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ORIGINAL PAPER

Comparison of response of moss, lichens and attic dust to geology and atmospheric pollution from copper mine

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Abstract Different sampling media (moss, lichen and attic dust) were used for monitoring the distribution of 15 elements, including certain trace elements, in the vicinity of an intensively exploited copper mine in the east of the Republic of Macedonia. Moss species (Hypnum cupressiforme and Campothecium lutescens), epiphytic lichens (Hypogymnia physodes and Evernia prunastri) and attic dust were collected for comparative analysis for monitoring air pollution. In both cases (lithological and anthropogenic affected areas) for the distribution of elements, the sampling media follows the expression capabilities: attic dust > moss > lichens. Enrichment factors M/L—moss vs. lichen, for plant response to elements distribution and D/L—attic dust vs. lichen, for historical response of elements distribution were significant for Cu and Ni, which were singled out as the main markers for anthropogenic and geogenic distribution. The factor analysis highlighted geogenic (F1: Ni-Cr-Cd-Fe-Al-K-Mn-Zn) and anthropogenic (F2: As-Cu-Pb) association of elements from three types of media samples. For anthropogenic affected areas, T value and F value for Cu content were significant at $p < 0.05$ and higher enrichment factors were obtained for lichen, moss and attic dust media (3.8, 5.0 and 5.7, respectively). Spatial distribution for element deposition (with emphasis on Cu and Ni) is not disturbed by the significant differences in the sampling media matrix. Treated sample materials (attic dust, moss, lichen) are shown to be useful in determining an anthropogenic impact, as well as the chemical properties or geological background on orographic diverse terrain in the presence of complex geological structure.

Keywords Attic dust · Bučim copper mine · Macedonia · Lichen · Moss · Spatial distribution

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Introduction

The environmental fate of heavy metals absorbed on to dust particles is of growing concern when addressing environmental issues for mine and processing plants environs (Pacyna et al. 2007). The complexity of the contamination sources and the large amounts of waste tailings produced is of high priority when investigating the contamination levels and the mechanisms that rule their distribution and deposition in the local environment (Järup 2003; Vallero 2008; Ashraf et al. 2011). Different media sampling is used for monitoring the possible air pollution by heavy metals around metal emission sources. Long-term and long-distance monitoring are sensitive for different types of sampling media and stability and responsiveness with respect to environmental and pollution conditions, present limitations for implementing air pollution monitoring (Artiola et al. 2004). The ability of moss and lichen to accumulate trace substances present in the lower atmosphere is well known and their potential as biomonitors of environmental pollution by heavy metals has been documented by numerous studies (Branquinho et al. 1999;

Garty 2001; Onianwa 2001; Jeran et al. 2002; Culicov et al. 2005; Chakrabortty and Tryambakro-Paratkar 2006; Market 2007; Balabanova et al. 2010, 2012). The different morphological and physiological properties of mosses and lichens partially account for the differences in metal-uptake efficiency. However, the extent to which humans spend time in their houses, household vacuum cleaner dust and especially attic dust, might preserve a record of human exposure to ambient air pollutants that infiltrate indoor environments, as well to those materials that were present outdoors. The use of undisturbed attic dust has the advantage of being a measurement, albeit indirect, of air pollution. An attic dust measurement provides an integrated measure based on the above variables over time; therefore, it is closer to the endpoint in the process continuum from source to exposure and ultimately, to effects. Attic dust allows investigations of historical air pollution on much smaller scales, including the micro-scale to regional scale. Attic dust is derived primarily from external sources through aerosol deposition and as a result of soil dusting, rather than household activities (Šajn 2003). The usefulness of different types of urban dust and especially of attic dust, as a suitable long-term monitor for determining the status and content in air, has been proven by numerous studies (Alijagić and Šajn 2011; Gosar et al. 2006; Cyrys et al. 2003; Jeffrey et al. 2005; Šajn 2003, 2005, 2006; Žibret 2008, 2012; Žibret and Rokavec 2010; Žibret and Šajn 2008; Balabanova et al. 2011).

Geochemical research on large lowland areas, mostly in Northern Europe, where there is little influence by local winds, or where the area lies on a unique geological structure (primarily large alluvial plains or glacial deposits), has shown that it is relatively straightforward to determine the source of pollution, or the state of the natural distribution of chemical elements in particular sampling media. In addition, a developed infrastructure (such as the roads, paved areas, buildings) is appropriate for the sampling of dust sediments, such as a street dust and household dust, which reveals the current chemical state of the environment.

To assess the state of the chemistry of the environment in mountainous, sparsely populated areas is much more difficult. Owing to the lack of infrastructure, it is almost impossible to collect a sufficient number of statistically significant samples of urban dust, such as street dust or household dust (Šajn 1999; Žibret and Rokavec 2010; Žibret 2012).

This problem can be solved by sampling various biogenic materials, such as moss and lichen, the usefulness of which has already been proven for the evaluation of environmental chemism (Branquinho et al. 1999; Garty 2001; Onianwa 2001; Jeran et al. 2002; Culicov et al. 2005; Chakrabortty and Tryambakro-Paratkar 2006; Market 2007; Balabanova et al. 2010, 2012). Chemical distribution in biogenic material, due to their nature (accumulation of airborne particles and the impact of rainfall), corresponds more to the distribution of street dust (Žibret and Rokavec 2010; Žibret 2012). Sampling of such materials can be a significant problem, particularly in Macedonia, because of the dry climatic conditions. Specifically, moss or lichen do not thrive on flat plains but are fairly common on the hilly or mountainous areas where there is more rainfall (Balabanova et al. 2010, 2012).

The characteristic difference between the attic dust and biogenic sampling material is that attic dust records historical air contamination, for the period of operation of a source of contamination (Šajn 2003, 2005, 2006; Gosar et al. 2006). On a roof constructed of wood we get an undamaged sample; the total air deposit that has accumulated since the period of construction until the moment of sampling. Unlike attic dust, biogenic materials give only the current state, or a maximum period of plant growth. Another important aspect is that the distribution of elements in biogenic material is affected by precipitation reactions, due to which certain chemical elements are redistributed. At the same time, they are strongly influenced by soil dust formed from the bedrock. In addition, attic dust is sampled at the greatest height above the ground, followed by lichen on branches and mosses on the soil surface. Thus, attic dust, moss and lichen have the potential for collecting complementary information on present and historical air pollution trends.

