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ORIGINAL PAPERS

EVALUATION OF LICHENS AS BIO-INDICATORS OF METAL POLLUTION

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Abstract

The objectives of this study have been to determine the impact of the distance from a combustor of a cement plant (downwind direction) and duration of exposure to pollution on the bioaccumulation of metals by four lichen species. Nickel, cadmium, chromium, copper and lead accumulated in lichen thalli, with the highest accumulation occurring at 50 m of the cement plant and upon prolonged exposure. In contrast, the concentrations of Al were not consistently affected by the distance from the plant or the duration of exposure. *Pseudevernia furfuracea* was most effective as an indicator of cement dust pollution. We concluded that transplantation of *Pseudevernia furfuracea* on trees or shrubs can be an easy and cost-effective means of Ni, Cd, Cr, Cu and Pb pollution monitoring.

Key words: cement plant pollution, enrichment factor, heavy metal pollution, lichens.

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OCENA POROSTÓW JAKO BIOLOGICZNYCH WSKAŹNIKÓW ZANIECZYSZCZENIA METALAMI

Abstrakt

Celem badań było określenie wpływu odległości od komory spalania w cementowni (przy dominującym kierunku wiatru) oraz długotrwałości wystawienia na zanieczyszczenie na bioakumulację metali przez cztery gatunki porostów. Najwyższy poziom akumulacji w plechach porostów takich metali, jak nikiel, kadm, chrom, miedź i ołów stwierdzono w odległości 50 m od cementowni i przy długotrwałym narażeniu na zanieczyszczenie. Natomiast stwierdzone zawartości Al w porostach nie były jednoznacznie powiązane z badanymi czynnikami. *Pseudevernia furfuracea* okazał się najbardziej skutecznym wskaźnikiem zanieczyszczenia powodowanego przez cementownię. Wyniki badań dowodzą, że obsadzenie drzew lub krzewów porostami z gatunku *Pseudevernia furfuracea* może stanowić łatwą i tanią metodę monitorowania zanieczyszczenia przez Ni, Cd, Cr, Cu i Pb.

Słowa kluczowe: zanieczyszczenie pochodzące z cementowni, czynnik wzbogacenia, zanieczyszczenie metalami ciężkimi, porosty.

INTRODUCTION

The cement industry generates cement dust, which contains metals such as Cd, Cr, Cu, Ni and Pb (AL-KHASMAN, SHAWABKEH 2006). Although cement factories usually stand far from city centers, their surroundings suffer from pollution. SCHUHMACHER et al. (2009) demonstrated that cement dust and associated chemicals can spread over a large area with wind and rain, accumulating in lichens, plants, animals and soils, located downwind from a cement plant.

Lichens have been used as indicators of air pollution and biosorption (YAZICI, ASLAN, 2006, CICEK et al. 2008, BINGOL et al. 2009). Owing to their peculiar anatomical, morphological and physiological characteristics, lichens are one of the most valuable biomonitors of atmospheric pollution (BATTAL et al. 2004). They can be used as sensitive indicators to estimate biological effects of pollutants by recording changes in a given community, and as accumulative monitors of persistent pollutants, which can be evaluated by assaying their trace element content. Many epiphytic lichen species are sensitive to air pollutants and have been used widely to detect changes in air quality (SHOWMAN 1988). As a bioindicator method, lichen mapping is useful because the fieldwork can be completed by one person without expensive equipment. In order to be a good indicator, a given lichen species should be expected togrow at every site (SHOWMAN 1988), and species should have been widespread in an area submitted to assessment before it became affected by air pollution (CALVELO, BACCALA 2009).

Our objectives were to evaluate the effectiveness of four lichen species as bioindicators of air pollution from the cement industry. Specifically, we studied metal accumulation in four lichen species exposed to air emissions (1) at some distance from the cement plant (50, 100 and 200 m), (2) for the duration of exposure equal four, eight, and twelve months. Two other factors analysed were (3) heavy metals originating from the factory or from natural parent material, according to the enrichment factor, and (4) the reliability of the tested lichens as biomonitoring tools for the evaluation of levels of atmospheric pollutants.

MATERIAL AND METHODS

The study area is located in eastern Turkey (N 39° 55′ 31′′, E 40° 40’ 12″). The region has a continental climate, characterized by hot, dry summers and cold, snowy winters. Eastern Anatolis is the coldest region in Turkey and has a very short vegetation period. Relative humidity averages 60%. The soil is classified as Vertisol according to the USA taxonomy, with parent materials mostly consisting of volcanic, marn and lacustrin transported material. The major type of plant cover is steppe. Forests are located in the higher parts of mountains in the north and northeast. Woodland communities include *Pinus sylvestris. Picea orientalis, Fagus orientalis, Quercus petrea, Juniperus oxycedrus, Abies nordmanniana, Ulmus minor,* and *Fraxinus excelsior* species and conifers, mostly at altitudes of 700-2500 m. The Aşkale cement plant is located 55 km west of the town of Erzurum. It has been operating in the area since 1974.

