen exposed in bags in the city of Naples (Italy), *Environmental Pollution*, 122 (2003) 91–103.

22. Godinho, R.M.; Verburg, T.G.; Freitas, M.C.; Wolterbeek, H.T. Accumulation of trace elements in the peripheral and central parts of two species of epiphytic lichens transplanted to a polluted site in Portugal. *Environmental Pollution* 157(2009).
23. Wolterbeek, H.T.; Garty, J.; Reis, M.A.; Freitas, M.C. Biomonitors in use: lichens and metal air pollution. In: Markert, A.M.B.B.A., Zechmeister, H.G. (Eds.), Trace Metals and Other Contaminants in the Environment.6 (2003). Elsevier, pp.377–419.
24. Sarret, G.; Manceau, A.; Cuny, D.; Van Halewyn, C.; Deruelle, S.; Hazemann, J.L.; Soldo, Y.; Eybert-Berard, L.; Menthonnex, J.J. Mechanisms of lichen resistance to metallic pollution, *Environment Science Technology*, 32 (1998) 3325–3330.
25. Wolterbeek,B. Biomonitoring of trace element air pollution: principles, possibilities and perspectives. *Environment Pollution* 120(2002) 11–21.
26. Rhoades, F. M. Review of Lichen and Bryophyte: Elemental content literature with reference to Pacific Northwest Species United States Department of Agriculture Forest Service (1999) 125.
27. Nimis, P.L.; Lazzarin, G.; Lazzarin, A; Skert, N. Biomonitoring of trace elements with lichens in Veneto N.E. Italy, *ScienceTotal Environment*.255 (2000) 97–111.
28. Nimis, P.L. Checklist of the lichens of Italy 3.0, University of Trieste, Dept of BiologyIN3.0/02(http://dbiodbs.univ.trieste.it) 2003
29. Agnan, Y. Bioaccumulation et la bio indication par les lichens de la pollution atmosphérique actuelle et passée en métaux et en azote en France Sources, mécanismes et facteurs d'influence, Thèse de Doctorat Université de Toulouse, (2013) 26-63.
30. Agnan, Y . ; Probst, A. Séjalon-Delmas. Evaluation of lichen species resistance to atmospheric metal pollution by coupling diversity and bioaccumulation approaches: A new bioindication scale for French forested areas, Ecological Indicator January (2017). 72 : 99-110, Doi:10.2016/j.ecolin.2016.08.006.
31. Kirschbaum, U. ; Wirth, V. Les lichens bioindicateurs les reconnaître pour évaluer la qualité de l'air. Ed. Eugen Ulmer, Paris(1997) 128.
32. Halimi, A. L'Atlas Blidéen : Climats et étages végétaux. O.P.U., Alger. (1980) 523.
33. State, G.; Poescu, I.V.; Gheboianu, A.; Radulescu, C.; Dullama, I.; Bancuta, I. Stirbescu. Identification of air pollution elements in lichens used as bioindiactors by the XRF and AAS methods Rom. *Journal. Physic*., Vol.56 (2011) , Nos.1-2, p.240-249 Bucharest, 2011.
34. Menezes, M.A.B.C.; Jacimovic, R. Validation of the k0_IAEA software using SMELS material at CDTN/CNEN, Brazil. Journal Radioanal Nucl Chem 278 (3)(2008) 607-611.
35. Burrough, P. A. Principles of Geographical Information Systems for Land Resources Assessment, Oxford University Press, New York (1986)189-190.
36. McBratney, A.B.; Webster, R. Choosing functions for semi-variograms of soil properties and fitting them to sampling estimates. *European Journal . Soil Science*. 37,(1986) 4 : 617-639.
37. Nimis, P.L. ; Andressi,S. ; Pittao, E. The performance of two lichens species as bioaccumulators of traces metals. The Science of the Total Environment 275 (2001) 43-51.