The main objective for this study was to represent a systematically model for monitoring of air pollution with heavy metals; developing a comparative methodology for monitoring the current and parallel historical records of heavy metals—air pollution. On the other hand, critical goal was also included: determination of the most stable and also the most responsive sampling medium for determining a long-term status of atmospheric chemism (with emphasis on heavy metals contents); determination of main markers for geogenic and anthropogenic influences in potentially polluted area. Intentionally, an area with intensive exploitation of Cu minerals (copper mine "Bučim", near the city of Radoviš, Republic of Macedonia), was selected as a study area in the period of September–October 2010. Disposed mining waste rock materials as well as fine particles from the flotation tailing dam create environmentally hazardous conditions for residents and ecosystems at a local level. Disposed waste rock (ore tailings) and flotation tailings present the main emission sources of dust in the atmosphere. Therefore, the purpose of the investigation was also to determine whether the comparison method has the potential to reconstruct air pollution histories since the launching of the mining activities as well as to determine the intensity of pollution in some certain periods in the past with a simple selection of the age of the sampled object (attic dust and biogenic materials: moss and lichens).

Materials and methods

Study area

An area of 400 km^2 was monitored, bounded by coordinates 41°32′–41°44′N and 22°15′–22°30′E, located in the eastern part of the Republic of Macedonia (Fig. 1). A copper mine (open pit) environment was monitored as an area potentially polluted with anthropogenically introduced higher contents of certain heavy metals. The region is characterised by a moderate continental climate. The altitude varies between 350 and 1,000 m. The average annual rainfall is 563 mm with large variations from year to year. Most frequent winds in the region are those from the west with frequency of 199 ‰ and 2.7 m s^{-1} speed and winds from the east with frequency of 124 ‰ and 2.0 m s^{-1} speed. Climatic conditions in the region allow the airborne distribution of fine dust particles generated by mining activities and exposed ore and flotation tailings. The intensively exploited copper mine is located in the centre of the study area, from where dust distribution occurs continually. The Bučim mine and ore processing plant have been in operation since 1979 and it is assumed that the mine has about 40 million tons of ore reserves. Ore tailings are deposited by the dampers from the open ore pit at an open site near the mine. The deposit contains about 130 million tonnes of ore tailings and occupies an area of 0.80 km^2. In the process of flotation of copper minerals, the average annual amount is about 3.95 million tons of flotation tailings. These tailings are drained and disposed of in a dump near the mine. The exposure of this great mass of ore and flotation tailings to constant air flow and winds leads to the distribution of fine dust in the air (Stafilov et al. 2010).

Geological description

The investigated area represents a part of the Vardar structural zone, separated from other structural zones during the Caledonian, and subjected to strong tectonic deformation during the Hercynian orogenesis. The structural relations were further complicated by the Alpine orogenesis.

According to Hristov et al. (1965) and Rakićević et al. (1969), the oldest formations are represented by the Precambrian gneisses and micashists and white marble lenses. The lower Paleozoic comprises sequences composed of amphibolite schists, marbles and schistose carbonate rocks.

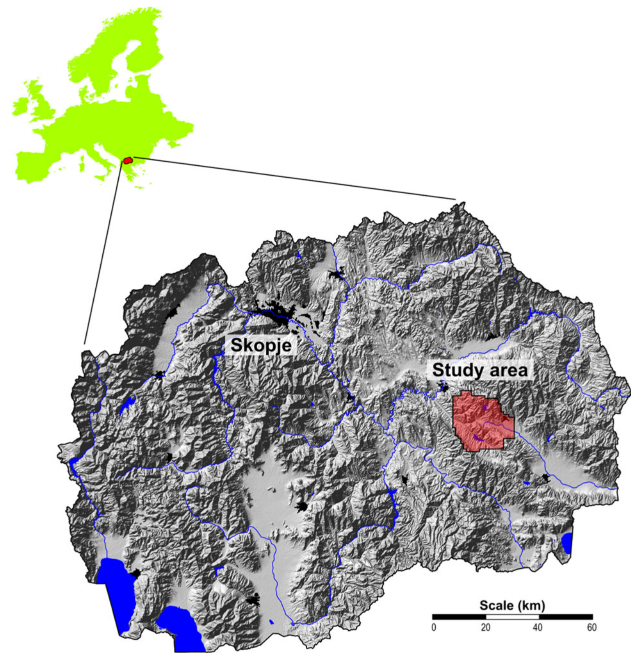

Fig. 1 Location of the study area

Except for minor intrusions, serpentines also occur as xenoliths in the granites. Mesozoic rocks outcrop in a very small part of the study area. The aforementioned rocks are covered by the narrow belt of tertiary deposits represented by the upper Eocene sediments that have been intruded by Neogene andesites and their pyroclastites. The Pliocene lacustrine sandy series is developed in a wide area of the Radoviš basin. Holocene deposits (river terraces and alluvial sediments) were also developed on the Radoviš basin.

The small metallogenic area of Bučim-Damjan-Borov Dol is characterised by deposits and mineralisations of iron, copper, gold and base metals. The Bučim Cu and Au mine is the only mine in the Republic of Macedonia that belongs to the Serbo-Macedonian metallogenic province. It was discovered in 1955, explored in the period 1962–1979 and production commenced in 1979. Bučim is Macedonias principal producer of Cu, operating as a mine and ore processing installation near Radoviš. In 1999, milled 4 Mt of ore were processed to yield 21,000 t of copper and 700 kg of gold in concentrates. Ore reserves amount to a total of 80 Mt grading 0.3 % Cu, 0.35 g/t Au in four discrete ore bodies (Stefanova et al. 2004). The map for generalized geology of the investigated area was previously published (Balabanova et al. 2011).

Sampling design and procedures

Specific types of moss were selected according to the protocol adopted within the European Heavy Metal Survey (Barandovski et al. 2008). Hypnum cupressiforme (Hedw.) and Campothecium lutescens (De Not.) were used as moss

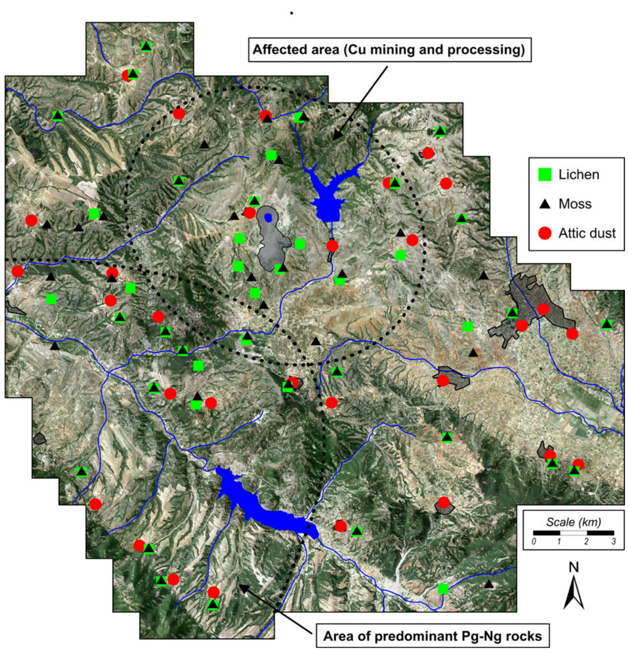

Fig. 2 The map of the study area with location of sampling points

biomonitors, characteristic of the flora of the Republic of Macedonia (Balabanova et al. 2010). Hypogymnia physodes (Nyl.) and Evernia prunastri (Ach.) were used as characteristic lichen species (Balabanova et al. 2012). Moss and lichen samples were collected according to the previously defined sampling network in the spring of 2010. Depending on the conditions and the accessibility of the locations, those species that were available and typical of the region were collected.

