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Heavy metal accumulation in lichens and soils a long main road from the north to the south parts of Erbil governorate

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Abstract

In 2012 during wet season (March, April, May) and dry season (July, August, September, October), ten locations were selected from extra north to extra south of Erbil, Kurdistan, Iraq to determine some roadside pollutants in lichens and soils. The most abundant species were Collema cristatum, Diploschistes scruposus, Lecanora dispersa, Lecanora murales, Pertusaria flavicunda, Placidium lacinulatum, Thelomma californicum and Verrucaria maura. In lichens pH, total nitrogen and sulfate (SO4) concentration were at the range of 6.96 - 8.05, 1.86 - 6.05ppm and 39 - 79ppm, respectively. Among heavy metals the concentration of Cd Cr, Cu, Fe, Mn and Zn levels were ranged from 0.79 to 1.56ppm, 70.21 - 293.57ppm, 26.44 - 38.23ppm, 12383.34 - 16948.32ppm, 228.54 - 583.04ppm and 24.30 - 2840.40ppm respectively. In studied soils, the concentration of above mentioned parameters were at level of normal range. There were a correlation between concentrations of studied pollutants in soil and lichens. The results of location pollution accumulation (LPA) revealed that Dibaga location was the most polluted area, while Barzewa location was the least polluted location. Based on the species pollutant accumulation (SPA), the best indicators for air quality monitoring assessment was Collema cristatum, *Licanora muralis.*

Keywords: Air quality, Erbil, heavy metals, Iraq, Kurdistan, Lichen species.

Introduction

The lichens comprises of fungal hypha and algal partners living together symbiotically [1]. The phycobiont is randomally intermixed or stratified with mycobiont 2]. Lichens are extremely slow growing organisms, increasing in size by 1mm-1cm per year, while they are living for very long time. They are also extremely widespread in nature;

they grow on a variety of habitats under extreme cold and dry conditions from arctic to Antarctica and from rocky shores of the sea to the desert area [3, 4 and 5]. Lichens are excellent bioindicators for air pollution because they are very sensitive to dry and wet deposition of airborne pollutants; and Lichens are very sensitive to SO_2, as well as they serve as an early warning signal for potential air pollution damage, as they absorb nutrients directly from the atmosphere, and readily accumulating atmospheric contaminants [6,7]. There are a huge number of different modes of studies related to lichens in the world [8, 9 and 10]. In Iraq and Kurdistan only 4 studies have been done in Kurdistan especially on identifications reviewed by [11]. The aim of the current study is to evaluate the quality of ambient air using the epipelic and epilithic lichens as bioindicators for assessment the concentration of roadside pollutants NO_2 and SO_2 and to determine the concentration of some common toxic heavy metals in the ambient air perhaps affected by vehicle exhaust.

Materials and methods

Description of the study area

Erbil governorate is the capital of Iraqi Kurdistan region, located at a longitude of 42°15´E to 46°30´E and latitude 34° 25´N to 37°50´N; at an elevation of 411m above sea level, Erbil is covers an area of about 164840 km^2.The climate of Erbil area is most approached to the Irano –Turanian type. Average temperature range in Erbil is under zero to above 48°C. Precipitation occurs from the late of autumn to the late of spring passing winter season, while heavy snowfall occurs in the mountains and at higher altitudes.

The geography, climate, geology and soil of Iraq and Kurdistan reviewed by Guest (1966 [12, 13]. The rocks of Iraqi Kurdistan region is calcareous because originated from limestone and dolomite of different formations [14]; also the soil is calcareous consist of gravel, sand, clay, silt or loam, topsoil contain 1– 4.5% of organic matter and suitable for agriculture [15]. In this study ten locations were selected starting from north to south part of Erbil governorate, starting from, Kawlokan, Zargali, Sisawa, Barzewa Aquban, Baraka, Sulawk villages, and Safin-Kawanian mountain, Dibaga foothills to Qarachugh Mountains. Each site nearly covering an area of 100 m^2.

Lichen collection and identification

For the purpose of identification epilithic and epipelic lichen were collected during dry season and wet season 2012 in ten locations by about 50 m on main roads from south to north part of Erbil governorate. Samples were scraped off with a knife and hummer with a chisel to chip off the some crustose species and in paper bag. Identification of lichen species have been done as proposed by lichenologists [2, 3, 4 and 5]. Lichnes and soil analysis was made according to [16, 17 and 18].

Heavy metals

Soil samples were digested following the procedure implemented by Luter *et al.* (2011), the concentration of cadmium (Cd^{+2}), chromium (Cr^{+2}), copper (Cu^{+2}), iron (Fe^{+3}), lead (Pb^{+2}), manganese (Mn^{+3}), and zinc (Zn^{+2}) were determined using atomic absorption spectrophotometer model (PYE UNICAM SP9).

