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Spatial Mapping of Heavy Metals Using Lichen Bioaccumulation Capacity to Assess Air Contamination in Morocco

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ABSTRACT

Spatial mapping of the distribution of heavy metals was performed with the Inverse Distance Weighted technique (IDW) of ArcGis-10 information system (GIS).We propose an innovative study based on information system technology and lichen biomonitoring to assess air pollution. The results demonstrated that the contamination of heavy metals (HM) fluctuates with certain hotspots with a high concentration of Cr, Pd, Cu, Cr, and Fe.The spatial mapping showed that "SidiYayha El Gharb" is the most contaminated area not only due to lithogenic sources but also from industries and traffic. Spatial mapping shows that the environment is highly affected by industrial discharges, and remediation activities should be carried out urgently to prevent serious health problems and ecological disasters.

INTRODUCTION

Air quality can be modified by pollutants either of natural or anthropological origin. Heavy metals(HM) contamination has been recognized as a serious pollution problem (Tchounwou et *al*.,2012). Because of their toxicity, pervasiveness, persistence and non-biodegradable nature, heavy metals exert considerable biological effects at many levels (Singh and Chandel,2006) and can be considered as serious health and environmental threats (Wu et *al*., 2010).

The concentration of elements, particularly trace elements, in lichens is used as an important parameter in biomonitoring of atmospheric deposition due to the direct correlation between trace element concentrations in lichens and the environment (Bari et *al*., 2001; Nash III et *al*., 1995). However, data from environmental contamination are very sparse and air-monitoring network insufficiently expanded to have a clear image of the situation.

Bioaccumulation of trace elements in lichens occurs through various mechanisms including surface complexation, biomineralisationand physical trapping in the intercellular spaces of the medulla (Nash III, 2008). The whole surface of the thallus is involved in the absorption so that elements present in the atmosphere as well as those present in the substrate can penetrate into the lichens' bodies (Basile et *al*., 2008; Nash III, 2008). Because lichens lack root systems, it's widely believed that atmospheric deposition is the main source of elements in the thalli (Bajpai and Upreti, 2012).

Morocco is a developing country that needs an expansion of its infrastructure and the exploitation of more energy. The related activities generate large availability and transfer of trace elements and other forms of pollutants (ElKhoukhi et *al*., 2004).With increasing urbanization and industrialization, Morocco is becoming heavy metal producer, resulting in the contamination of air and other abiotic compartments According to the results of many studies, lichens, are the most suitable biological matrix for the biomonitoring purposes. The spatial mapping could be an effective approach to support decision making for regional contaminated forest and urban area (El Khoukhi et *al*., 2004)

In this study, we used epiphytic lichens as bio-accumulators to reveal air contamination in Morocco. We measured the total concentrations of 5 HM and the data obtained were used to perform a spatial interpolation that can be associated further with health and epidemiological data. Our main objectives are to *i)* identify the origin of trace elements in lichens and*ii)* produce maps with environmental blackheads.

MATERIALS AND METHODS

Study area

The study area is located on the Atlantic coast between Kenitra and Mohammedia (Fig. 1), Morocco. It has a Mediterranean climate with oceanic influences. The summer is dry and sunny, but banks of mist and dew, are both quite common during this period. However, rainfall is very variable between the north and the south. The total mean annual rainfall is 600 mm in Kenitra, 560 mm in Rabat and 400 mm in Casablanca. Temperatures are rather similar, the average temperature in January is 12-13°C; while in summer it is around 23°C.The prevailing winds are from South-West (SW) to North-East (NE).

In addition to intensive agricultural activities and a well-developed road network supporting heavy traffic, the area is very industrialized (wood processing, road construction and petrol refinery and cement production,etc).

Sampling and chemical analysis

Due to their bioaccumulation capacity (Shukla et *al*., 2012), samples of lichens: *Xanthoria parietina* and *Evernia prunastri* were collected from 20 localities in the northeast of Morocco especially in forest sites. Lichens have been prepared and cleaned from dust and analyzed in the lab with inductively coupled plasma (ICP-AES) and atomic absorption spectrometry (AAS) to determine heavy metals (Fe, Cr, Zn, Pb and Cu) concentrations.

