POTENTIAL AND LIMITS OF MOSS AND HUMUS INDICATORS TO MONITOR ATMOSPHERIC DPOSITION LEVELS OF ELEMENTS IN THE CZECH REPUBLIC

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The concentration of fourteen elements in moss and forest floor humus samples gave reliable information about the distribution about of the current and historic atmospheric loads of these elements in the Czech Republic. The distribution of current and historic relative deposition loads for the mentioned elements was drawn in classed post maps and isoline maps. Multielement analyses of moss provide a credible, quick and relatively cheap means of identifying even the absolute actual loads in large territories. In order to test the biomonitoring techniques on a fine scale, moss and humus matrices were taken in a dense grid of sampling points near the city of Příbram - a multielemental source of pollution. Analyses of 36 elements reliably determined the impacts of mining and smelting of polymetallic ores, recycling Pb wastes and mining uranium ore. In the maps, the distribution of historic and current contaminations was located in a radius of 15 km from the city. The obtained results justify us in recommending moss and humus biomonitoring for wider use, especially since these monitoring techniques are used in other European countries.

Introduction

Researchers have been seeking an effective means of monitoring atmospheric deposition loads of elements, because thirty-two European countries and the USA signed the Protocol on Heavy Metals in the framework of the Convention on Long-range Transboundary Air Pollution in Aarhus, Denmark, in 1998.

Levels of atmospheric deposition of elements are most often measured at special stations through analyses of individual forms of deposition (dry, wet, bulk depositions, etc.) of pollutants. However, large-scale measuring of atmospheric deposition levels is a time-consuming and expensive activity. Hence monitoring of atmospheric deposition usually covers only densely settled or industrial regions, and only a limited number of elements and compounds are monitored. This is why alternative cheaper and more effective techniques are required, mainly for the open countryside. Analyses of elements in common natural matrices may provide an alternative way, as the element content in them correlates significantly with the local atmospheric deposition level.

We decided to use analyses of suitable biomonitors, such as moss and forest floor humus, for large-scale biomonitoring of current and historic atmospheric loads throughout the Czech Republic (50˚N; 15˚E, abbreviated ´the CZ´ in the following text) and for fine-scale monitoring around the city of Příbram (49˚41´N; 14˚ 00´E).

a) Mosses – bioindicators of current atmospheric deposition loads

Mosses do not have genuine roots but long unicellular rhizoids, which can take up water from soil covers only through diffusion. The surface of the above-ground parts of ´feather´ (exohydric, pleurocarpous) mosses adsorbs crucial if not entire amounts of nutrients from atmospheric deposition. The cation exchange capacity of moss tissue may reach 150-200 meq/100g or more. No wonder that the content of elements in mosses correlates significantly with the atmospheric deposition levels in a given area.

Moss segments that grew up one, two or three years ago can be analysed. Even dead moss tissues preserve their adsorption capacity and can be exposed in the form of a ´moss-bag´ to monitor the current atmospheric deposition. If the moss production and coefficients of element uptakes are known, it is easy to calculate the absolute atmospheric deposition levels of elements at a given place, e.g., in $\mu g/m^2$/year, from the analysed moss samples. The first successful moss monitoring was introduced in the Nordic countries as early as the late 1960s [1], [2]. Moss monitoring techniques have been progressively improved and have become highly standardised. About 30 countries have taken part in the European moss monitoring programmes recently [3], [4].

b) Forest floor humus – an indicator of historic loads

Some natural matrices have been tested for retrospective determination of atmospheric deposition loads. Analyses of individual layers of known age cored from peat bogs, glacials or tills have been used [5], [6]. To solve the shortage of the above materials, we tested forest floor humus as an alternative matrix with a long memory. Coniferous forest floor humus is a long-time stable organic material widely available in boreal and temperate climatic zones. Cation exchange capacity of humic substances reaches 500-550 meq/100g. Litter (L), fermentation (F) and humic (H) horizons are easily distinguishable along a vertical forest floor profile. A humus-rich A horizon of mineral soil is situated under the H organic horizon of the forest floor. H and A horizons are mixed through natural or man-made processes. The natural content of the mineral admixture, mainly quartz grains, typically reaches 5-20% in the H horizon of coniferous forests. Selective digestion of organic matter in humus samples is needed to eliminate this geogenic influence. Unfortunately, humus analyses can find only relative historic atmospheric deposition loads due to the mixing of humic compounds of different ages in the H horizon. However, the forest floor memorises deposition loads as old as old the forest trees are, or older, i.e. usually up to 80-120 years.