Statistical analysis

The results were statistically analyzed according to the statistical program Graph Pad. Prism, version 5. The mean and standard division values of were calculated for each variable. One- way analysis of variance

(ANOVA) followed by least significant difference (LSD) test, which was applied for multiple comparisons, according to the following formula (Le,2003):

$$LSD = t^* \frac{\sqrt{2EMS}}{r}.$$

The simple correlation equation was applied to determine the relationship between the concentrations of all pollutants in soil and lichen species in the studied locations.

The pollution statuses of studied locations were determined by the proposed Location Pollution Accumulation (LPA), according to the following formula:

$$LPA = \frac{\text{Sum concentration of all pollutants at specific studied location}}{\text{No.of lichen species at this location}}$$

While to identify the indicator species among the common lichen species the modified Species Pollution Accumulation (SPA) has been used as per the following formula (Shukla and Gupta, 2001):

$$SPA = \frac{\text{Density of a specific species at all studied locations}}{\text{Total number of studied locations}} * \text{Total concentration of all pollutants in the specific species.}$$

Results and discussion

In ten studied locations during Mar to Sep 2012, the most common lichen were 8 species that abundant in either in all or most studied sites (Table 1) represented by *Collema cristatum, Diploschistes scruposus, Lecanora dispersa, Lecanora murales, Pertusaria flavicunda, Placidium lacinulatum, Thelomma californicum* and *Verrucaria maura*. While, the rare species was *Acarospora impressula, Buellia spuria, Lecidella stigmatea, Neofuscelia pulla, Parmelina quercina.* The differences in species richness may be due to weather variations such as high relative humidity, rainfall and low to moderate temperature during the year [8]. However, the type of rocks and vegetation cover are factors affecting on lichens abundance and distribution. Air pollution especially SO_2 is another main factor limiting lichens growth and abundance, because lichens are very sensitive this gas [19, 20, 21, 22 and 23].

Table 1. Common lichen species at all studied.

Lichen species	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6	St. 7	St. 8	St. 9	St. 10	Total
Collema cristatum	+	+	+	+	+	+	+	+	+	+	10
Diploschistes scruposus	+	+	+	+					+	+	6
Lecanora dispersa	+	+	+	+	+	+	+	+	+	+	10
Lecanora murals	+	+	+	+	+	+	+	+	+	+	10
Pertusaria flavicunda	+		+	+	+	+			+	+	7
Placidium lacinulatum	+	+	+	+		+		+			6
Thelomma californicum	+		+	+	+	+	+	+	+	+	9
Verrucaria Maura	+	+	+	+	+	+	+	+	+	+	10

it is appear from Table 2 that the cadmium (Cd) concentration in lichens, was ranged from 0.13 to 1.78ppm; the highest concentration was recorded in both *Fulgensia fulgens* and *Lecanora dispersa* at Sulawk and Barzewa sites during dry and wet seasons respectively, while the minimum concentration was recorded at Safin-Kawanian mountain in *Dermatocarpon miniatum*during during wet season. The concentrations of chromium (Cr) at all sites was ranged between 18.69 and 182.30ppm, the highest value was recorded in *Collema cristatum* at Baraka site during dry condition, while the lowest concentration was recorded in *Aspicilia caesiocinerea* at Barzewa sites during same season. Copper (Cu) concentration ranged from 10.19 to 223.91ppm, the maximum value was recorded in *Placidium lacinulatum* during wet condition at Kawlokan site, while the minimum value was recorded in *Aspicilia leprosescens* at Baraka, *Caloplaca auranta* at Sulawk and *Thelomma californicum* at Aquban location all during wet condition. The iron (Fe) concentration was between 1285.08 and 17631.36 ppm, the highest value was recorded in *Thelomma californicum* during wet season at Baraka village, whereas the minimum value was observed in *Psora lurida*at Kawlokan during same season. Concerning manganese (Mn) concentration it was ranged from 86.74 to 842.10ppm; the lowest value was recorded in *Pertusaria aspergilla* during dry condition at Baraka velage, the maximum value was recorded in *Lecanora murales* at Qarachugh mountain during same season. Lead (Pb) was not detected in the lichen species in any sites. Zinc (Zn) was ranged from 10.38 to 127.94ppm; the lowest concentration was recorded at Sisawa site in *Aspcilia calcarea* during wet season, the highest value was recorded at Kawlokan site during dry condition.