The moss and lichen sampling protocol was performed according to set standard rules for the collection of such samples (Tuba et al. 2007) and it was done in the following order: one sampling spot is formed by collecting five sub-spots in an area of 50 × 50 m^2. Every spot of the sampling network must be a minimum distance of 300 m from main roads, 100 m from local roads and 200 m from villages. Moss and lichen samples were collected using polyethylene gloves to prevent any further contamination. The collected material was stored in paper bags. After it was cleaned of other plant species and soil, individual plant samples were separated and air-dried for several days. Dry samples were again placed in paper bags until the analyses were performed. Moss samples were collected at 52 studied localities and lichen samples were collected from 50 localities as presented at Fig. 2.

Attic dust samples were collected from houses in the settlements within the study area (Fig 2). In every settlement, attic dust was collected from two or three houses on different sites (year of construction up until 1970) to establish the long-term accumulation of heavy metals in the study area (Balabanova et al. 2011). The collection of attic dust samples was performed according to the adopted protocol (Šajn 2003, 2005): the surface of the attic beams was first cleaned of rough dust and then the finest dust was collected with a plastic brush and placed in polyethylene bags. In each settlement, dust samples from two or three houses were collected to determine the average content of heavy metals in the samples. Sixty-four dust samples were collected from twenty-nine locations (settlements).

Sample preparation

The preparation of moss and lichen samples was performed by cleaning, drying, chopping and digestion. For the digestion of moss and lichen samples, a microwave digestion system was applied. A precisely measured mass (0.5 g) of each moss sample was placed in Teflon digestion vessels to which 5 ml of concentrated nitric acid (HNO_3) and 2 ml hydrogen peroxide (H_2O_2 30 %, m/V) were added. The vessels were closed, tightened and placed in the rotor of a microwave digestion system. Finally, the vessels were cooled, carefully opened and the digests quantitatively transferred to 25 ml calibrated flasks.

For the digestion of attic dust samples, open wet digestion with a mixture of acids was applied. The digestion was carried out in the following order: a precisely measured mass of dust samples (0.5 g) with the accuracy of 0.0001 g was placed in Teflon vessels. After this, 5 ml concentrated nitric acid (HNO_3) was added until brown vapours were emitted from the vessels. Nitric acid is a very suitable oxidant for the digestion of environmental samples. For the total digestion of inorganic components 5–10 ml hydrofluoric acid (HF) was added. When the digest became a clear solution, 2 ml of $HClO_4$ was added. Perchloric acid was used for the total digestion of organic matter. After cooling, the vessels for 15 min, 2 ml of HCl and 5 ml of H_2O were added to totally dissolve the metal ions. Finally, the vessels were cooled and the digests quantitatively transferred to 50 ml calibrated flasks.

Analysis of element contents

Analyses for a total of 15 elements (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Sr, and Zn) within the digest samples were performed using atomic emission spectrometry with inductively coupled plasma, (ICP-AES, Varian 715-ES). As and Cd were analysed by electrothermal atomic absorption spectrometry (ETAAS). The optimisation of the instrumental condition for the analysed elements was done previously (Balabanova et al. 2010, 2011).

The QC/QA of the applied techniques was performed by the standard addition method and it was found that the recovery for the investigated elements ranges for ICP-AES was 98.5–101.2 % and for ETAAS was 96.9, 103.2 %. The same methods were applied for the determination of the analysed elements in the reference materials JSAC 0401 (soil) for the dust samples and M2 and M3 (moss) for the moss and lichen samples. The sensitivity with regard to the lower limit of detection was done.

Data processing

For the statistical analysis of data, both parametric and nonparametric statistical methods were used. The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics (Table 1). Data distribution was examined with the application of normality tests. The application of bivariate statistics showed how chemical elements correlate between their content in different sampling media. For that issue, the linear coefficient of correlation was used.

Enrichment factors were considered to evaluate the response of individual media samples. Coordination is made to determine how to express the values obtained for the contents of the elements (divide mean values for element contents).

Multivariate statistical methods (cluster and R-mode factor analyses) were used to reveal the associations of the chemical elements. Factor analysis was performed on variables standardised to zero mean and unit standard deviation (Reimann et al. 2002; Filzmoser et al. 2005; Žibret and Šajn 2008). As a measure of similarity between variables, the product-moment correlation coefficient (r) was applied. For orthogonal rotation, the varimax method was used. Those elements with low communalities were excluded because of their lack of significant associations.

To verify the results obtained by factor analysis, clustering multivariate methods were applied to the data. Cluster analysis encompasses a number of different classification algorithms that can be used to develop similarities between grouped elements.

Significant difference of the aforementioned population is additionally verified by the statistical T test and F test.

Results and discussion

Comparative analysis

The comparative analysis of the mean and range values for the analysed elements in lichen, moss and attic dust samples are given in Table 1. Enrichment factors M/L—moss vs. lichen, for plants response to elements distribution and D/L—attic dusts vs. lichen, for historical response of elements distribution, is presented in Table 1.