Study area and climatic condition

Four lichen species were collected from ten different provinces in Eastern Anatolia, Turkey, in July 2008. The species, identifed using various keys (ASLAN 2000, ASLAN et al. 2002), were *Cetraria islandica* (L.) Ach.*, Lobaria pulmonaria* (L.) Hoffm.*, Pseudevernia furfurace*a (L.) Zopf., and *Usnea longissima* Ach. Lichen species were transplanted on trees on the cement plant premises, placed 50, 100 or 200 m downwind from the combustion unit of the plant, in 10 replications. Both soil and lichens samples were taken four, eight and twelve months after the transplantion of the lichens into the area. Twenty surface (0-10 cm) soil and 20 lichens samples were taken at each sampling time.

Soil Analysis

Soil samples were air-dried, crushed and passed through a 2-mm sieve prior to chemical analysis. Total Cu, Pb, Ni, Al, Cr and Cd were determined after wet digestion using a HNO_3-HCl acid mixture 10 ml (1:3 v/v) according to MERTENS (2005a,b), using a Bergof Speedwave MWS-2 microwave (Bergof Speedwave Microwave Digestion Equipment MWS-2) and an Optima 2100 DV Inductively Couple Plasma spectrophotometer (Perkin-Elmer, Shelton, CT, USA).

Lichen Analysis

Lichen samples were oven-dried at 68°C for 48 h and ground to pass through a 1-mm sieve. Total Cu, Pb, Ni, Al, Cr and Cd were determined after microwave wet digestion using a HNO_3-H_2O_2 acid mixture (2:3 v/v) according to MERTENS (2005a,b) in a Bergof Speedwave MWS-2 microwave (Bergof Speedwave Microwave Digestion Equipment MWS-2) (BRODO et al. 2001), and an Optima 2100 DV Inductively Couple Plasma spectrophotometer (Perkin-Elmer, Shelton, CT, USA).

Statistical analysis

Data gathered from individual exposure times (four, eight, and twelve months) were subjected to analysis of variance (ANOVA) and mean separation using Duncan's test at $P<0.05$ of SPSS 13.0 statistical program,with the distance (50, 100 and 200 m) as a fixed effect and replications as random effects.

RESULTS AND DISCUSSION

Soil transition and essential, non-essential and basic metal content

Essential (Cu), non-essential (Ni, Cr, Cd), and basic metal (Al and Pb) concentrations in the soil samples varied with the distance (50, 100 or 200 m) from the combustor of the cement plant (predominant wind direction). It was demonstrated that cement fumes increased the content of all of the metals, especially non-essential and basic ones. There were statisitically significant differences between the distances in respect of the total element concentration (Table 1). The total Cu, Ni, Cr, Cd, Al and Pb content near the cement plant soils (50 m) was considerably higher than in samples taken far away from the cement plant (100 and 200 m) – Table 1. The levels of the determined metals decreased rapidly with the distance, reaching the background amounts at a distance of 100 m. In general, Cu, Ni, Cr, Cd and Pb were more abundant in the topsoil (0-10 cm) than the deeper soil layers (10-30 cm) (data not given). These metals originating from industrial operations are distributed in soil by the atmospheric deposition as a function of the distance.

Lichen transition and essential, non-essential and basic metal content

It was shown that cement fumes raised the content of non-essential and basic metals in lichens. Essential (Cu), non-essential (Ni, Cr, Cd) and basic metal (Al and Pb) concentrations in lichen samples varied with the distance from the combustor of the cement plant and duration of exposure. There were statisitically significant differences between the distance and duration

Table 1

Mean (n=10) and ranges for the descriptive parameters of 50 soil samples (0-10 cm depth) from 50, 100 or 200 m downwind from the combus-tion unit of the plant before the lichens transplant