Atomic absorption spectrometry analysis

Thalli were put in the oven to dry at 120°C. The dried samples of *E. prunastri* were then ground to a powder and separated into 0.5 g amounts for metal analysis. Lichen samples were chemically analyzed after extraction with a mixture of HCl and HNO_3 (3:1) and heating to 80° for 24h. Digestion was completed with the addition of a few drops of perchloric acid. This digest was filtered and the filtrate diluted. The total metal concentrations in the solutions were determined by using a PerkinElmer 2380 spectrometer in a flame correcting for Ca, Si and Al with HACH DR 30.

Inductively coupled plasma analysis

Lichens samples were ashed in glass vials at 550°C in a muffle furnace. The resulting ash was digested in an acid mixture of 8 ml of 65% HNO_3, 2 ml of 35% H_2O_2 and 0.5 ml of 38-40% HF of approximately 200 mg dry weight in a microwave oven in preparation for the analysis

Data analysis

Geo–statistics interpolation and mapping was carried throught the Inverse Distance Weighted (IDW) technique by using ArcGIS10. IDW method is commonly used in spatial interpolation and has been introduced for the contaminated site assessment (Chen et *al*., 2015). This method assumes that the influence of the variable being mapped decreases with distance from its sampled location and relies mainly on the inverse of the distance raised to a mathematical power which controls the significance of known points on the interpolated values based on their distance from the output point (Watson and Philip, 1985). It is a type of deterministic method for multivariate interpolation with a set of known scattered points. The values assigned to unknown points are calculated based on the weighted averages of values available at known points. It applies the inverse distance to each known point when assigning weights, given by

$$Z = \sum_{i=1}^{n} \frac{1}{(D_i)^p} Z_i / \sum_{i=1}^{n} \frac{1}{(D_i)^p}$$

where Z denotes the value of the interpolation points, $Zi(i= 1 \sim n)$ is the value of the sample points; n denotesthe number of calculated sample points; Di is the distance from sample point I to the interpolation point and $p$is a positive power parameter determined by the minimum mean absolute error and significantly influences the outcome of interpolation. Additionally, '*n-1*cross validation' was implemented to ensure the IDW interpolation accuracy in this study (Bin et *al*., 2017).The outputs of HM were subjected to Kriging interpolation and mapped to visualize spatial patterns. The method generates 5 monometallic maps, which can be considerate as a data of air contamination based on lichens biomonitoring.

RESULTS AND DISCUSSION

Heavy metal concentrations in epiphytic lichens

Concentrations of elements in lichens recorded in this study (Table 1) were generally higher than the values found in the literature for different lichen species from different locations, even in urban, forest and industrial sites (Agnan et *al*., 2013; Rizzio et *al*., 2001). This finding could suggest a much higher crustal particulate input in the study area due to a greater impact of human activities on natural element cycles. A variety of human activities in the study area has released substantial quantities of heavy metals particulates into the atmosphere.

Agglomerative hierarchical clustering (AHC) AHC analysis (Fig. 2) was performed using an Excel