From the obtained values for elements content (Table 1), it is clearly visibly that lichens have lower retention power for accumulation for almost all the

Table 1 Descriptive statistics of analyzed chemical elements in various sampling materials (n = 50—lichen; n = 52—moss; n = 64—attic dust; 15 analyzed elements)

Element	Lichen		Moss		Attic dust		ER	ER
	X	Range	*X*	Range	*X*	Range	(M/L)	(D/L)
Al	580	150–2,500	2,100	470–8,500	11,000	1,800–22,000	3.7	19
As	0.89	0.10–3.8	2.6	0.14–14	8.1	0.50–52	2.9	9.1
Ba	14	3.8–30	32	12–66	4,600	3.9–39,000	2.3	330
Ca	6,500	1,300–20,000	6,400	4,500–11,000	6,000	340–19,000	0.99	0.93
Cd	0.12	0.10–0.38	0.54	0.18–1.8	2.0	1.1–3.1	4.6	17
Cr	2.3	1.0–6.9	3.1	1.0–11	39	17–110	1.4	17
Cu	**12**	**1.5–130**	**21**	**2.1–199**	**52**	**11–420**	**1.7**	**4.3**
Fe	710	190–4,500	3,300	740–12,000	12,000	1,100–18,000	4.6	17
K	2,400	1,200–3,700	3,200	1,900–4,500	8,800	5,600–12,000	1.4	3.8
Mn	57	14–150	170	59–440	210	110–450	2.9	3.7
Na	71	16–250	46	25–82	6,800	330–29,000	0.65	96
Ni	**2.8**	**1.5–10**	**7.4**	**2.1–30**	**23**	**8.9–59**	**2.6**	**8.2**
Pb	6.7	0.61–120	8.8	2.7–40	29	3.1–120	1.3	4.3
Sr	14	2.9–37	26	13–55	36	3.6–140	1.8	2.5
Zn	21	10–39	29	17–54	51	21–93	1.4	2.4

Bold values indicate anthropogenic distribution for Cu and geogenic distribution for Ni in the study area

X mean; Range (min–max); *ER* enrichment ratio; *M/L* moss vs. lichen; *D/L* attic dust vs. lichen; *n* number of observation

Table 2 *T* test, *F* test and enrichment ratios of 11 selected elements in sampling materials according to the determined main geological units

Element	Material	*X* (Ng–Pg)	*X* (Pz–Pt)	*T*		*F*		EF
Al	Lichen	490	620	−1.00	NS	1.01	NS	0.79
Al	Moss	2,200	2,100	0.38	NS	0.15	NS	1.1
Al	Attic dust	12,000	11,000	−1.77	NS	0.72	NS	1.1
As	Lichen	0.64	1.0	−2.22	*	4.91	*	0.64
As	Moss	2.8	2.5	0.28	NS	0.08	NS	1.1
As	Attic dust	5.4	9.5	2.87	*	2.84	NS	0.57
Cd	Lichen	0.12	0.11	0.62	NS	0.38	NS	1.1
Cd	Moss	0.54	0.54	−0.05	NS	0.00	NS	0.99
Cd	Attic dust	2.2	1.9	−1.48	NS	6.60	*	1.2
Cr	Lichen	2.3	2.3	0.10	NS	0.01	NS	1.0
Cr	Moss	3.9	2.8	1.80	NS	3.26	NS	1.4
Cr	Attic dust	56	30	−4.89	*	31.7	*	1.9
Cu	**Lichen**	**6.4**	**15**	**−1.38**	**NS**	**1.91**	**NS**	**0.44**
Cu	**Moss**	**6.8**	**26**	**−1.94**	**NS**	**3.76**	**NS**	**0.26**
Cu	**Attic dust**	**22**	**68**	**3.26**	*****	**5.54**	*****	**0.33**
Fe	Lichen	550	780	−1.15	NS	1.33	NS	0.70
Fe	Moss	3,200	3,300	−0.25	NS	0.06	NS	0.95
Fe	Attic dust	13,000	11,000	−2.01	*	2.49	NS	1.1
K	Lichen	2,300	2,400	−0.96	NS	0.93	NS	0.94
K	Moss	3,000	3,300	−2.27	*	5.13	*	0.89
K	Attic dust	8,600	9,000	0.92	NS	1.16	NS	0.96
Mn	Lichen	69	52	1.93	NS	3.73	NS	1.3
Mn	Moss	180	160	1.17	NS	1.36	NS	1.2
Mn	Attic dust	250	190	−3.04	*	12.2	*	1.3
Ni	**Lichen**	**4.0**	**2.3**	**4.36**	*****	**19.0**	*****	**1.7**
Ni	**Moss**	**11**	**5.9**	**4.24**	*****	**17.9**	*****	**1.9**
Ni	**Attic dust**	**35**	**17**	**−6.20**	*****	**61.5**	*****	**2.1**
Pb	Lichen	4.5	7.7	−0.60	NS	0.36	NS	0.59
Pb	Moss	8.4	9.0	−0.30	NS	0.09	NS	0.93
Pb	Attic dust	30	28	−0.47	NS	0.16	NS	1.1
Zn	Lichen	21	21	0.10	NS	0.01	NS	1.0
Zn	Moss	27	30	−1.47	NS	2.17	NS	0.90
Zn	Attic dust	45	54	2.62	*	6.04	*	0.83

Bold values indicate anthropogenic distribution for Cu and geogenic distribution for Ni in the study area

X (Ng–Pg) average concentration of chemical elements in area of predominant Pliocene sediments, Eocene flysch series and andesites and piroclastites ($n = 15$ lichen; $n = 15$ moss; $n = 22$ attic dust); *X* (Pz–Pt) area of predominant Precambrian and Paleozoic rocks ($n = 35$ lichen; $n = 37$ moss; $n = 44$ attic dust)

t result of *t* test; *F* result of *F* test for sampling materials between defined areas; *NS* no significance; * significance at $p < 0.05$; *ER* enrichment ratios (area of Ng–Pg rocks vs. area of Pz–Pt rocks)

analysed elements compared with mosses. This phenomenon is due to the higher porous structure of lichen, the rain washing effect and the strong influence of acidic surfaces to the accumulation of these elements. Moss species accumulate higher concentrations of lithophile elements (Al, Ba, Ca, Cr, K, Li, Mg, Na, Sr). However, lichen more easily accumulates chalcophile elements (Cd, Pb, Cu, Zn).

Correlations of element contents between lichen, moss and attic dust samples were examined. Correlation coefficients (*r*) between the various sampling materials (lichen-moss; lichen-dust and moss-dust) collected from the same sampling locations ($p < 0.05$) were accounted. The moss-dust significant correlation was singled out for Cd, Cu and Pb (0.41, 0.80 and 0.41, respectively). Lichen-dust correlation was significant for Cu and Pb (0.41 and 0.37, respectively). Copper is the most expressed element in the correlations of the three sampling media. The statistical observation included only values for elements contents from sampling materials collected from the same sampling locations.

The whole study area was monitored as two sub-areas: an area of predominantly Pliocene sediments, Eocene flysch series and andesites and pyroclastites (Ng–Pg) and an area of predominantly Precambrian and Paleozoic rocks (Pz–Pt). This approach was considered to determine the impact of geogenic effects as natural phenomena on the elements distribution in the different sampling media (Table 2). For Cu, no significant values were obtained for the *T* and *F* values; only for the sampling media of attic dust were significant values for the *T* and *F* values found (3.26 and 5.54, respectively), indicating strong response of this media to geogenic enrichment for Cu.

