ACCUMULATION OF SOME HEAVY METALS IN LICHENS IN GIRESUN CITY, TURKEY

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Abstract

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Biomonitoring properties of some foliose and crustose lichen species were studied in a polluted area of Giresun city, in the northern part of Turkey caused by high traffic density. Heavy metal concentrations were usually ranked in the order of Fe > Zn > Mn > Cu > Pb in the studied lichen species. Fruticose *Cladonia* species were significantly different from foliose species in terms of heavy metal concentrations except for Pb and Zn. Interspecific differences with respect to heavy metals were observed between the studied species except for Pb. According to Principal Component Analysis (PCA) the main loading factors in the first axis were Fe and Mn in the positive zone. However, Zn followed an opposite behaviour in relation to other heavy metals and occured in the negative zone.

Key words: biomonitoring, crustose lichens, foliose lichen, heavy metal pollution, traffic density

Introduction

Lichens are extremely sensitive symbiotic organisms which react to even slightly polluted air and they have certain characteristics, which meet several requirements of the ideal biomonitor i. e. large geographical ranges allowing comparison of metal concentration from diverse region; a morphology which does not vary with seasons, thus enable accumulation to occur throughout the year. Biological monitoring can be very effective as an early warning system to detect environmental changes (Markert, 1993; Loppi et al., 2000).

Lichens accumulate heavy metals to a very high degree, with concentrations reflecting environmental levels of these elements (Herzig et al., 1989; Loppi et al., 2000). The use of lichens in biomonitoring of particulate pollutants has gained increasing acceptance in recent years. Due to their different sensivity to air pollution they are potentially useful for air monitoring purposes (Herzig et al., 1989; Garty et al., 2000; Pandey et al., 2002).

However, there is a scarce information on intra- and inter-specific variability in heavy metal accumulation, that is of obvious importance for assessing data quality in applied studies (Nimis et al., 2001).

The aim of the present study is to determine Fe, Zn, Mn, Cu and Pb concentrations in some foliose and crustose lichens which occured in Giresun city and to examine whether interspecific differences were occurred or not in the studied lichen species in terms of heavy metal accumulation.

Material and methods

Study area

Giresun city is situated in the northeastern part of Turkey and its population density is 533 390. During the study period SO2 levels in Giresun city ranged from 12–122 $\mu g.m^3$ and maximum SO2 levels were observed from November to March, while minimum SO2 levels were observed in spring and summer months (Anonymous, 2004). Most of lichen samples were collected from Giresun Castle which is situated in the centre of the city. There is a tea factory near Giresun Castle. Only *Collema furfuraceum* and *Xanthoparmelia conspersa* were collected from the seashore and roadside, respectively to examine the effects of high traffic density (Table 1). Selected lichen species were different from each othere with respect to thallus types. *Cladonia* species have fruticose thallus type while other lichen species have foliose thallus type.

In the laboratory, the lichens were carefully removed from rocks, using a snapper blade and were oven dried to a constant weight at 70 ^oC with a microwave oven. 0.5 g of the dried lichen samples were then powdered and they were extracted with a mixture of concentrated HCl and HNO3 (3 : 1). This digest was filtered through a Whatman

T a b l e 1. Sampling areas.

Species	Sampling site [m]	Substrate	Traffic density*
Cladonia rangiformis	Giresun Castle, 110	soils	47.600
C. convoluta	north-west of Giresun Castle, 100	soils	47.600
C. pyxdidata	north of Giresun Castle, 100	soils	47.600
C. furcata	north of Giresun Castle, 100	soils	47.600
Flavoparmelia caperata	north-west of Giresun Castle, 120	siliceous rocks	47.600
Dermatocarpon luridum	north of Giresun Castle, 90	siliceous rocks	47.600
D. miniatum	south-east of Giresun Castle, 140	siliceous rocks	47.600
Xanthoria calcicola	north-west of Giresun Castle, 120	siliceous rocks	47.600
Peltigera malacea	north of Giresun Castle, 110	mosses	47.600
Collema furfuraceum	Giresun, sea shore	siliceous rocks	141.400
Xanthoparmelia conspersa	Giresun roadside, 110	siliceous rocks	141.400

* Traffic density is expressed as the mean number of cars per 24 hours integrated for the year.

filter paper No. 42. Concentrations of heavy metals (µg. g^{-1} dry wt) were determined by a Perkin Elmer 2280 atomic absorption spectrophorometer, using the air/acetylene flame (Allen et al., 1986; Kutbay, Kılınç 1991; Pandey et al., 2000). The following heavy metals were analyzed: Pb, Mn, Cu, Zn and Fe.