2. Methodology

a) Moss monitoring

Moss monitoring was carried out in the CZ (78,864 km^2) in 1991 and 1995. In the latter monitoring programme, 196 moss samples were taken in a grid of sampling points of 20x20 km. Representative samples influenced exclusively by atmospheric deposition were taken in accordance with the instructions and methods of the European biomonitoring programme [4]. Preferably *Pleurozium schreberi* moss was taken, and two-year-old segments (1994-1995) were analysed. The concentration of 14 elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, S, V, Zn) was measured by means of the ICP-OES technique. Standard reference materials, moss laboratory standards and recovery tests were used to check the digestion and analytical processes. Classed post maps and isoline maps of the distribution of the analysed elements in the moss were run through the Surfer PC programme. In order to count the absolute atmospheric deposition loads the moss production was determined. The current load in the territory of the CZ was evaluated through the index of the general deposition load weighted through the deposition levels of all 14 elements.

b) Humus monitoring

In contrast to moss monitoring, there was no available standardised method for taking and analysing forest floor humus for large scale monitoring. A technique for sampling and analysing forest floor humus was therefore developed and tested in the CZ in 1993-1995. Retrospective historic loads of the 14 elements were determined throughout the CZ in 1995-1997. About 200 samples of humic substances from H horizons were taken in mull or moder forest floors of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) or mixed forest stands, usually 60-90 years old. The upper L and F horizons were removed, and using a plastic pipe organic matter from the H horizon was cut out. At the location, 6-7 (sub)samples were taken and joined in a representative mixed sample. The volume density and mineral content of the taken matrix was measured. Powdered samples were digested through nitric acid and hydrogen peroxide in a microwave pressure digestion system, and solid quartz and silica gel were removed. Pseudo-total concentrations of the 14 elements were measured using an ICP-OES instrument. Standard reference materials and laboratory humus standards [7] were analysed in parallel. Recovery tests did not show any serious problems in digestion and analytical procedures. Assuming that all the atmospheric pollutants had been bound exclusively to the organic fraction of the taken samples, the analytical results were related to the so-called ash-free samples. The distributions of the element concentrations in the humus were expressed through classed post maps and isoline maps.

c) Fine-scale monitoring

The moss and humus monitoring techniques described above were tested for monitoring current and historic atmospheric deposition loads on a fine scale around the city of Příbram. Polymetallic Ag, Pb, Zn ores with many minority elements were extracted near the city and processed in a local smelting works as recently as the 1970s. Now the smelter located close to the abandoned mine recycles Pb wastes and metals from electronic components and produces special non-ferrous alloys. From 1949-1992 uranium ore (uraninite) was extracted from pits on the opposite (eastern) side of the city.

In 1999, samples of coniferous forest floor humus and moss (*Pleurozium schreberi*) were taken along linear transects 15 km in length running radially from the smelter chimney. The transects were 30º apart, and the distance between the sampling points at the transects was 2000 m. Samples were taken and treated in the same ways as in the large-scale monitoring operation. Analyses of 36 elements (see Table 3) were carried out by means of the ICP-MS technique.

Results

a) Large-scale moss monitoring

Extreme and average absolute deposition loads of the investigated elements in the territory of the CZ in 1994-1995 determined through the moss analyses are shown in Table 1. Very high atmospheric deposition loads of Al, As, Co, Cr, Hg, Mo, Ni, S, V and Zn were found in the lignite basin and in Krušné Mts. in the northwestern part of the CZ. The power plants and chemical industry are concentrated in this basin. Very high deposition of the above elements and As, Cd, Cu, Pb was found in the mountains on the northern border of the CZ (Jizerské Mts. and Giant Mts.) Pollutants are transported to this area from distant sources located in so-called the Black Triangle and are intensively washed out through precipitation in these mountains. Very high current deposition levels of Cd, Fe, Mo, Pb, S, and Zn were found in the black coal basins in the northeastern part of the CZ, where coal processing, metallurgical engineering and chemical industries are concentrated. The highest deposition loads are found to the east, in the nearby Beskydy Mts., due to the transport of pollutants by the wind and through more intensive washing of pollutants. 6.8%, 13.0%, 43.7% and 36.5%, respectively, of the CZ territory suffered from very high, high, moderate and small general atmospheric deposition loads weighted through the concentration of all 14 elements in the moss samples. Analyses of samples taken at identical places in 1991 and 1995 demonstrated a significant decrease in all measured element deposition by between 16% (Cd) and 77% (As), due to the enormous decrease in industrial production and the introduction of a desulphurization programme for the power plants in the CZ in the 1990s. The average concentrations of the elements in the moss samples were very close to the average data published for Germany and Poland. Slightly lower concentrations (about -20%) were found in Austria and, on the contrary, two to three times higher average atmospheric deposition levels were indicated in the Slovak Republic. Colour maps of the current atmospheric deposition loads, and results with a commentary, can be found in the latest Czech moss monitoring surveys [8], [9].