Table 3 *T* test, *F* test and enrichment ratios of 11 selected elements in sampling materials according to the defined affected areas

Element	Material	*X* (affected)	*X* (rest)	*T*		*F*		ER
Al	Lichen	660	520	1.11	NS	1.24	NS	1.3
Al	Moss	2,500	1,900	1.83	NS	3.33	NS	1.3
Al	Attic dust	12,000	11,000	0.50	NS	0.25	NS	1.1
As	Lichen	1.0	0.80	1.29	NS	1.67	NS	1.2
As	Moss	3.7	1.9	2.06	*	4.23	*	1.9
As	Attic dust	13	7.1	1.89	NS	3.57	NS	1.8
Cd	Lichen	0.13	0.11	1.31	NS	1.71	NS	1.2
Cd	Moss	0.67	0.45	3.02	*	9.10	*	1.5
Cd	Attic dust	2.3	2.0	2.52	*	6.33	*	1.2
Cr	Lichen	2.5	2.1	1.23	NS	1.52	NS	1.2
Cr	Moss	3.4	3.0	0.61	NS	0.37	NS	1.1
Cr	Attic dust	31	40	−1.34	NS	1.81	NS	0.77
Cu	**Lichen**	**21**	**5.4**	**3.01**	*****	**9.05**	*****	**3.8**
Cu	**Moss**	**41**	**8.1**	**3.83**	*****	**14.67**	*****	**5.0**
Cu	**Attic dust**	**160**	**28**	**6.99**	*****	**48.80**	*****	**5.7**
Fe	Lichen	880	580	1.67	NS	2.80	NS	1.5
Fe	Moss	4,000	2,800	2.28	*	5.19	*	1.4
Fe	Attic dust	10,000	12,000	−1.84	NS	3.37	NS	0.83
K	Lichen	2,400	2,300	0.89	NS	0.80	NS	1.0
K	Moss	3,200	3,200	−0.31	NS	0.09	NS	1.0
K	Attic dust	9,100	8,800	0.78	NS	0.60	NS	1.0
Mn	Lichen	51	61	−1.19	NS	1.43	NS	0.84
Mn	Moss	180	160	1.42	NS	2.02	NS	1.1
Mn	Attic dust	200	210	−0.78	NS	0.60	NS	0.95
Ni	**Lichen**	**2.6**	**3.0**	**−1.11**	**NS**	**1.23**	**NS**	**0.84**
Ni	**Moss**	**7.1**	**7.5**	**−0.34**	**NS**	**0.11**	**NS**	**0.94**
Ni	**Attic dust**	**17**	**25**	**−2.05**	*****	**4.20**	*****	**0.67**
Pb	Lichen	10	3.8	1.38	NS	1.91	NS	2.7
Pb	Moss	12	6.6	3.28	*	10.73	*	1.9
Pb	Attic dust	29	29	0.00	NS	0.00	NS	1.0
Zn	Lichen	23	20	1.68	NS	2.81	NS	1.1
Zn	Moss	32	27	2.91	*	8.49	*	1.2
Zn	Attic dust	53	50	0.60	NS	0.37	NS	1.1

Bold values indicate anthropogenic distribution for Cu and geogenic distribution for Ni in the study area

X (affected) average concentration of chemical elements in area around open pit and Cu processing plant—polluted area ($n = 22$ lichen; $n = 15$ moss; $n = 12$ attic dust); *X* (rest) non-polluted area ($n = 28$ lichen; $n = 32$ moss; $n = 52$ attic dust)

t result of *T* test; *F* result of *F* test for sampling materials between polluted and unpolluted area; *ns* no significance; * significance at $p < 0.05$; *ER* enrichment ratios (polluted area vs. unpolluted area)

On the other hand, the anthropogenic effect (mine-affected and non-affected areas) was also considered. Collected samples were grouped in two sub-areas: affected area (close to the mine) and the rest of the study area (distant from the mine). The anthropogenic impact of copper, as the main anthropogenic metal introduced in the study area was singled out. The *T* and *F* values were significant at $p < 0.05$ and higher enrichment factors were obtained for lichen, moss and attic dust media (3.8, 5.0 and 5.7, respectively), as presented in Table 3.

Multivariate analysis

Factor analysis, from a total of 15 elements, identified two synthetic variables: geogenic (F1) and anthropogenic (F2) association of elements from three types of samples. Factor 1 includes Ni-Cr-Cd-Fe-Al-K-Mn-Zn correlations, with a total variance of 51 %, while the factor 2 includes As-Cu-Pb correlations, with a total variance of 23 %. Matrix of dominant factor loading, from total 166, samples of lichen, moss and attic dust was constructed, with communality value 74 %. Factor loadings for F1 (Ni-Cr-Cd-Fe-Al-K-Mn-Zn) were 0.89, 0.88, 0.86, 0.85, 0.82, 0.72, 0.64, respectively. Factor loadings for F2: Cu-As-Pb were 0.84, 0.76, and 0.67, respectively. Correlation matrix was used to detect structure in the relationships between variables. Elements: Ba, Na, Ca and Sr were excluded from further analysis because of the very low factor loading (<0.60) or tendency to form an independent factor and therefore, do not belong to any factor group. However, the correlation

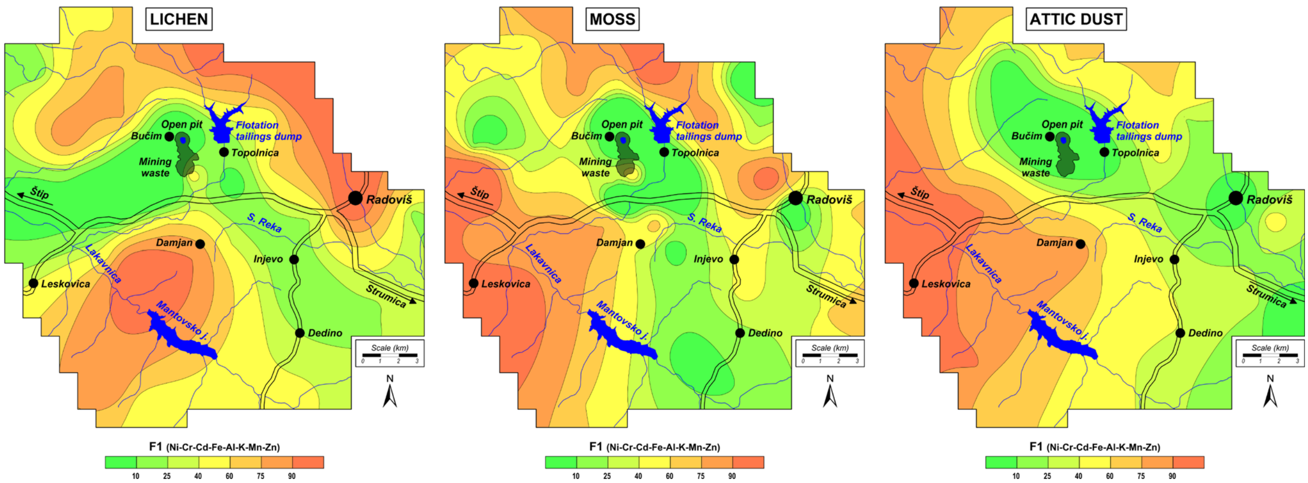

Fig. 3 Spatial distribution of factor 1 loadings (Ni-Cr-Cd-Fe-Al-K-Mn-Zn) in lichen, moss and attic dust