Nomenclature of lichens followed that of Purvis et al. (1992) and Wirth (1995).

To show the grouping of species in terms of heavy metal concentrations, principal component analysis (PCA) and average-linkage were performed by using the CAP 1.5 version (Anonymous, 1999a) software programmes. The first two axes of PCA are now the theoretical variables minimizing the total residual sum of squares among all possible choices of two explanatory variables (Jongman et al., 1995).

One- and two-way analysis of variance (ANOVA) tests and Pearson correlation coefficients were carried out by using SPSS 10.0 version. Tukey' s honestly significant difference (HSD) test was used to rank means following the analysis of variance by using SPSS 10.0 version (Anonymous, 1999b).

Results

Heavy metal concentrations were usually ranked in the order of Fe > Zn > Mn > Cu > Pb. However, there was a minor change in the order of Cu and Pb in *Cladonia rangiformis*, *C. convoluta*, *C. furcata*, *Flavoparmelia caperata* and *Xanthoparmelia conspersa*. Interspecific differences were observed between the studied species except for Pb according to Tukey's HSD test (Table 2).

T a b l e 2. Heavy metal concentrations (µg. g^{-1} dry weight) in the studied species. Means followed by the same letter are not significantly different at the 0.05 level using Tukey's HSD test.

Species	Thallus	Pb	Mn	Cu	Zn	Fe
Cladonia rangiformis	fruticose	10.9083 ^{a}	13.1867 ^{a}	4.7067 ^{a}	65.8267 ^{ab}	623.4900 ^{a}
C. convoluta	fruticose	10.5083 ^{a}	79.9200 ^{a}	9.8067 ^{c}	140.2800 ^{cde}	3121.250 ^{e}
C. pyxdidata	fruticose	7.7667 ^{a}	42.0167 ^{a}	8.9533 ^{bc}	157.9867 ^{de}	1270.710 ^{ab}
C. furcata	fruticose	7.3100 ^{a}	23.7500 ^{a}	5.7667 ^{ab}	96.5067 ^{abc}	856.6500 ^{a}
Flavoparmelia caperata	foliose	19.0167 ^{a}	79.8267 ^{a}	13.7033 ^{d}	132.9767 ^{cde}	2432.490 ^{cde}
Dermatocarpon luridum	foliose	11.4200 ^{a}	74.8967 ^{a}	14.6933 ^{d}	182.9233 ^{e}	2097.490 ^{bcd}
D. miniatum	foliose	6.8533 ^{a}	63.0233 ^{a}	7.6100 ^{ab}	53.2267 ^{a}	1972.870 ^{bc}
Xanthoria calcicola	foliose	6.3367 ^{a}	79.4633 ^{a}	8.5300 ^{bc}	120.3367 ^{cd}	2996.630 ^{de}
Peltigera malacea	foliose	4.1133 ^{a}	52.5200 ^{a}	7.8933 $^{a\,ab}$	118.3967 ^{cd}	1494.490 ^{ab}
Collema furfuraceum	foliose	9.5933 ^{a}	205.5133 ^{b}	9.8067 ^{c}	112. 7967 ^{bcd}	3216.390 ^{e}
Xanthoparmelia conspersa	foliose	12.3333 ^{a}	45.6700 ^{a}	8.6000 ^{bc}	116.2667 ^{bcd}	2713.890 ^{cde}

Fruticose *Cladonia* species were significantly different from foliose species in terms of heavy metal concentrations except for Pb and Zn (Table 3).

There were significant correlations between Mn–Cu, Zn–Cu, Fe–Mn and Fe–Cu (Table 4).

Across all study sites and species heavy metals, fall into three groups. The first group consists of only Fe. However, the second and third groups consist of Mn and Zn and Pb and Cu, respectively (Fig. 1).

The main loading factors in the first axis were Fe and Mn in the positive zone according to PCA analysis.

T a b l e 3. Comparison of fruticose *Cladonia* species with foliose species by one-way ANOVA.

Element	F-Value
Pb	0.115 NS
Mn	6.908 *
Cu	7.578 *
Zn	0.095 ns
Fe	10.499 **

Ns- not significant. * $P < 0.05$, ** $P < 0.01$

T a b l e 4. Pearson correlation coefficients between element pairs.