		Unpolluted area		Polluted area					
Parameter	units	mean	range	mean 50 m	range	mean 100 m	range	mean 150 m	range
General soil properties									
pH		7.8 ^{b*}	7.20-8.10	8.2 ^{a}	7.25-8.70	7.96 ^{ab}	7.15-8.40	7.82 ^{b}	7.10-8.14
EC	(ms cm^{-1})	366 ^{b}	310-430	405 ^{a}	320-460	394 ^{ab}	325-445	370 ^{b}	310-420
OM	(%)	1.2 ^{c}	0.8-2.2	1.4 ^{a}	0.7-2.8	1.4 ^{a}	0.6-2.6	1.3 ^{b}	0.4-1.9
$CaCO_3$	(%)	9.1 ^{c}	6.8-23.5	13.6 ^{a}	6.0-30.5	11.4 ^{b}	6.4-24.7	8.9 ^{c}	6.4-20.5
CEC	(cmolc kg^{-1})	43.5 ^{ab}	33.5-69.7	48.2 ^{a}	35.5-74.3	42.8 ^{b}	30.5-60.2	40.8 ^{c}	31.4-58.7
Essential transition metals									
Cu	(mg kg^{-1})	3.4 ^{c}	2.2-5.2	7.8 ^{a}	2.2-10.8	6.2 ^{b}	2.4-8.4	4 ^{c}	2.0-6.1
Non-essential transition metals									
Cd	(mg kg^{-1})	10.1 ^{d}	6.8-15.9	24.9 ^{a}	7.4-60.6	18.6 ^{b}	7.04-48.4	13.2 ^{c}	7.22-27.5
Cr	(mg kg^{-1})	121 ^{d}	98-155	197 ^{a}	114-205	154 ^{b}	102-196	134 ^{c}	98-172
Ni	(mg kg^{-1})	31 ^{d}	27-44	68 ^{a}	28-74	51 ^{b}	22-63	34.8 ^{c}	23-42
Basic metals									
Pb	(mg kg^{-1})	0.6 ^{d}	0.2-2	2.3 ^{a}	0.2-4	1.8 ^{b}	0.2-3.1	1.2 ^{c}	0.2-2.8
Al	(mg kg^{-1})	10 940 ^{c}	9 760-21 456	11 430 ^{a}	9 760-23 423	11 000 ^{b}	9 620-20 300	10 900 ^{b}	9 500-20 000

*Means followed by different letters are significantly different (α</0.05) tested in rows.

of exposure variants in respect of total element concentrations (Figures 1, 2). *Pseudevernia furfuracea* was the most effective indicator of cement dust pollution. Nickel, Cd, Cr, Cu and Pb accumulated the highest in lichen thalli within 50 m of the plant and 12-month period of exposure, while the concentrations of Al were not consistently affected by the distance from the plant and duration of exposure.

Concentrations of some essential (Cu), non essential (Ni, Cd, Cr,) and basic (Pb) metals in soil and in lichen species near the cement plant were higher than in samples taken far away from it. They decreased rapidly with the distance from the road, and reached the background level within the 100 m transect. The relationship between the content of metals in soil and in lichens versus the distance from the cement plant can be described using a power function (Figures 1, 2). But cement fumes did not affect the basic metal (Al) content in lichens and the mean differences for this element were not statistically significant.

The above findings provide evidence that the cement plant and industrial waste incinerator are sources of metals that influence the elemental composition of the nearby topsoil. In the study area, higher concentrations of Ni, Cd, Cr, Cu and Pb may be explained by rock crushing during cement production. Cement is made through the reaction of crushed and ground calcareous rocks (limestone or chalk) and argillaceous rocks (clay or shale) at high temperatures.

The distribution pattern of the total concentration of an element can be used to judge whether the enrichment with that element is caused by the fume pollution, farming practice or natural parent material. The enrichment factor (EF) (EF_{soil}= $(M/Fe)_{soil}/(M/Fe)_{control}$) is also used as an index to distinguish whether a given element in soil originates from natural or anthropogenic sources. According to OLIVIA and ESPINOSA (2007), the enrichment factor value >2 is considered as a critical level of enrichment contributed mainly by anthropogenic inputs.

Solid particles can have a negative effect on the air quality, and cement manufacturing is among the industries responsible for particle pollution. Although cement factories are generally established far from city centers, local areas are affected negatively. Cement dust spreads over a large area through wind, rain, etc., accumulates in and on plants, animals and soil, and can be very harmful to human health (AYVAZ 1992).

Agricultural soils receive metals mainly from fertilizers, manure, pesticides, wastewater and other scattered point pollution sources such as industries, traffic emissions, incineration facilities, etc. The geographical distribution of copper in the investigated area is mainly dominated by the cement plant emissions. The lowest value was measured in the most distant sites from the cement plant, where it fell down to 5.6 mg kg^{-1} dry lichen (Figure 1). This proves that anthropogenic activities are the main source of the metal in soil.