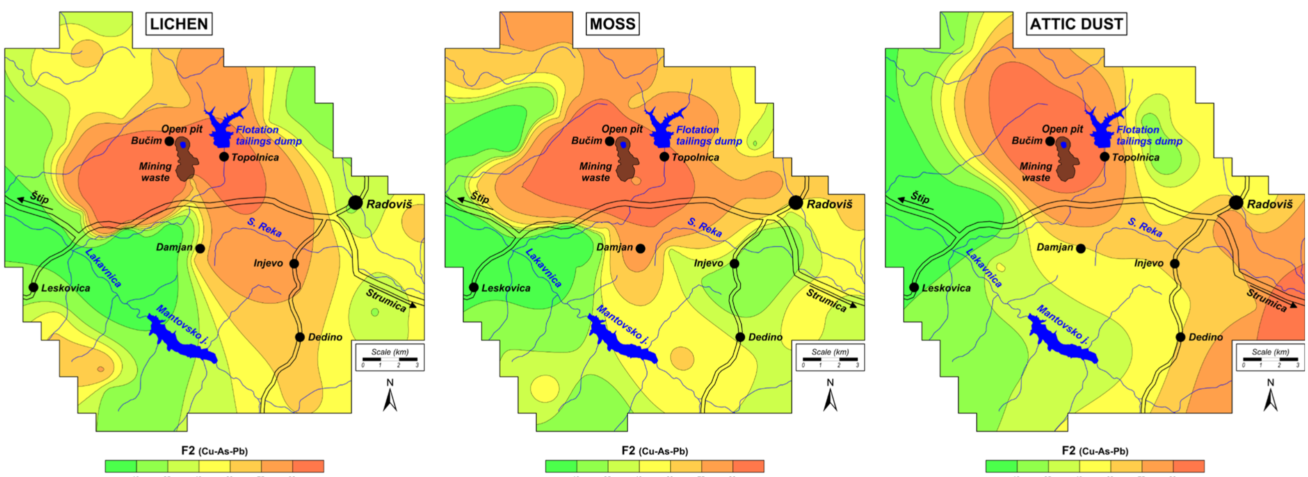

Fig. 4 Spatial distribution of factor 2 loadings (Cu-As-Pb) in lichen, moss and attic dust

matrix explains their occurrence as natural phenomena, grouping them as Ca-Sr and Ba-Na.

Spatial distribution

Spatial distribution for factor groups was done based on the three types of media samples. For the geogenic association, F1 (Ni-Cr-Cd-Fe-Al-K-Mn-Zn) has a significantly similar distribution pattern with minor variations, especially in the biogenic samples. In all observed materials, higher concentrations are observed in the area of predominant Pliocene sediments (Factor 1, as presented in Fig. 3). Significant deviations from the aforementioned data are represented by the high values in moss and lichen in the area where Pz rocks, mainly schist, occur. This type of observation was not included for attic dust.

Attic dust occurs in places that have the greatest distance from the ground and most probably can be attributed to the smallest dust particles that are released by weathering processes. Larger particles formed by the weathering of schist settle on lower-lying material, such as moss and lichen. This means that the moss and lichen are much more exposed to the local composition of soil and geological background, respectively, whereas the particles formed by the weathering of Pliocene sediments have much smaller dimensions and can reach higher elevations, this resulted in significant enrichment in all sampled materials (Fig. 3).

The spatial distribution pattern of anthropogenic factor F2 (As, Cu and Pb) is very similar for all three sampled materials. For this distribution, data similar to those obtained from F1 can be applied. Seemingly, they are more similar to the distributions of F2 in attic dust and moss. The