	Pb	Mn	Cu	Zn	Fe
Pb	**1**	0.1213 ns	0.2000 ns	0.0812 ns	0.2475 ns
Mn		**1**	0.4068 *	0.2822 ns	0.6544 **
Cu			**1**	0.6604 **	0.5420 *
Zn				**1**	0.3292 ns
Fe					**1**

Ns- not significant, * $P < 0.05$, ** $P < 0.01$

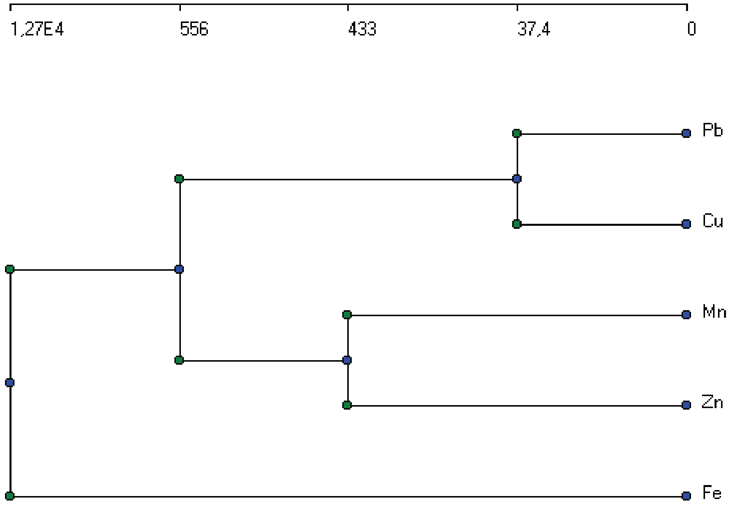

Fig. 1. Dendrogram of the studied heavy metals by Euclidian distance.

However, Zn followed an opposite behaviour in relation to other heavy metals and occurred in the negative zone (Fig. 2).

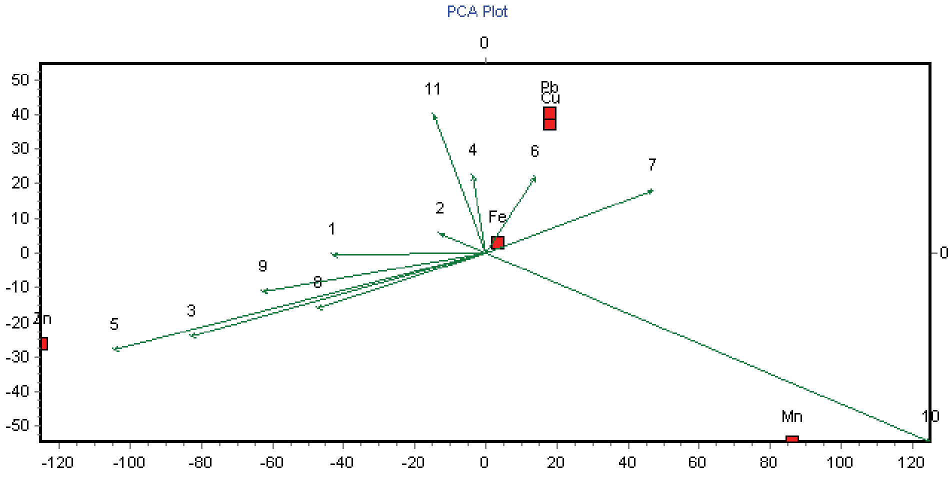

Fig. 2. PCA of the studied species and heavy metals.

1 = *Cladonia rangiformis*
2 = *Flavo parmelia caperata*
3 = *Dermatocarpon luridum*
4 = *Cladonia convoluta*
5 = *Cladonia pyxidata*
6 = *Xanthoria calcicola*
7 = *Dermatocarpon miniatum*
8 = *Peltigera malacea*
9 = *Cladonia furcata*
10 = *Collema furfuraceum*
11 = *Xanthoparmelia conspersa*

Discussion

The normal level of Pb, Mn, Cu, Zn and Fe in the plants growing in uncontaminated areas have been reported to vary in the ranges 2–10 µg. g^{-1} dry wt, 20–300 µg. g^{-1} dry wt, 5–20 µg. g^{-1} dry wt, 20–100 µg. g^{-1} dry wt and 50–250 µg. g^{-1} dry wt, respectively (Markert, 1992; Markert, 1994; Aksoy, Öztürk, 1996). Taking these values into account, the results of the present study show that the area is polluted by Pb, Zn and Fe. One of the sources of emission of Pb and Zn is motor vehicles. Zn exists as alloys in accumulators of motor vehicles or in carburetors and it is released as combustion product. Much of the bodywork of motor vehicles is galvanized, and Zn oxides are also released by wear and tear on car tyres (Bereket, Yücel 1990; Bloemen et al., 1995). Elevated concentrations of these elements may therefore have been caused by the effects of high traffic density (Kutbay, Kılınç 1991; Türkan et al., 1995; Aksoy, Öztürk, 1997).