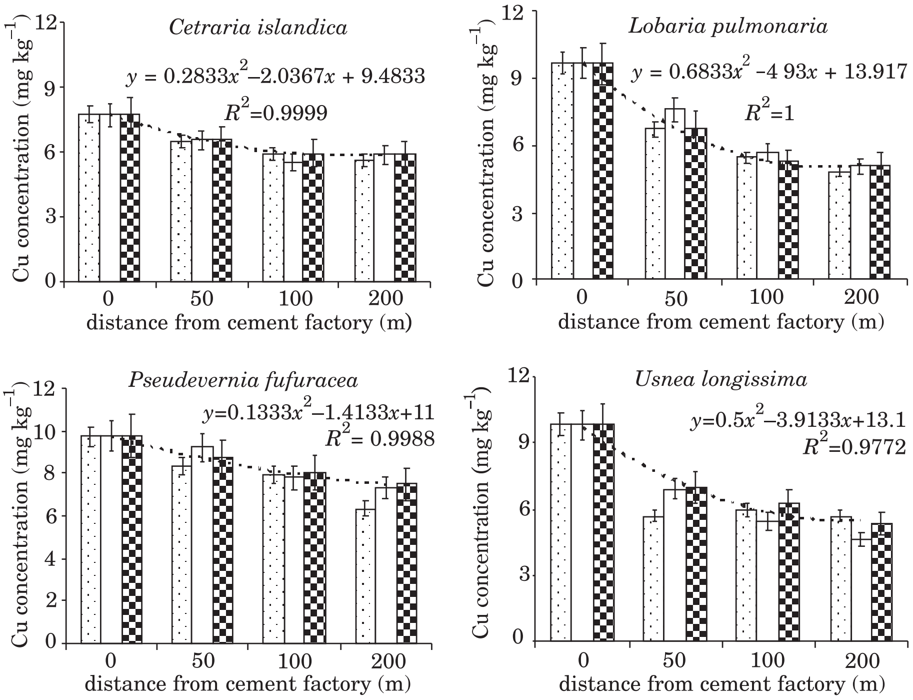


Fig. 1. Impact of location (distance relative to a cement factory) and duration of exposure on the Cu (essential transition metals) content of four lichen species

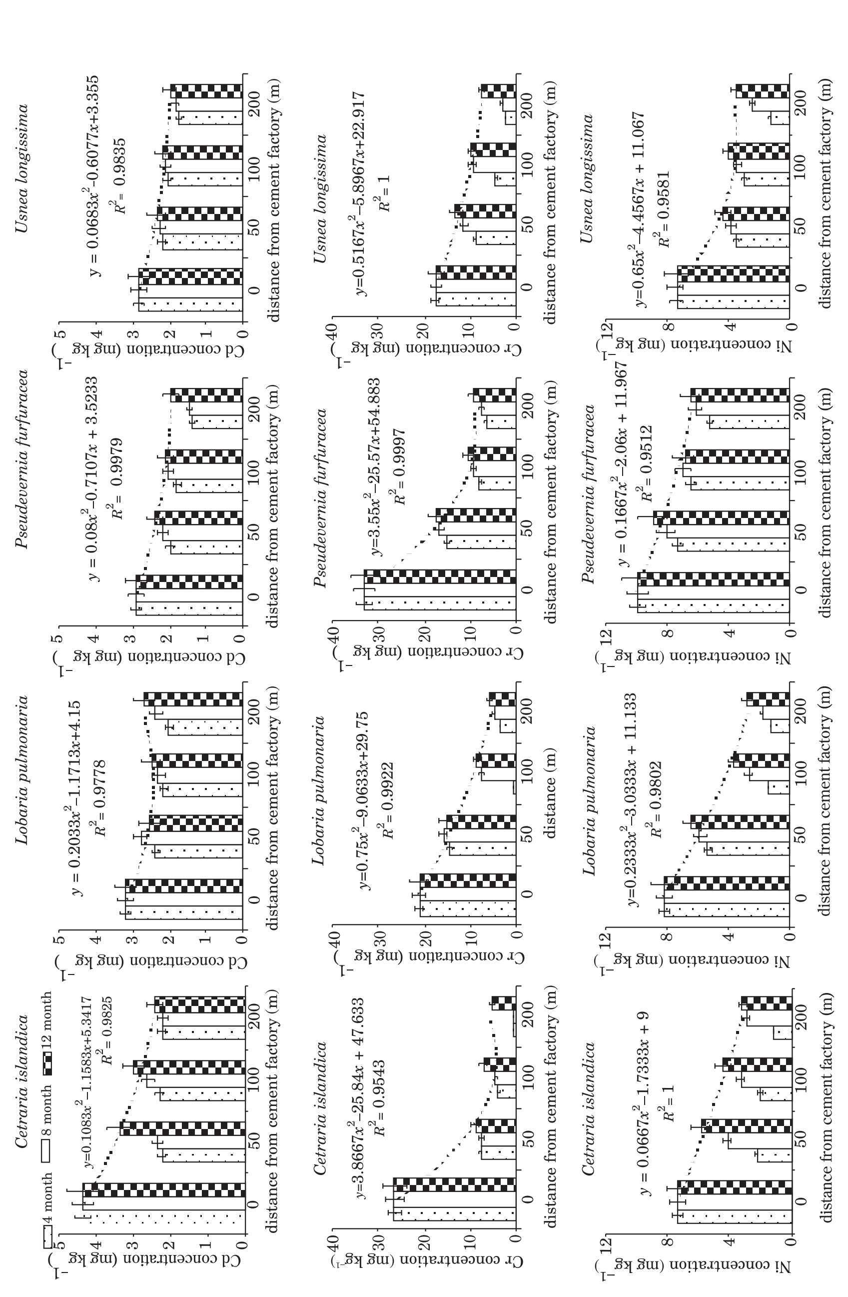
Copper is a trace element in most of soils. It is an essential element for plants, animals and people, but has also been implicated as a toxic element to all organisms. According to the WHO, the copper content in soil ranges between 2 and 60 mg kg^{-1} (WHO, 1998).The toxic concentration was set at 130, 70 and 100 mg kg^{-1} by the ICRCL (1987), ERD (1999) and Efroymson et al. (2007), resepectively, In the Netherland, UK, Hong Kong, and Turkey, the governments defined such levels at 36 mg kg^{-1}, 27 mg kg^{-1}, 24.8 mg kg^{-1}, and 140 mg kg^{-1}. Accordingly, the concentation of total Cu of all lichen samples (ranged from 5.6-7.73 mg kg^{-1}) in this study area was not toxic.