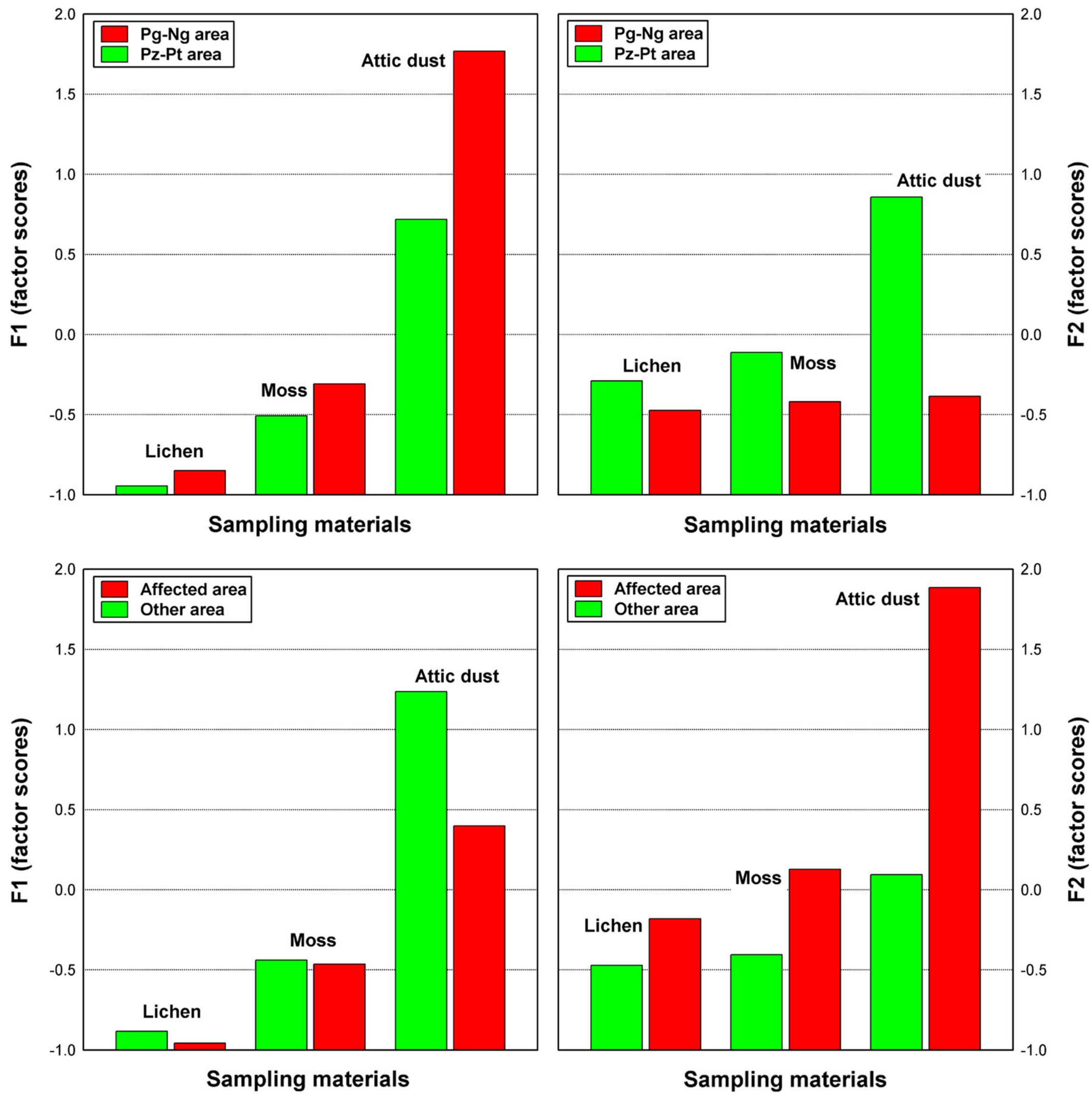

Fig. 5 Distribution of factors 1 and 2 loadings in sampling materials according to basic lithological units (*above*) and according to defined areas (*below*)

anthropogenic factor F2 (As, Cu and Pb) presents a distribution of high contents of potentially high-risk elements close to the anthropogenic source, as can be seen in Fig. 4.

Almost identical results were obtained for the ultimate effect of spatial distribution, but the main problem was to separate them in terms of their capabilities and responsiveness to the geogenic and anthropogenic distribution of elements. For that issue, values for factor loadings were grouped separately for different sampling media. Anthropogenic factor F2 follows the trend from F1 with emphasis for attic dust where the expression of the media goes for the anthropogenic affected area (Fig. 5). The distribution of F1 and F2 according to basic lithological areas for the sampling media follows the expression capabilities: attic dust > moss > lichens (Fig. 5).

The main markers for the geogenic and anthropogenic influence were identified as Ni and Cu, respectively (Fig. 7). Consequently, these two elements were analysed separately for their spatial distribution and expression of sampling media capabilities. Nickel's spatial distribution strongly relies on geogenic enrichment, as presented in F1 distribution and individual Ni distribution (Figs. 1 and 7).

The spatial distribution of Cu was almost identically expressed by lichen, moss and attic dust (Fig. 6). When considering the distribution of Cu in the sampling materials according to basic lithological units, a similar expression was found; however, considering the defined areas (affected and other), the attic dust media has the strongest expression when anthropogenic influences are considered.