Heavy metal concentrations in the present study were concurred with the data obtained by Nimis et al. (2001) who studied foliose lichens. Higher concentrations of largely terrigenous elements such as Fe was found in *Collema furfuraceum* and *Xanthoria calcicola*. Nimis et al. (2001) reported high Fe concentrations in *Xanthoria parietina* and high Fe concentrations were explained on the basis of the dominance of siliceous rocks. Siliceous rocks made up of Fe and Al hydroxides are also very widespread in the study area. In addition to this, Fe is the most abundant heavy metal in the other studied lichen species. Lichens have been shown to demonstrate special affinity for Fe (Pandey et al., 2002).

According to dendrogram of the studied species Pb and Cu are belonging to the same group and significant correlations were found between different element pairs except for Pb. These findings were consistent with the studies of Bennett, Wetmore (1999) and Garty et al.'s (2000).

Fruticose *Cladonia* species were significantly different from foliose species in terms of heavy metal concentrations except for Pb and Zn. Pandey et al. (2001) stated thallus types play an important role in determining the accumulation of heavy metals. *Collema furfuraceum*, *Dermatocarpon luridum* and *Xanthoria calcicola* were the best accumulator of heavy metals as compared to the other species in the present study and all of these lichen species are foliose lichens. McCune et al. (1997) stated these genus are heavy metal-tolerant and based on the results of the present study these species can be used safely in biomonitoring.

Conclusions

Lichens accumulate heavy metals to a very high degree, with concentrations reflecting environmental levels of these elements (Herzig et al., 1989; Loppi et al., 2000). Due to their different sensivity to air pollution they are potentially useful for air monitoring purposes (Herzig et al., 1989; Garty et al., 2000; Pandey et al., 2002). Fruticose and foliose lichen samples were taken from Giresun city which is situated in the northeastern part of Turkey near the roads that have high traffic density. High Pb, Zn and Fe values were found. Elevated concentrations of these elements may therefore have been caused by the effects of high traffic density (Kutbay, Kılınç, 1991; Türkan et al., 1995; Aksoy, Öztürk, 1997). Higher concentrations of largely terrigeneous elements such as Fe was found in *Collema furfuraceum* and *Xanthoria calcicola*. High Fe concentrations were may be due to the dominance of siliceous rocks. Siliceous rocks made up of Fe and Al hydroxides are also very widespread in the study area. According to the dendrogram of the studied species Pb and Cu are belonging to the same group and significant correlations were found between different element pairs except for Pb. Fruticose *Cladonia* species were significantly different from foliose species in terms of heavy metal concentrations except for Pb and Zn. *Collema furfuraceum*, *Dermatocarpon luridum* and *Xanthoria calcicola* were the best accumulator of heavy metals as compared to the other species.

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References

Aksoy, A., Öztürk, M., 1996: *Phoenix dactylifera* L. as a biomonitor of heavy metal pollution in Turkey. Journal of Trace and Microprobe Techniques, *14* p. 605–614.