Element	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg***	**Mo**	**Ni**	**Pb**	**S**	**V**	**Zn**
Min.	70395	49	26	42	125	965	28945	(3.7)	13	230	535	346740	125	3720
Max.	468190	925	480	540	635	5184	1269435	(15.1)	230	4385	22400	869250	1720	78850
Mean	115123	238.8	84.3	119.5	357.0	2445	114208	(9.3)	46.2	607.3	1981	685420	626.2	11114
* Uptake efficiency of analysed moss for Hg was not reliable known. (Coefficient = 100% have been used for the CZ).														

Tab. 1. The minimum, maximum and average absolute values of atmospheric deposition levels of given elements ($\mu g/m^2/year$) in the CZ in 1995, determined through moss analyses (n=196).

b) Large-scale humus monitoring

Table 2 provides information about concentrations of measured elements in the CZ forest floor humus. Humus analyses showed that the distribution of historic (humus) and current (moss) loads had similar patterns. The reason for this is that industrial centres grew up at certain sites in the second half of the 19th century, and industrial production has continued mainly in these regions in the territory of the present-day CZ. Very high levels of old contaminations were found for Cd, Co, Fe, Hg, Mo, Ni, Pb, V and Zn mainly around the historic centres of the metallurgical and engineering industries in central Bohemia, e.g., the cities of Prague, Kladno, Rokycany, and Příbram. In the industrial region of the lignite basin in the northwestern cross-border area, very high historic loads of Al, As, Co, Cr, Cu, Fe, Mo, Ni, S, and V were found. Large hot spots of high historic contaminations of Cd, Cr, Cu, Fe, Mo, Pb, and Zn were found in the industrial region surrounding the black coal mines in the northeastern part of the CZ. Smaller hot spots were found around some of the larger industrial cities. Generalised data show that, respectively, very high, high, moderate and low historic deposition loads related to all partial deposition loads of individual elements were found, respectively, in 18%, 24% 30% and 28% of the CZ territory. Compared to the northern half, the southern half of the CZ is shown to be very little affected by atmospheric deposition loads. The humus monitoring results identified more atmogenic impacts than geogenic factors in the local environment. Detailed interpretation of large scale humus monitoring in the CZ was presented in the CZ national humus survey [10], [11].

Element	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mo**	**Ni**	**Pb**	**S**	**V**	**Zn**
Min.	3575	5.49	0.328	1.45	7.48	8.37	3043	0.329	0.665	6.26	52.1	2259	9.86	42.1
Max.	30075	167.0	5.82	17.5	94.5	214.0	36998	2.26	7.97	52.6	4872	4747	125	446
Mean	9120	23.8	0.865	5.15	26.5	29.6	10874	0.676	1.97	18.8	185	3045	37.5	89.1
S.D.	4168	17.79	0.559	2.69	13.28	19.13	5738	0.205	1.079	8.11	348.4	417	19.30	42.7
Median	8124	19.20	0.708	4.41	23.40	25.30	9019	0.656	1.750	17.20	141.0	2955	33.20	79.3

Tab. 2. Statistics for a set of element concentrations in forest floor humus samples (n=192) taken in the CZ in 1995.