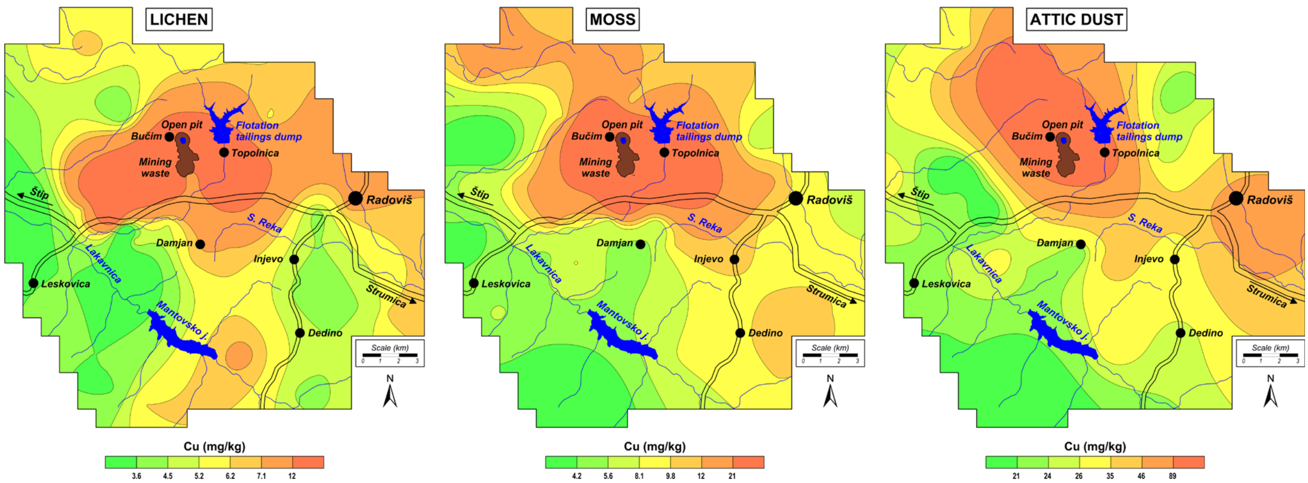

Fig. 6 Spatial distribution of Cu in lichen, moss and attic dust

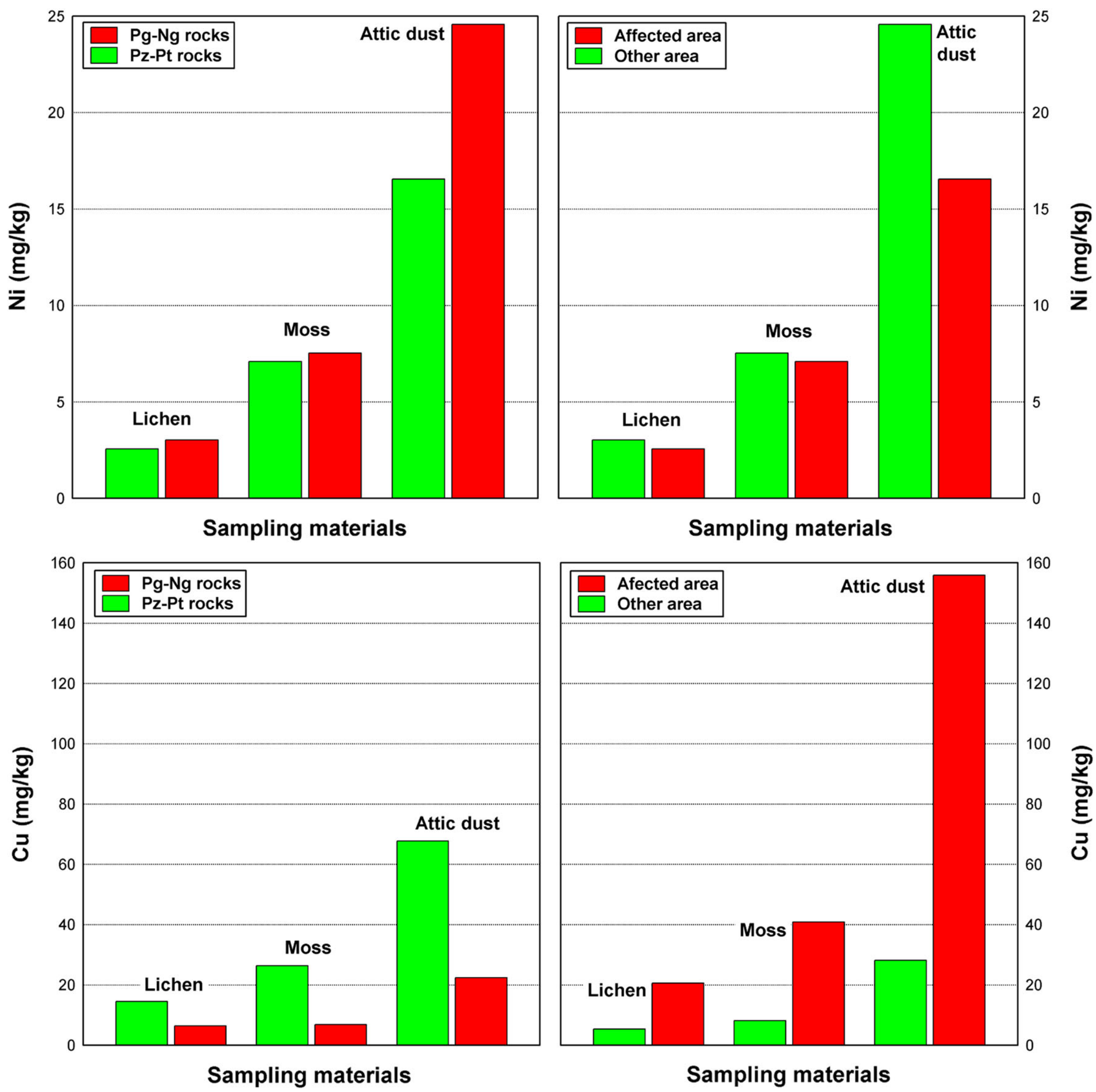

Fig. 7 Distribution of Cu (*below*) and Ni (*above*) in sampling materials according to basic lithological units (*left*) and defined areas (*right*)

Plant species can be very sensitive to higher Cu content, which has been proven with conducted studies (lower contents for Cu in lichen-moss). In contrast, attic dust is more useful in terms of direct accumulation (or simple deposition) of atmospheric dust, distributed by an anthropogenic emission source (Fig. 7).

Functional interdependence of Cu concentrations in the lichen, moss and attic dust samples was analysed according to the distance from the pollution source. Proportionality in data dispersion was determined for all three types of media, with the correlation values for lichens, $r = -0.51$; moss, $r = -0.54$; attic dust, $r = -0.47$. Just as spatial distribution had shown higher contents of Cu contaminated dust deposits in close proximity to the dust emission source, long-distance distribution had not occurred.

Based on these assumption and the results from the present study, it can be considered that attic dust is the most stable and also the most responsive sampling medium for determining a long-term status of atmospheric chemism. It is also the only indication of conditions in the past, because the period of accumulation of air deposits is equal to the age of the building, and the distribution of elements is not affect by precipitation. Previous studies (Šajn 2003, 2005, 2006; Gosar et al. 2006; Žibret 2008; Žibret and Šajn 2008) have already determined that the distribution of elements is minimally affected by population activity, taking into consideration that the particles are only collected from roofs of wooden construction.

Using attic dust, it is possible to determine the intensity of pollution in some certain periods in the past with a simple selection of the age of the sampled object, which is not possible with other sampled material. The big problem with sampling attic dust is that it is associated with the presence of settlements and buildings with a roof construction and obtaining the samples can be very difficult and sometimes dangerous.

On the other hand, biogenic samples are very widespread in the environment, particularly in areas with more rainfall and sampling is quite simple. Problems can occur in dry climates with little rainfall, which is the case in the lowland parts of Macedonia. Both biogenic materials are an indication of the current state of the environment and are very useful for monitoring and predicting environmental changes in chemistry. According to the results, moss is a more stable and more responsive sampling tool than lichen and its sampling procedure is easier.

Conclusion

The comparative analysis between elements content from mosses (Hypnum cupressiforme, Campothecium lutescens), the epiphytic lichens (Hypogymnia physodes and Evernia prunastri) and attic dust showed: (a) stability to higher contents of Cu, Pb, Fe (<0.01 %, < 0.01 % and 1 %, respectively); (b) moss species accumulate higher concentrations of lithophile elements (Al, Ba, Ca, Cr, K, Li, Mg, Na, Sr) and lichen more easily accumulates chalcophile elements (Cd, Pb, Cu, Zn); (c) mosses and lichens cannot be used interchangeably as biomonitors of metals in areas with Cu mineral deposits and ore processing; (d) attic dust presents a very suitable medium in terms of direct accumulation (or simple deposition) of atmospheric dust distributed by an anthropogenic emission source.

The main markers for geogenic and anthropogenic influences were identified as Ni and Cu, respectively. The ultimate effect is that spatial distribution for element deposition (with emphasis on Cu and Ni) is not disturbed by the significant differences in the sampling media matrix. In both cases (lithological and anthropogenic affected areas) for distribution of elements, the sampling media follows the expression capabilities: attic dust > moss > lichens. All three treated sample materials (attic dust, moss, lichen) are shown to be useful in determining an anthropogenic impact, as well as the chemical properties or geological background on orographically diverse terrain in the presence of complex geological structures with an assumption that attic dust is the most stable and responsive to environmental changes and lichen is the worst. Based on the research results, the combination of attic dust and moss gives the best results in the determination of anthropogenic impact on the environment, as well as the natural enrichment. Attic dust shows very stable historical reconstruction of contamination and moss reveals the current state, related to a period of growth and to a period of accumulation of chemical elements. Because the influence of the parental material (bedrock) on chemistry of biogenic samples, as well as attic dust is rather vague, would be interesting and necessary to include topsoil as a direct indicator of the parental material in further investigation.

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