Aksoy, A., Öztürk, M.A., 1997: *Nerium oleander* L. as a biomonitor of lead and other heavy metal pollution in Mediterranean environments. Sci. Total Environ., *205*, p. 145–150.
Allen, S.E., Grimshaw, N.M., Parkinson, J.A., Quarmby, C., Roberts. J.D., 1986: Chemical Analysis. In Chapman, S.B. (eds): Methods in Plant Ecology. Blackwell Scientific Publications, Oxford, p. 411–466.
Anonymous, 1999a: CAP 1.5. Designed by Henderson, P.A., Seaby, R.M.H., Pisces Conservation LTD.
Anonymous, 1999b: SPSS 10.0 for Windows. SPSS Inc., New York.
Anonymous, 2004: Turkish Ministry of Health. Public Health Laboratory. SO2 Levels in Giresun city.
Bennett, J. P., Wetmore, C.M., 1999: Changes in element contents of selected lichens over 11 years in northern Minnesota, USA. Environ. Exp. Bot., *41*, p. 75–82.
Bereket, G., Yücel, E., 1990: Monitoring of heavy metal pollution of traffic origin in Eskişehir. Turk. J. Chem., *14*, p. 266–271.
Bloemen, M.L., Markert, B., Lieth, H., 1995: The distribution of Cd, Cu, Pb and Zn in topsoils of Osnabrück in relation to land use. Sci. Total Environ., *166*, p. 137–148.
Garty, J., Weisssman, L., Tamir, O., Beer, S., Cohen, Y., Karnieli, A., Orlovsky, L., 2000: Comparison of five physiological parameters to assess the vitality of the lichen *Ramalina lacera* exposed to air pollution. Physiol. Plant., *109*, p. 410–418.
Herzig, R., Liebendörfer, L., Urech, M., Amman, K., 1989: Passive biomonitoring with lichens as a part of an integrated biological measuring system for biomonitoring air pollution in Switzerland. Int. J. Environ. Analyt. Chem., *35*, p. 43–57.
Jongman, R.H., ter Braak, C.J.F., Tongeren, O.F.R., 1995: Data Analysis in Community and Landscape Ecology. Cambridge University Press, Cambridge, 299 pp.
Kutbay, H.G., Kılınç, M., 1991: Heavy metal pollution in plants growing along motor roads. In Öztürk, M.A., Erdem, Ü., Görk, G. (eds): Urban Ecology. Ege University Press, İzmir, p. 62–66.
Loppi, S., Putortiİ, E., Pirintsos, S.A., Dominicid, V.De, 2000: Accumulation of heavy metals in epiphytic lichens near a municipal solid waste incinerator (Central Italy). Environ. Monit. Assess., *61,* p. 361–371.
Markert, B., 1992: Presence and significance of naturally occuring chemical elements of the periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems. Vegetatio, *103,* p. 1–30.
Markert, B., 1993: Plants as Biomonitors – Indicators for Heavy Metals in the Terrestrial Environment. VCH Publishers, Weinheim, New York, Tokyo.
Markert, B., 1994: Plants as biomonitors – Potential Advantages and problems. In Adriano, D. C., Chen, Z.S., Yang, S. S (eds): Biogeochemistry of Trace Elements. Science and Technology Letters. Northwood, p. 601–603.
McCune, B., Dey, J., Peck, J., Heiman, K., Will-Wolf, S., 1997: Regional gradients in lichen communities of the southeast United States. Bryologist, *100*, p. 145–158.
Nimis, P.J., Andreussi, S., Pittao, E., 2001: The performance of two lichen species as bioaccumulators of trace metals. Sci. Total Environ., *275*, p. 43–51.
Pandey, V., Upreti, D.K., Pathak, R., Pal, A., 2002: Heavy metal accumulation in lichens from the Hetauda industrial area Narayani zone Makwanpur District, Nepal. Environ. Monit. Assess., *73*, p. 221–228.
Purvis, O.W., Coppins, B.J., Hawsksworth, D.L., James, P.W., Moore, D.M., 1992: The Lichen Flora of Great Britain and Ireland. National History Museum, London.
Türkan, İ., Henden, E., Çelik, Ü., Kıvılcım, S., 1995: Comparison of moss and bark samples as biomonitors of heavy metals in a highly industrialised area in Izmir. Turkey Sci. Total Environ., *166*, p. 61–67.
Wirth, V., 1995: Die Flechten Baden-Württembergs. Teil 1–2. Ulmer, Stuttgart.

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Kınalıoğlu K., Horuz A., Kutbay H.G., Bilgin A., Yalçın E.: **Akumulácia niektorých ťažkých kovov v lišajníkoch v meste Giresun, Turecko.**

V oblasti mesta Giresun nachádzajúcej sa v severnej časti Turecka znečistenej hustou dopravou sme skúmali biomonitorovacie vlastnosti niektorých krovitých a listnatých druhov lišajníkov. U skúmaných lišajníkov boli

koncentrácie ťažkých kovov v poradí Fe > Zn > Mn > Cu > Pb. V koncentráciách ťažkých kovov okrem Pb a Zn sa krovité druhy *Cladonia* značne líšili od listnatých druhov. U skúmaných druhov sme zistili vnútrodruhové rozdiely z hľadiska ťažkých kovov okrem Pb. Podľa Principal Component Analysis (PCA) boli hlavným záťažovým faktorom v pozitívnej zóne Fe a Mn, avšak Zn sa vo vzťahu k ostatným ťažkým kovom správal opačne a objavil sa v negatívnej zóne.