38. Samsonov, Y.N.; Koutesengii, K. p.; Makarov, V. I.; Ivanov, A.V.; Ivanov, V.A.; McRae, Dj.; Conard, S. G.; Baker, S. P.; Ivanova, G. A.; USDA, F.S. Particulate emissions from fires in central siberian scots pine forests. *Canadian Journal of forest research* 35(2005) 2207-217.
39. Tsurumi, M. Sources of elements in cedar bark collected near a highway (Japan). *The Science of the Total Environment*, 86 (1989) 239-250.
40. Birmili, W.; Allen, A. G.; Bary, F.; Harrison, R. M. Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environmental Science Technology*.40(2006) 1144-1153.
41. Rauch, S.; Morrison, G.M.; Motelica-Heino, M.; Donard, O.F.X.; Muris, M. .Elemental Association and Fingerprinting of Traffic-Related Metals in Road Sediments. *Environmental Science Technology* 34(2000) 3119-3123
42. Yenisoy- Karakas, S.; Tuncel, S.G. Geographic patterns of elemental deposition in Aegean region of Turkey indicated by lichen, Xanthoria parietina (L) Th. Fr. *Science of Total Environment* 329 (2004) 43-60.
43. Andraud-Dieu, A. Recherche de molécules antimicrobiennes d'origine lichénique : Etude phytochimique de trois lichens, approche synthétique de deux composés actifs. Thèse de Doctorat, Université de Limoges (2015) 341.
44. Nieboer, E.; Richardson, D.H.S.; Tomassini, F.D. Mineral uptake and release by lichens: an overview. Bryologist 81: 226- 246.
45. Rakotondramanana, H.T.; Randriamanivo, L.V.; Andriambolona, R.; Rasolofonirina, M. Studies of particulate matter and heavy metals of urban air pollution in Antananarivo city, Madagascar using total reflexion X-ray fluorescence. Pollution atmospherique n°178-Avril-Juin( 2003) 273-283.
46. Plat, H.; Krenn, B. E.; Wever, R. The bromoperoxidase from the lichen Xanthoria parietina is a novel vanadium enzyme. *Biochemy. Journal* 248 (1987) 277-279.
47. Kabata-Pendias, A.; Pendias, H. Trace elements in soils and plants. CRC Press, Inc. Boca Raton (1984) 315.
48. Lin, C.C.; Chen, S. J.; Huang, K.L.; Hwang, W.I.; Chang-Chien, G.P.; Lin, W Y. Characteristic of metals in nano/ultrafine/fine/coarse particles collected beside a heavily trafficked road. *Environmental Science. Technology*., 37 (2005).
49. De Miguel, E.; Llamas, J.F.; Chacon, E. ; Berg, T. ; Larssen, S. ; Royset, O. ; Vadset, M. Origin and patterns of distribution of trace elements in street dust: unleaded petrol and urban lead. *Atmospheric Environmental*., 31 (1997) 2733-2740.
50. Sternbeck, J.; Sjodin, A.; Andreasson, K.. Metal emissions from road traffic and the influence of resuspension - results from two tunnel studies. Atmosheric Environmental. 36(2002) 4735-4744. http://dx.doi.org/10.1016/S1352-2310(02)00561-7
51. Weckwerth, G. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). *Atmospheric Environmental* 35(2001) 5525-5536.
52. Gydesen, H.; Pilegaard K.; Rasmussen, L.;Rühling,A. .Moss analysis used as a means of surveying the atmospheric heavy metal deposition in Sweden, Denmark and Greenland. Bulletin Statens Naturvardsverket 1670 (1983) 44.
53. Forget, E.; Courchesne, F.; Kennedy, G.; Zayed, J. , Response of blue spruce (Piceapungens) to manganese pollution from MMT, Water. Air and Soil Pollution, 73 (1994) 319-324.
54. Semadi., A. Effets de la pollution atmosphérique (pollution globale, fluorée et plombique) sur la végétation dans la région de Annaba(Algérie). Thèse Doctorat d'État. Université Pierre et Marie Curie (1989) Paris :339.