This study, however, has demonstrated that the main source of Cu pollution in the analysed soil was the cement plant, and the affected area was only in the direct vicinity to the plant (Figure 1). There were correlations beetwen the soil and lichen Cu content versus the distance (50, 100 or 200 m) from the combustor of the cement plant, and the Cu concentrations in the polluted soil and lichens revealed similar trends. The Cu content in lichens determined in our study was higher than reported by Bajpai et al. (2010) for north India. On the other hand, the Cu content in the polluted soil determined in our study was higher than observed by Al-Khasman and

SHAWABKEH (2006) in Jordan but lower than obtained by THORNTON (1991) in London, PATERSON et al. (1996) in Aberdeen, WONG et al. (1996) in Hong Kong, LI et al. (2001) also in Hong Kong, and BANAT et al. (2005) in central Jordan.The relationships between the content of the metal in soil or in lichens and the distance from the cement plant can be described using a power function. The coefficient of determination for the fitted regression model was significant (r^2 = 0.99). The EF values of Cu ranged from 1.40 to 2.2 and increased nearer the cement plant (Figure 1). The EF value of Cu can be a good criterion for distinguishing the pollution from cement plant emissions. The highest Cu uptake was detected by *Pseudevernia furfuracea* species at 12-month period. This finding supports the claim that the cement plant emissions contributed to the Cu pollution. Moreover, Cu accumulated in the investigated area at an accumulation rate similar to that of Cd, both of the metals being the main pollutants from the cement plant's emissions.

Chromates are among allergens that are unavoidably widespread in the environment. Because chromate salts are used in the machine industry and cement forms contain a certain amount of chromate, chromium sensitivity is considered an industrial problem (WHO 1998). Chromium is a trace element in most of soils. It is not an essential nutrient of plants, but is a trace essential element for animals and people. It is also considered toxic, especially of its Cr (VI) form. The toxic concentrations were set at 100 mg kg^{-1} by ANON (1983), while PATERSON et al. (1996) set the threshold at 24 mg kg^{-1}, and the BALL et al. (1991) claimed it was 84 kg^{-1}. The concentration of the soil total Cr in the study area ranged from 0.6 to 26.5 mg kg^{-1} (134 1-197 mg kg^{-1} in Table 1) . Thus, the soil Cr content data showed that the study area was polluted with Cr. The Cr content in the polluted soil and lichens had similar trends in respect to the distance (50, 100 or 200 m) from the combustor of the cement plant (Figure 2). The Cr content in lichen tissues determined in our study was higher than obtained by TUNCEL and YENISOY-KARAKAS (2003) in Western Anatolia, JERAN et al. (1996) in Slovenia, STEINNES et al. (1992) in Norway and BAJPAI et al. (2010) in north India, but lower than achieved by SLOOF and WOLTERBEEK (1991) in the Netherlands. On the other hand, the Cr content in the polluted soil determined in our study was higher than reported by AL-KHASMAN and SHAWABKEH (2006) in Jordan, THORNTON (1991) in London, PATERSON et al. (1996) in Aberdeen, WONG et al. (1996) in Hong Kong, LI et al. (2001) in Hong Kong, BANAT et al. (2005) in Central Jordan and CALZONI et al. (2007) in Italy. The Cr pollution of arable lands was mainly from the cement plant emission, with the atmospheric deposition being the major source. The total concentration of Cr in the analysed soil decresed with an increase in the distance from the cement plant, while thee total Cr content in lichen tissues rose with the increasing duration of exposure. These correlations proved that the predominant pollution source of Cr in this area was the cement plant's emission and the affected area was only the immediate surroundings of the main cement plant facilities (Figure 2). The relationship between the content of Cr in soil or lichens and the distance from the cement plant can be described using a power function. The coefficient of determination for the fitted regression model was significant ($r^2 = 0.99$). The EF values of Cr ranged from 1.20 to 1.6 and increased nearer to the cement plant (Figure 2). The EF value of Cr can be a good critical value to distinguish the pollution from cement plant emission. The highest Cr uptake was detected by the *Pseudevernia furfuracea* species. This justifies the claim that emmissions from the cement plant are the principal contributor to the local Cr pollution. This also support the thesis that Cr was accumulated in the study area, and the accumulation rate was similar to that of Cd, both of the metals being the main pollutants from the cement plant. In the cement industry, the linings for rotaries contain chromium, which could be liberated by wear and friction, thus becoming a source of chromium in the soil and lichen samples (ANON 1983).