Table 1: Concentration of heavy metals in lichen thallus in mg/Kg

Station	*Sample Code*	*Zn*	*Pb*	*Fe*	*Cu*	*Cr*
Sidi Yahya ElGharb	S1	1366 ± 0.62	45.75 ± 0.77	15000 ± 443.84	13.86 ± 0.01	1774 ± 0.96
Kenitra	S2	85 ± 2.99	5,7 ± 0.17	1990 ± 3.10	32.5 ± 0.31	570.33 ± 8.50
Rabat (Forêt Ibn Sina)	S3	95 ± 0.79	2.85 ± 0.06	2640 ± 4.54	66.66 ± 0.72	59.98 ± 0.73
Mehdia	S4	69 ± 0.48	4.27 ± 0.05	2700 ± 99.83	31.96 ± 0.94	404.2 ± 1.947
Dar Essalam	S5	67 ± 0.48	4.03 ± 0.016	1360 ± 2,07	7,34 ± 0.18	17.99 ± 0.82
Harhoura	S6	103 ± 0,62	4,85 ± 0,08	2050 ± 10.80	42.65 ± 0.71	716.63 ± 1.09
Plage des Nations	S7	109 ± 0.89	5.62 ± 0.18	2150 ± 3.60	17.64 ± 0.01	478.74 ± 1.73
Plage Sidi Abed	S8	25 ± 0.65	4.32 ± 0.21	1120 ± 4.28	13.07 ± 0.12	868.99 ± 1.79
Bouznika	S9	92 ± 0.40	27.89 ± 0.36	3150 ± 3.49	38.31 ± 0.24	683.99 ± 1.79
Forêt Mansouriya	S10	77 ± 0.48	27.6 ± 0.19	2450 ± 58.49	30.05 ± 0.48	675.61 ± 0.81
Mohammedia du côté de la zone industrielle	S11	108 ± 28.52	4,6 ± 0.12	1550 ± 5.28	31.89 ± 0.06	80.14 ± 0.66
Forêt provinciale de Kenitra	I1	218.99 ± 1.52	22.82 ± 1.43	8422.01 ± 12.42	22.52 ± 1.27	1242.32 ± 40.34
Forêt urbaine de Kenitra	I2	121.67 ± 0.84	17.059 ± 1.17	3339.82 ± 0.91	7.95 ± 0.48	257.89 ± 1.25
Forêt de Sidi Boughaba	I3	42.84 ± 1.08	2.852 ± 0.10	1974.96 ± 0.56	4.69 ± 0.11	74.98 ± 0.11
Forêt de Mkhinza	I4	38.34 ± 1.17	15,74 ± 0.52	1591.68 ±1.07	4.06 ± 0.57	142.054 ± 1.027
Ceinture Verte de Temara	I5	110.99 ± 0.57	42.05 ± 1.02	5744.53 ± 1.27	85.14 ± 1.04	183.38 ± 1.19
Ceinture Verte proche de Sidiel Abed	I6	38.77 ± 0.67	7.22 ± 0.78	851.34 ± 0.85	3.14 ± 0.07	32.995 ± 0.70
Skhirate	I7	25.08 ± 1.35	6.23 ± 0.56	1157.24 ± 1.42	4.61 ± 0.67	21.58 ± 1.41
Forêt de Bouznika	I8	31.17 ± 3.53	22.63 ± 1.06	1872.03 ± 20.2	20.12 ± 0.70	68.15 ± 2.12
Forêt de Mohammedia	I9	22.02 ± 1.42	5.23 ± 1.23	479.97 ± 1.41	4.69 ± 1.35	44.55 ± 0.70

program plug-in XLSTAT version 7.5.2., using Euclidean distance dissimilarity. This method has segregated sites into 5 clusters. Class1 includes site I1with an important concentration of Cr (1242 mg/kg), Cu (22,524 mg/kg), Zn (218,994 mg/kg) and Fe (8422). Class 2 includes I2; S2; S3; S4; S6; S7; S10; S11and S9.Class 3 includes I3; I4; I6; I7; I8; S8; S11; S5; I9 (Table 2).

Class 4 is represented by I5 which is "Temara" recognized by its copper contamination(85.14 mg/kg). Class5 includes S1 that is highly contaminated with Cu (13,860 mg/kg), Zn (1366mg/kg), Pb (45,750mg/kg), Fe (15000 mg/kg) and Cr (1774 mg/kg).