55. Rahali, M. Etude de la pollution plombique et globale dans la région d'Alger en utilisant les lichens comme indicateurs biologiques. Thèse de Doctorat d'Etat. INA (2003), Alger, 302.

56. Harrison, R.M.; Tilling, R.; Callen Romero, M.S.; Harrad, S.; Jarvis, K.. A study of trace metals and polycyclic aromatic hydrocarbons in the road side environment.*Atmospheric Environmental*., 37(2003) 2391-2402.
57. Councell, T. B.; Duckenfield, K. U.; Landa, E. R.; Callender, E. Tire-wear particles as a source of zinc to the environment.*Environ.Science Technology*. 38(2004) 4206 4214.
58. Baturin, G. N. Phosphorites on the Sea Floor. Volume 33 1st Edition, *Elsevier Science*, January (1982)342.
59. Lella, L. A.Di.; Frati, L.; Loppi, S.; Protano, G . ; Riccobono, F.( 2004). Environmental distribution of uranium and other trace elements at selected Kosovo sites. Chemosphere. 6 (2004) 861–865.
60. Allen-Gil, S. M.; Ford J.; Lasorsa, B K..; Monetti, M.; Vlasova, T.; Landers, D. H. Heavy metal contamination in the Taimyr Peninsula Siberian Arctic . *Science Total Environmental* 201 (2003) 119-138.
61. Bargagli, R.; Mikhailova I. Accumulation of inorganic contaminants. In: Nimis, P. L.; Scheidegger, C.; Wolseley, P. (Eds.). Monitoring with Lichens - Monitoring Lichens, Kluwer/NATO. Science Series, Dordrecht (2002) 65-84.
62. Chiarenzelli, J.; Aspler, L.; Dunn, C.; Cousens, B.; Ozarko, D.; Powis, K. Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the Central Barrenlands, Nunavut, Canada, Appl. Geochem. 16 (2001) 245–270
63. Riget, F.; Asmund, G.; Aastrup, P..The use of lichen (Cetrarianivalis) and moss (Racomitriumlanuginosum) as monitors for atmospheric deposition in Greenland". Science Total Environmental 245 (2000) 137–148.
64. Tan,O.H.Ng. B. C.; Obbard, J.P. Lichens as bioindicators of atmospheric heavy metal pollution in Singapore. Environment .Monitoring. Assessement 123 (2005) 63-74.
65. Scerbo, R.; Ristori, T.; Possenti, L.; Lampugnani, L.; Barale, R.; Marchigiani, C.Lichen (Xanthoria parietina) biomonitoring of trace element contamination and air quality assessment in Pisa Province (Tuscany, Italy)". *Science Total Environment* 286 (2002) 27–40.
66. DogrulDemiray, A.; Olcubal, I.; HakanAkyol, N.; Çabonoglu, G. Biomonitoring of airborne metals using the lichen Xanthoria parietina in KOCAELI PROVINCE,Turkey. Ecological indicators 18 (2012) 632-643.
67. Agnan, Y. ; Séjalon-Delmas, N. ; Claustres, A. ; Probst, A. Investigation of spatial and temporal metal atmospheric deposition in France through lichen and moss bioaccumulation over one century. *Science of The Total Environment*, May 529 (2015) 285-296.
68. Dron, J.; Austruy, A. ; Agnan, Y. ; Ratier, A. ; Chamaret, P. Biomonitoring with lichens in the industrial oportuary zone of Fos-sur-Mer (France): Feedback on three years of monitoring at a local collectivity scale. Pollution atmosphérique N° 228 - Janvier-Mars (2016)
69. Augusto, S.; Pinho, P.; Branquinho C.; Pareira, M. J; Sores, A.; Catarino, F. Atmospheric Dioxin and Furan deposition in relation to land used and other pollutants: A survey with lichens. *Journal of atmospheric chemistry* 49 (2004) (1-3): 53-65, .