Cadmium is a trace element in most of soils. It is not an essential nutrient of plants, but is a toxic element to plants, animals and human beings. Cadmium is emitted into the atmosphere from natural sources, mainly basalt rocks, and from anthropogenic sources. Metallurgy (drying of zinc concentrates and roasting, smelting and refining of ores) is the largest source of anthropogenic atmospheric cadmium emissions, followed by waste incineration and other sources, including the production of batteries, fossil fuel combustion and generation of dust by industrial processes such as cement manufacturing (YAMAGATA 1970). Generally, cadmium is found in lower concentration than other metals in soil. In the investigated area, the high levels of Cd in lichens are associated mainly with emissions from the cement industry. According to ELLIS and REVITT (1982), zinc and cadmium may be derived from the mechanical abrasion of vehicles and also associated with tyre wear. Cadmium is also a common component of leaded petrol, diesel oil and even unleaded petrol (HUANG et al. 1994). Cadium pollution is associated with the wearing out of tyres and brakes, and with industrial fumes (BALL et al. 1994). The toxic concentrations were set at 1 and 3 mg kg^{-1} by ANON (1983), while BANAT et al. (2005) quote the amount of 5 mg kg^{-1}, and the municipalities of London, and Hong Kong sets target level at 1 and 2 mg kg^{-1} (THORNTON 1991, LI et al. 2001). The concentration of the total Cd in the analysed soil ranged from 2.0 to 4.3 mg kg^{-1} (13.2 to 24.9 in Table 1). Thus, the data showed that the study area suffered from Cd pollution. The cadmium pollution of arable lands was mainly due to the cement plant's emissions; the contribution of Cd from the atmospheric deposition prevailed (BAJPAI et al. 2010). The Cd content in the polluted soil and lichens showed similar trends in respect to the distance (50, 100 or 200 m) from the combustor of the cement plant. The Cd content in lichens determined in our study results was higher than obtained by TUNCEL and YENISOY-KARAKAS (2003) in Western Anatolia, JERAN et al. (1996) in Slovenia, or FREITAS et al. (1999) in Portugal. Moreover, the Cd content in the polluted soil determined in



Cetraria islandica
4 month
8 month
12 month
y=0.1083x²−1.1583x+5.3417
R² = 0.9825
Cd concentration (mg kg⁻¹)
distance from cement factory (m)
Lobaria pulmonaria
y = 0.2033x²−1.1713x+4.15
R² = 0.9778
Pseudevernia furfuracea
y = 0.08x²−0.7107x + 3.5233
R² = 0.9979
Usnea longissima
y = 0.0683x²−0.6077x+3.355
R² = 0.9835
Cetraria islandica
y=3.8667x²−25.84x + 47.633
R² = 0.9543
Cr concentration (mg kg⁻¹)
Lobaria pulmonaria
y=0.75x²−9.0633x+29.75
R² = 0.9922
distance (m)
Pseudevernia furfuracea
y=3.55x²−25.57x+54.883
R² = 0.9997
Usnea longissima
y=0.5167x²−5.8967x+22.917
R² = 1
Cetraria islandica
y = 0.0667x²−1.7333x + 9
R² = 1
Ni concentration (mg kg⁻¹)
Lobaria pulmonaria
y=0.2333x²−3.0333x + 11.133
R² = 0.9802
Pseudevernia furfuracea
y = 0.1667x²−2.06x + 11.967
R² = 0.9512
Usnea longissima
y=0.65x²−4.4567x + 11.067
R² = 0.9581