c) Fine-scale monitoring of current and historic loads

The distributions of element concentrations in both the moss and the humus matrices generally displayed four types of pattern for monitored area around the city of Příbram. The concentrations of elements in the moss and humus matrices correlated significantly (α=0,01; r=0.33-0.99), except for the Cs, Rb, and S concentrations. The existence of hot spots of high element concentrations of moss and humus in the same locations, e.g., for Fe, Ni, Se indicated long-term operation of same local sources of pollution. Large humus hot spots together with small moss hot spots for Ag, Cd, In, Pb, Sb, U, and lanthanides, for example, indicated the positive influence of recently-introduced technology for cleaning the fumes in the smelter works, and the termination of polymetallic and uranium ores extraction. The distribution of moss and humus concentrations did not correspond with the distribution of mother rocks. Only the occurrence of increased Sr concentrations in the humus was found on Sr-rich plutonic granite. Table 3 gives information about the range of the absolute current (1998-1999) atmospheric loads of the elements in the investigated area, determined by moss analyses. ´Typical values´ of deposition are related to the medium loads affecting the largest area of the investigated landscape segment. The northern and eastern parts of the city have suffed from very high deposition loads of many elements. Ignoring other elements, only Pb or Cd intoxications have been under investigation in the area up to now, e.g. [10].

The results of principal component analysis showed four factors that may explain the individual element distribution in the analysed matrices. The factors were easily identified. The precinct of the smelter works (chimney, slag piles and the area of the former polymetallic mine) has evidently contaminated the landscape with Ag, As, Bi, Cd, Cu, Fe, Hg, In, Ni, Pb, S, Sb, Se, Tl, Zn (old loads) and Ag, As, Cd, Cu, In, Ni, Pb, Sb, Se, Zn (current loads). About 30-200 km^2 of the landscape is affected by this source, not including old Pb and Cd loads, which have affected more than 800 km^2. Wind effects scatter dust particles from piles of rubbish abandoned near the former uranium mine in an eastern suburb of the city. This source has contaminated the adjacent area of 20-150 km^2 with Al, Be, Cr, Cs, Ga, Li, Mn, Rb, Sc, Sr, Th, U, V (old loads) and Al, Be, Ce, Cr, Fe, Ga, La, Li, Nd, Pr, Sc, Th, U, V, Y (current loads). Our moss and humus analyses showed that the heat-resistant steel foundry situated 15 km from the city of Příbram has been contaminating the surroundings mainly with Mo. The distribution of Cs, Hg, Rb, Tl, Ce, Co, La, Nd, Pr, and V in parts of the analysed matrix can be explained by a geogenic anomaly of element concentrations in the ground, or contaminations through human spreading of mine wastes. Complete analytical and graphical results of fine-scale monitoring were presented in [13]. Figure 1, as a specimen, demonstrates the potential of information obtained from the fine-scale monitoring.

Element	**Ag**	**Al**	**As**	**Bi**	**Cd**	**Ce**
Uptake coef.	1.10	0.45	0.39	(0.77)	0.72	0.46
Min.-Max.	3.75-124.31	70807-223027	109.2-1409.1	3.07-14.74	41.21-1067.83	100.96-333.72
Typical	4.69-7.04	143333-157667	132.31-198.46	8.38-9.21	107.50-125.42	182.28-196.30
	Co	**Cr**	**Cu**	**Fe**	**Ga**	**La**
Uptake coef.	0.45	0.60	0.46 (0.35-0.57)	0.60	0.49	0.49
Min.-Max.	45.87-286.67	120.4-365.5	3870-308478	43860-143835	29.22-95.04	43.18-152.96
Typical	86.0-114.67	215.0-279.5	7010-9815	86000-107500	47.39-52.65	78.98-92.14
	Li	**Mo**	**Ni**	**Pb**	**S**	**Sb**
Uptake coef.	0.42	0.53	0.46	1.00	0.39	(1.05)
Min.-Max.	46.07-137.91	23.85-258.0	269.22-1318.04	869.5-127452.0	317208-539154	18.43-2899.43
Typical	76.79-92.14	36.51-48.67	56.09-84.13	1935-2580	396923-463077	18.43-36.86
	Th	**U**	**V**	**Y**	**Zn**	*Ba, Be, Cs, Hg In, Mn, Nd, Pr, Rb, Sc, Se, Sr, Tl.
Uptake coef.	0.43	0.865	0.59	0.48	0.85	
Min.-Max.	6.0-39.6	3.58-71.88	218.64-1051.68	23.92-86.00	4598-36727	
Typical	21.0-27.0	5.97-7.46	327.97-437.29	37.63-48.38	7588-9106	
**For Ba, Be, Cs, Hg, In, Mn, Nd, Pr, Rb, Sc, Se, Sr and Tl the uptake coefficients were not reliably known.*						

Tab. 3 Absolute current atmospheric deposition loads (μg/m^2/year) in the city of Příbram and its surroundings assessed from moss analyses in 1999.