70. Jeran, Z.; Mrak, T.; Jacimovic, R.; Batic, F.; Kastelec, D.; Mavsar, R.,;Simoncic, P. Epiphytic lichens as biomonitors of atmospheric pollution in Slovenian forests. *Environmental pollution* 146(2007) 324-331.
71. Saiki, M. ; Alves, E.R.; Marcelli, M.P. Analysis of lichen species for atmospheric pollution biomonitoring in the Santo Andre municipality, São Paulo, Brazil. *Journal of radioanalytical and nuclear chemistry*, Vol, 273, N°3(2007)543-547.
72. Cuny, M.A. Evolution spatiale et temporelle des concentrations en éléments traces métalliques de thalles de Xanthoria parietina récoltés sur la zone industrialo-portuaire de Dunkerque. Air pur- N°77(2009) 43-49
73. Hissler, C. ; Stille, P.; Krein, A.; Geagea, M.L.; Perrone, T.; Probst, J.L.; Hoffmann, L. Identifying the origins of local atmospheric deposition in the steel industry basin of Luxembourg using the chemical and isotopic composition of the lichen Xanthoria parietina. *Science of the Total Environment* 405(2008)338-344
74. Herzig, R.; Liebendorfer, L.; Urech, M.; Ammann, K.. Passive biomonitoring with lichens as a part of an integrated biological measuring system for monitoring air pollution in Switzerland.*Journal environment, Anal.Chem* vol. 35 (1989) 43-57.
75. OualiAlami, F. ; Elabidi, A. ; Mouhir, L. ; Fekhaoui, M. ; Serghini, A. Utilisation des lichens comme bio-indicateurs de la pollution atmosphérique par le plomb, cadmium et zinc de la région de Rabat-Salé-Zemmour-Zaër (Maroc) *Afrique Science* 10 (3) (2014) 89 – 106.
76. El Rhazoui, G.; Divakar, P. K.; Crespo, A.; Tahiri, H. ; El-Alaoui-Faris, F. Xanthoria parietina as biomonitor of airborne heavy metal pollution in forest sites in the north east of Morocco. Lazaroa 36(2015) 31-41.
77. Sarmoum, M. ; Djebbar, R. ; Latreche, K.. Bioaccumulation de trois métaux lourds (Pb, Zn et Cd) par le lichen, Xanthoria parietina, dans la région Algéroise. *Revue Ecologie-Environnement* ISSN: 1112-5888 : 10 (2014) 27-28.
78. Maatoug, M.; Medkour, K.; Ait Hamou, M.; Ayad, N, . Cartography of atmospheric pollution by the lead from road traffic using transplantation of lichen bioaccumulation Xanthoria parietina in Tiaret city (Algeria). Atmospheric pollution N ° 205-January-March 2010 p93
79. Belhadj, H. ; Hellal, B. ; Ayad, N. ; Ayyach, A. Quantification de l'émission de plomb dans le milieu urbain de Sidi Bel-Abbès (Algérie occidentale). *European Scientific Journal*( 2015) 11(6) 8-94.
80. Douibi, C.; Ramdani, M.; Khelfi, A.; Benharket, R.; Lograda, T.; Chalard, P. Biomonitoring of heavy metals by lichens in Setif area, east of Algeria. United *journal environmental science and toxicology* vol.1(1) August (2015) 001-013.
81. Berrayah, M. ; Maatoug, M. ; Azzaoui, M. ; Diallo, O., Sidibé, A. ; Manaa, K. H. Bio surveillance de la qualité de l'air d'un milieu urbain par des mousses et des lichens. Cas de la ville de Tlemcen (Algérie). *European Scientific Journal* ( 2016) 12 (9) 151-163.
82. Adjiri, F. ; Ramdani, M.; Lograda, T. ; Chalard, P., Bio-monitoring of metal trace elements by epiphytic lichen in the BordjBouArreridj area, east of Algeria. Der PharmaChemica,(2018) 10 (3) 1-8.

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