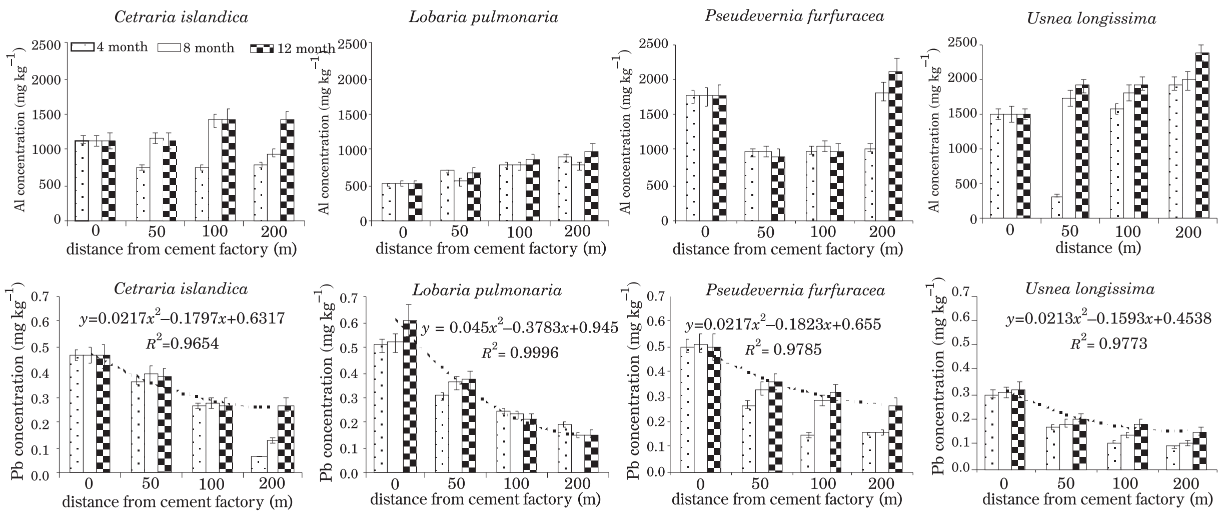


Fig. 2. Impact of location (distance relative to a cement factory) and duration of exposure on Cd, Cr and Ni (non-essential transition metals) and Al and Pb (basic metal) content of four lichen species

our study was higher than reported by AL-KHASMAN and SHAWABKEH (2006) in Jordan, THORNTON (1991) in London, and BANAT et al. (2005) in Central Jordan.

The concentration of the total Cd in soil in the study area decresed at larger distances from the cement plant, while the total Cd content in lichen species rose with the longer exposure time. These facts proved that the dominant source of pollution with Cd in this area's soil was the cement plant's emission and the affected area was limited to the nearest environs of the plant (Figure 2). The relationship between the content of Cd in soil or lichens and the distance from the cement plant can be described using a power function. The coefficient of determination for the fitted regression model was significant (r^2 = 0.97). The EF values of Cd ranged from 1.40 to 2.5 and increased with nearer to the cement plant (Figure 2). The EF value of Cd can be a good critical value to distinguish the pollution from cement plant emission. The highest Cd uptake was detected by *Cetraria islandica* species. This justifies the conclusion that emmissions from the cement plant contribute to the Cd pollution, but without more sophisticated calculations it is impossible to weigh out how much of it comes fromm the cement plant. The achieved data give a warning about the pollution with Cd in the analysed area.

Nickel is a trace element in soils. It is an essential element for animals and some plants. Some reports found it was richer in soils near cement plants, but no direct evidence has been produced to conclude that the said enrichment came from cement plants' emissions (MONACI et al. 2000, OLIVIA, ESPINOSA 2007). However, it was found that fossil fuel emissions contribute to nickel contamination The toxic concentration was set at 70, 38, 75 and 300 mg kg^{-1} by ICRCL (1987), ERD (1999), ANON (1983) and EFROYMSON et al. (2007), respectively, while the Netherland government sets their target level at 35 mg kg^{-1} (LIJZEN et al. 2002, ANON 2007). The concentration of the total Ni in all the lichen samples in the study area ranged from 1.2 to 9.3 mg kg^{-1} (Figure 2).

The Ni content in the polluted soil and lichens had similar trends in respect to the distance (50, 100 or 200 m) from the combustor of the cement plant. The Ni content in lichen tissues determined in our study was lower than obtained by BAJPAI et al. (2010) in North India. On the other hand, the Ni content in the polluted soil determined in our study results was higher than obtained by CALZONO et al. (2007) in Italy. This proves that the source of Ni pollution in the analysed soil was mainly the emission from the cement plant, and the affected area was the plant's immediate surroundings (Figure 2). The relationship between the content of Ni in soil or lichens and the distance from the cement plant can be described using a power function. The coefficient of determination for the fitted regression model was significant (r^2 = 0.95). The EF values of Ni ranged from 1.20 to 2.1 and increased nearer to the cement plant (Figure 2). The EF value of Ni can be a good critical value to distinguish the pollution from the cement plant's emissions. The highest Ni uptake was detected by *Pseudevernia furfuracea* species at the 12-month sampling period. This justifies the thesis that emssions from the cement plant contribute to the local Ni pollution.

Aluminum is the third richest element in soil, but it is not an essential nutrient for most plants. Although it was supposed to be a traffic pollutant, as it was found in cars' emissions due to being used in catalytic mufflers (LIJZEN et al. 2002), or in fumes emitted by car manufacturing plants, there is no evidence to prove that these sources pollute soils (MONACI et al. 2000). The Al content in the analysed soil and lichens had similar trends in respect to the distance (50, 100 or 200 m) from the combustor of the cement plant. The Al content in lichens determined in our study was lower than obtained by TUNCEL and YENISOY-KARAKAS (2003) in Western Anatolia, and by BAJPAI et al. (2010) in North India, but higher than reported by STEINNES et al. (1992) for Norway. The soil's total Al concentration decreased with an increase in the distance from the cement plant (Figure 2). The highest Al uptake was determined by *Usnea longissima*, and but all of the EF values were in a narrow range (0.9 to 1.0), which was due to the excessively high Al concentration in soil and the fact that the cement plant was not the main source of Al pollution. When the elemental composition of lichen tissues was compared to the sampling time, the highest Al content in lichens was determine at the 12-month period (Figure 2).