Chemical composition of soils of study locations:

It is appear from Table 3 the hydrogen ion concentration was ranged from 6.96 to 8.05.This is agree with General soil characteristics of Erbil province which is either alkaline or slightly in acid condition [13, 14]), in this study the pH value did not exceed 6.9. This support the fact that lichens are acidophilus and they less influenced by the chemistry of the soil, whereas they are strongly influenced by the air chemistry in, dry or wet precipitation [20, 21]. The difference between the same species in different locations may be contributed to rainfall and anthropogenic activity mainly from motor exhaust. The total nitrogen concentration was between 1.86 to 6.05ppm, and sulfate concentration was ranged from 39 to 79ppm.The Cd, Cr, Cu, Fe, Mn and Zn were ranged from 0.79 to 1.56ppm, 70.21 to 293.57ppm, 26.44 to 38.23ppm, 12383.34 to 16948.32ppm, 228.54 to 583.04ppm and 24.30 to 2840.40ppm respectively (Table 4).

Table 2. The concentration of studied variables in most abundant species during studying period in studied sites.

Variables	Valuse		Species	Condition	Locations
Temperature	Min	6.2 C°	-	Wet	Barzewa
	Max	37.1C°	-	Dry	Qarachugh
Humidity	Min	20.44	-	Dry	Qarachugh
	Mix	74.22	-	Wet	Barzewa
Rainfall mm/year	Min	146.43	-	Dry	Qarachugh
	Max	689.88	-	Wet	Barzewa
Ph	Min	5.13	*Dermatocarpon miniatum*	Dry	Kawlokan
	Max	6.9	*Lecanora dispersa*	Wet	Barak
T. nitrogen (ppm)	Min	4.02	*Verrucaria Maura*	Wet	Qarachugh
	Max	19.53	*Aspecilia calcarea*	Dry	Kawanian
Sulphate (ppm)	Min	32.00	*Collema cristatum* *Diploschistes sruposus* *Dermotocarpon miniatum*	Dry	Aquban
	Max	651.20	*Dermtaocarpon miniatum*	Wet	Kawanian
Cd^{+2} (ppm)	Min	0.13	*Dermatocarpon miniatum*	Wet	Kawanian
	Max	1.78	*Fllugensia flugens* *Lecanora dispersa*	Dry-wet	Sulawk, Barzewa
Ca^{+2} (ppm)	Min	18.69	*Aspecilia caecinerea*	Dry	Barzewa
	Max	182.30	*Collema cristatum*	Dry	Barka
Cu^{+2} (ppm)	Min	10.19	*Aspecillia leprosescens*	Wet	Sulawk, Iquban
	Max	223.91	*Placidium lacinulatum*	Wet	Kawlokan
Fe^{+2} (ppm)	Max	1763. 36	*Psora lurida*	Wet	Kawlokan
	Min	1285.08	*Thelomma californica*	Wet	Baraka
Mn^{+2} (ppm)	Min	86.74	*Pertusaria flavicunda*	Dry	Baraka
	Max	842.10	*Lecanora uales*	Dry	Qarachugh
Zn^{+2} (ppm)	Min	10.38	*Aspceilia calcaria*	Wet	Sisawa
	Max	127.94	*Placidium lacinulatum*	Dry	Kawlokan
Pb^{+2} (ppm)	Not detected				

Table 3. Hydrogen ion, total nitrogen and sulfide concentration (ppm) in soil samples of studied locations during period of the study

Locations	pH	Total nitrogen	Sulfide
Barzewa location	8.05	4.19	39
Kawlokan location	7.34	1.86	41
Zargali location	7.07	2.79	54
Sisawa location	7.14	1.86	40
SAquban location	7.02	4.65	67
Baraka location	6.96	4.65	79

Sulawk location	7.20	2.79	39
Safin-Kawanian location	7.03	6.05	48
Dibaga location	7.50	2.79	47
Qarachugh location	7.25	1.86	70
Mean	7.26	3.05	52.4
SE	0.1	0.39	4.6

Maximum and minimum are shaded

Table 4. Trace elements Cd, Cr, Cu, Fe, Mn and Zn concentrations ppm in the soil of the studied locations during period of the study

Locations /Elements	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Barzewa location	1.01	195.85	38.23	15013.04	412.88	N.D	144.72
Kawlokan location	0.90	112.09	24.75	14216.16	228.54	N.D	2289.60
Zargali location	0.90	146.99	34.86	16948.32	583.04	N.D	56.16
Sisawa location	0.79	293.57	28.12	14785.36	398.70	N.D	534.60
Aquban location	1.23	167.93	38.23	14557.68	356.16	N.D	28.08
Baraka location	0.79	133.03	28.12	10345.60	242.72	N.D	2840.40
Sulawk location	1.12	126.05	18.01	8296.48	228.54	N.D	24.30
Safin-Kawanian location	0.90	77.19	18.01	10231.76	242.72	N.D	248.40
Dibaga location	1.01	70.21	14.64	10345.60	299.44	N.D	426.60
Qarachugh location	1.56	119.07	21.38	9093.36	285.26	N.D	2829.60
Mean	1.02	144.20	26.44	12383.34	327.80	-	942.25
SE	0.07	20.00	2.70	955.00	36.00	-	380.00