Spatial mapping of heavy metals around industrial sites

The kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps of each heavy metal obtained from lichen concentration samples. The Interpolation mapping of spatial spread of Pb, Cu, Cr, Cd and Zn using Inverse Distance Weighted technique of ArcGIS10 is shown in Figures (4 a-e). As shown in the maps, a similar pattern of hotspots (high HM concentrations) around industrial sites is observed in the spatial distribution of all the metals except for Cr. High concentrations of Pb and Cu was also observed. Most

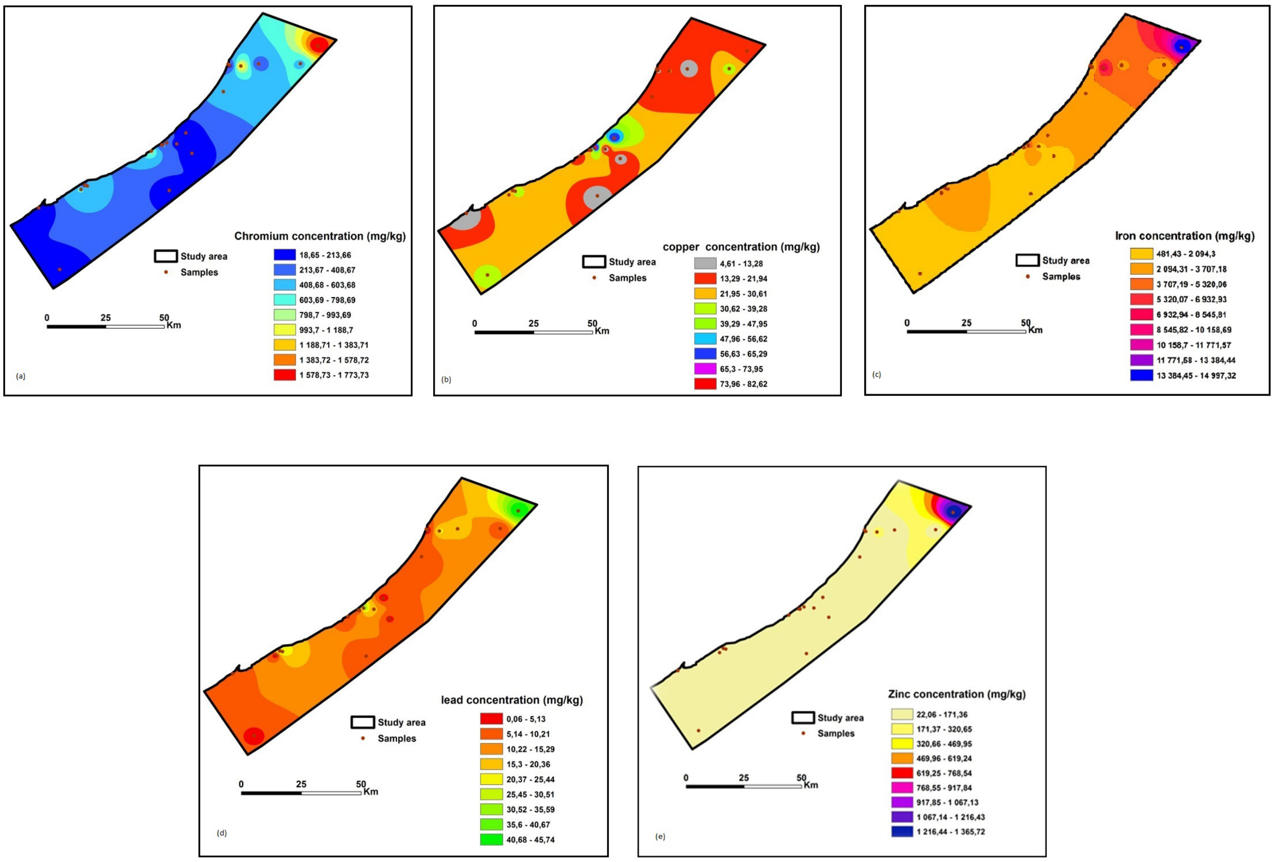

Figure 4 (a-e): Spatial distribution of metals (Cr, Cu, Fe, Pb and Zn) in lichens using Inverse Distance Weighted technique (Arc GIS 10).