Lead is a trace element in soil, known for its toxicity to organisms. It is a component of leaded petrol, diesel oil and even unleaded petrol (<0.015 g L^{-1}). It is implicated as a main pollutant from traffic and industrial activities (SWIETLICKI et al. 1996, JANSSEN et al. 1997). The toxic concentration was set at 500 and 813 mg kg^{-1} by the ICRCL (1987), while EFROYMSON et al. (2007) and ERD (1999) set it at 50 and 120 mg kg^{-1}, respectively, and the governments in London, Hong Kong and Turkey set their target level at 85 mg kg^{-1}, 30 mg kg^{-1}, 93 mg kg^{-1} and 300 mg kg^{-1} (ANON 1983, THORNTON 1991, LI et al. 2001, LIJZEN et al. 2002, ANON 2007). The concentration of total Pb in the study area ranged from 0.1 to 1.8 mg kg^{-1} (1.2 to 2.3 in Table 1). Thus, the data from soil analyses showed that the Pb pollution was not severe. The concentration of the total pB in soil in the study area decresed with an increase of the distance from the cement plant, while an increase in the total Pb content in lichen species occurred with the increasing sampling time. This proved that the source of Pb pollution of soil in this area was mainly the cement plant, and the affected area was only the land near to the main cement plant facilities (Figure 2). The relationship between the content of Pb in soil or lichens and the distance from the cement plant can be described using a power function. The coefficient of determination for the fitted regression model was significant (r^2 = 0.97). This could be attributed to the fact that thee cement industry requires substantial amounts energy for the process and production of cement, which is supplied by burning fossil fuel. Another source of Pb pollution could be the traffic in and around the cement plant (ICRCL 1987). The Pb content in the polluted soil and lichen had similar trends in respect to the distance (50, 100 or 200 m) from the combustor of the cement plant. The Pb content in lichens determined in our study was lower than obtained by BAJPAI et al. (2010) in north India. Moreover, the Pb content in the polluted soil determined in our study was lower than obtained by AL-KHASMAN and SHAWABKEH (2006) in Jordan, THORNTON (1991) in London and CALZONI et al. (2007) in Italy. The EF values of Pb ranged from 1.20 to 2.1 and increased closer to the cement plant (Figure 2). The EF value of Pb can be a good critical value to distinguish the pollution from a cement plant's emissions. The highest Pb uptake was detected by *Pseudevernia furfuracea* species at a 12-month sampling period. The Pb concentration reached a constant level over 100 m distance from the cement plant. This justified the claim that the cement plants could contribute to Pb pollution.

CONCLUSIONS

The data obtained in this study demonstrate that metal concentrations in urban soils can be used as a powerful geochemical indicator for monitoring the impact of anthropogenic activity, provided that the background levels have been correctly interpreted and established. The distribution of metals in the analysed soil indicated that the area had been affected by anthropogenic activity, in particular by the cement industry, leading to a high accumulation of heavy metals compared with the natural background levels. The distribution of the metal concentration of the soil in the study area indicated that the cement industry together with other industrial activities were responsible for most of the metal pollution, as the highest metal concentrations were found close to the cement factory. The conclusion regarding anthropogenic influences was further corroborated by analyses of soil and lichen samples collected around the cement factory at sites chosen according to the prevailing wind direction. The results of the statistical analysis and distribution of the pollutant metals suggested that cement emissions represented the most important source of contaminants for the investigated area. The contamination of soils near the cement lant with heavy metals emmited by the factory is rarely detected at a distance of over 200 m, but closer than 100 m from the factory soil is found to be contaminated with Ni, Cd, Cr, Cu and Pb. Further away from the cement plant, the EF factor reached values that proved the contamination was not predominantly from the cement emission. They included the critical value of about 1.5. In conclusion, it can be said that an appropriate and safe distance of over 200 m from a cement plant should be selected for residential purposes in order to avoid contamination with Ni, Cd,Cr, Cu and Pb. In our studz, this was the distance where the background levels of Ni, Cd, Cr, Cu and Pb were almost reached. The coefficient of determination for the fitted regression model was significant (r^2 = 0.95). This implies that the Ni, Cd, Cr, Cu and Pb content of soil and lichens was strongly dependent on the distance from the cement plant.These findings suggest that the lichen species *Pseudevernia furfuracea* and *Usnea longissima* present in the region can be used to monitor pollution originating from a cement plant origin, that particularly *Pseudevernia furfuracea* is a very good indicator of such contamination. Because lichens grow very slowly and are rarely encountered in polluted areas, lichen transplantation seems to be a solution. Transplantation of *Pseudevernia furfuracea* could be an easy and cost-effective means of air pollution monitoring and could provide valuable data for undertaking preventive measures. In this work, our goal was to contribute to lichen studies, which are of great importance for bio-monitoring, and this article disucsses metal pollution originating from a cement plant, using structural features of lichens. Further studies should be conducted, including determinations of pollution in different soil profile depths near cement plants and of the hiperaccumlator capacity of lichen species across the region.

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