Location pollution accumulation (LPA) and species pollution accumulation assessment (SPAA):

Based on location pollution accumulation assessment (LPAA) represented in Table 4, the results revealed that Dibaga location was the most polluted location among all the studied locations within Erbil governorate, followed by Qarachugh mountain and Aquban site, while Barzewa location was the least polluted location, followed by Safin-Kawanian mountain and Kawlokan site. On the other hand, based on species pollutant accumulation assessment (SPAA), it was found that the best indicators for air quality monitoring and assessment are *Collema cristatum, Licanora dispersa, Lecanora murales,* and *Verrucaria maura*. These may be contributed to the high precipitation of pollutants due to petroleum and gypsum activities at these areas, whereas Barzewa location showed to be the least polluted, followed by Safin - Kawanian site (Table 3). This is agree with findings of [25, 26]

It's also concluded from the results of LSPAA (Table 4) that *Collema cristatum, Lecanora dispersa, Lecanora murales,* and *Verrucaria maura* are the for air quality monitoring and assessment may be due the resistance of these species to different environmental stresses (Table 4). The results of this study is agree with the study of [22] who indicated that lichens closest to the road were contained higher amount of elements than lichen species far away from the road by 100m. Also [23] performed a study on lichens in India; they found that the highest metal concentration was in samples collected from roadside areas having heavy vehicular activities. The similar results found in air by [24]. The results of current study showed that the heavy metal concentration in soil samples were lower than of lichen samples. Previously [27] revealed that the elemental content of lichens strongly influenced by the chemistry of the air and precipitation. Also [7] has repeated the same fact that lichens lack a vascular system and roots, therefore not influenced by elements in soil. In this study no correlation relationship was found between concentrations of studied pollutants in soil and lichen species (Fig.1). This support the fact that lichens are acidophilus and they less influenced by the chemistry of the soil, whereas they are strongly influenced by the air chemistry, dry or wet precipitation [22, 28].

Table (5). Location pollutant accumulation (LPA) values In the lichens of all studied locations.

Location / Pollution	Barzewa	Kawlokan	Zargali	Sisawa	Aquban	Baraka	Sulawk	Safin-Kawanian	Dibaga	Qarachuh
Total nitrogen	9.53	9.59	11.04	10.33	9.49	9.11	8.89	9.60	11.23	6.24
Sulfate	96.08	77.70	99.52	101.61	72.20	71.50	141.70	134.67	217.87	120.73
Cd	1.11	1.11	1.40	0.96	1.00	1.20	1.17	0.99	1.13	1.11
Cr	63.51	61.87	84.97	86.56	86.56	84.53	70.20	58.40	88.67	75.81
Co	67.78	84.94	55.04	43.55	40.98	30.99	37.34	27.08	76.10	41.58
Fe	7437.51	7800.32	10241.23	10304.62	9036.17	9962.63	8927.48	9169.45	11646.47	8906.44
Mill	224.25	305.65	254.11	236.52	216.75	258.48	192.00	193.77	440.34	370.76
Za	40.87	42.73	32.11	26.26	24.76	26.20	34.70	27.06	48.82	34.57
Total	7940.64	8383.91	10779.41	10810.41	9487.90	10444.63	9413.44	9621.02	12530.63	9557.24
LPA	610.82	762.17	829.19	900.87	948.79	870.39	941.35	740.08	963.89	935.72

LSD (0.01)= 5914.62

Table 6. Species pollutant accumulation for common lichen species.

Lichen species	Total nitrogen	Sulfate (SO_4)	Cd	Cr	Cu	Fe	Pb	Mn	Zn	Total	SPA
Colima cristatum	10.26	86.09	1.08	85.42	65.21	10860.21	N.D	295.55	44.00	11447.82	14308.75
Diploschistes scruposus	10.43	96.33	1.15	67.62	76.24	9704.77	N.D	275.91	37.11	10269.57	7702.18
Lecanora dispersa	10.30	96.49	1.21	79.44	48.27	9977.17	N.D	346.61	39.16	10598.65	13248.31
Lecanora murals	10.02	89.41	1.09	82.68	38.10	9549.81	N.D	317.27	36.26	10124.63	12655.79
Perttaaria flavicunda	9.84	132.76	0.95	81.50	45.49	9004.86	N.D	242.88	31.51	9549.79	8356.07
Placidium lacinulatum	8.22	83.57	1.15	88.12	72.60	11592.62	N.D	248.92	44.76	12139.96	9104.25
Thelomma califbrnicum	8.54	110.81	1.46	70.57	38.64	9354.94	N.D	257.13	29.14	9871.23	11105.13
Vetrucaria Maura	9.42	115.52	1.10	67.38	55.58	9456.65	N.D	318.16	36.25	10060.07	12575.09

LSD (0.01) = 608.01

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