Table 2: Class barycenter's

Class	*Zn*	*Pb*	*Fe*	*Cu*	*Cr*
C1	218,994	22,822	8422,018	22,524	1242,326
C 2	93,959	11,980	2558,728	33,466	480,922
C 3	44,251	8,097	1328,582	10,403	150,161
C 4	110,996	42,050	5744,538	85,14	183,385
C 5	1366,000	45,750	15000,000	13,860	1774,000

Table 3: Sites segregated in classes according to HM concentrations in lichen thallus

Class	*Sites*
Class 1	I1
Class 2	I2 ; S2 ; S3 ; S4 ; S6 ; S7 ; S10 ; S11 ; S9
Class 3	I3 ; I4 ; I6 ; I7 ; I8 ; S8 ; S11 ; S5 ; I9
Class 4	I5
Class 5	S1

likely the source of Pb, Fe, Zinc and Cu contaminations are industrialization and traffic activities.

According to the map (Fig. 3), all urban sites are contaminated with chromium. This distribution of low Cr concentrations may be attributed to pollution from traffic vehicles. The increase in the environmental concentrations of chromium in S1 site can be linked to the air release of chromium, mainly from metallurgical, refractory, and chemical industries especially wood and paper industry.

The spatial distribution shown in Fig. 4(b) indicates that the Kenitra region is the most contaminated site with copper followed by Rabat and Mohammedia. The main source of Cu is probably Diesel as a source of energy (Seaward and Richardson (1989). Transport vehicles are the main transmitters. Combustion process, use of fossil energies, the material of construction may also enhance the release.

According to Fig. 4(c), the most iron contaminated site is the S1 site, where concentration is exceeding 15000 mg/kg. The main source of iron are incinerators, these obvious results suggested that the exhaust from the iron smelting industry had a telling effect on the nearby ecosystems. Urban site is contaminated which can be due to high traffic density. Bajpai and Upreti (2012) had reported significantly higher levels of Cr, Fe, Pb and Zn ($p<0.01$), Cd and Cu ($p<0.05$) in the lichens especially in samples collected from road sites.

For Lead (Pb), it is noteworthy that this heavy metal exploited in Morocco contaminates the lower atmosphere (Monna et *al*., 2012). First, because from several mines are stocked in the open air, and because indigenous lead is commonly used by local industries and craftsmen. Unfortunately, literature is particularly scanty for trace elements especially lead analyses of Moroccan environmental samples (Monna et *al*., 2012). In our case (Fig 4(d), Mohammedia seems to be highly contaminated, huge petrol refinery may be the cause, followed by Bouznika and Rabat region; these sites also had a high concentration of iron. According to Gao et *al*. (2002), the combination of the 2 elements Pb and Fe indicates the use of fossil fuels.

The region of Mohammedia is a hotspot it's due to fossil fuels burning, mining, waste incinerators, lead-acid battery manufacturers contribute to the release of high concentrations of lead. The highest air concentrations of lead are usually found near lead smelters. In Rabat region, one of the most factors of contamination of lead is pottery and tannery. The wood production processing, chemical and parachemical industry in Kenitra region are the main source of lead release.

The concentrations of Zn vary between 218.995 and 22.027 mg/kg, the most important one are localized in the S1 site (Figure 4(e)).The main source of Zn is fuel (Dubey et *al.,* 1999).Other sources of Zn are the use of pesticides and fertilizers (Scerbo et *al.,* 2002).The agricultural activities can be considered then as a possible factor of Zn enrichment.

CONCLUSION

The mapping shows that the whole area is affected by industrial and traffic release. Lead and iron are the most devastating ones. The most contaminated area is the "SidiYayha El Gharb" site affiliated to "Kenitra" area followed by "Mohammedia"; prevailing winds affect even non-polluted and rural sites. So these mapping can be used as tools of a decision in the management of territories and remaining environmental disparities. Reforestation and promoting urban greening could prevent heavy metals dispersion. The government should take urgent and drastic measures for remediation to prevent an ecological disaster.

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