Conclusion

Multielement moss and humus analyses can be used as a very reliable and efficient method for both large-scale and fine-scale monitoring of current and historic loads of atmospheric deposition of many elements.

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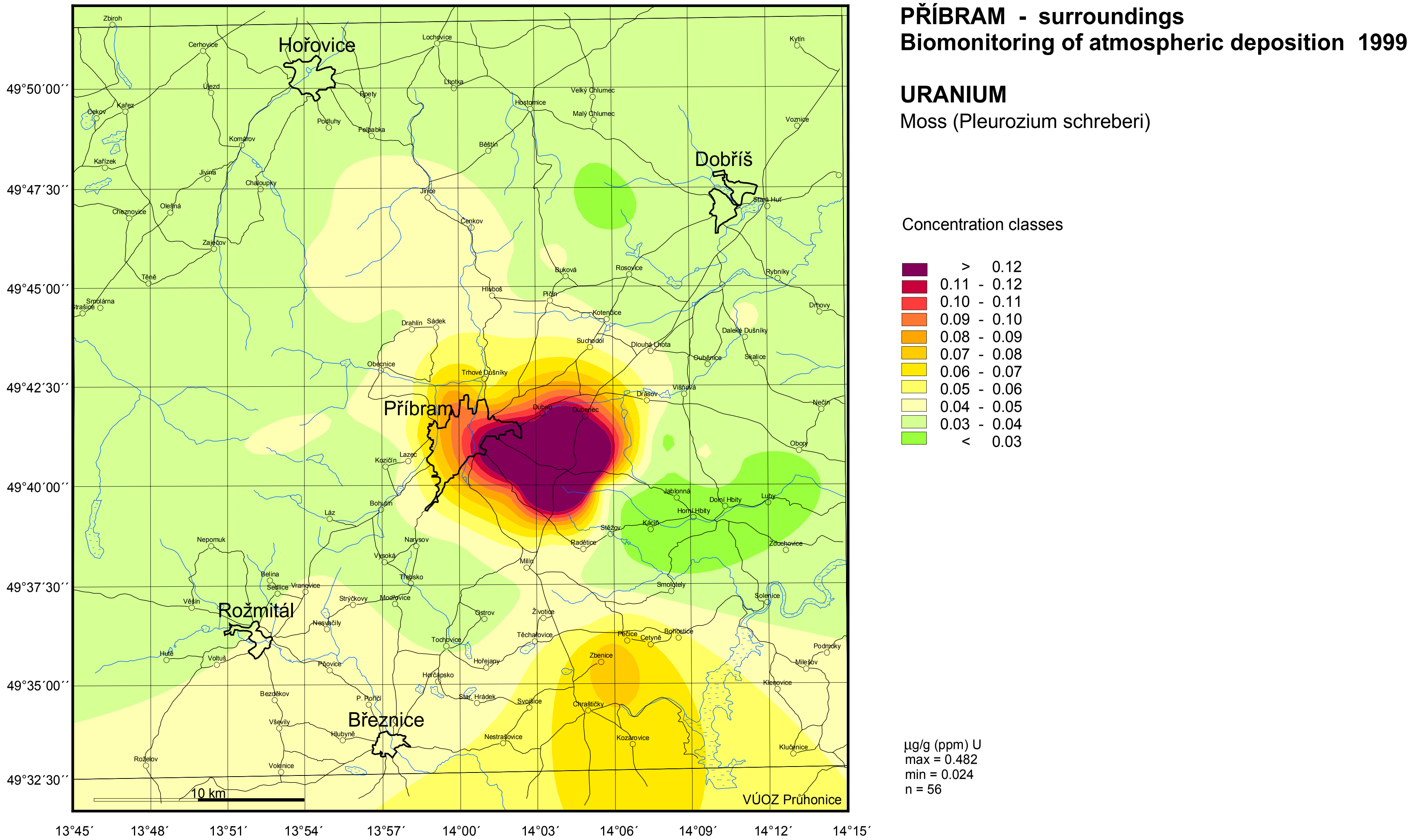

Fig. 1. The distribution of current (1998/1999) atmospheric deposition of uranium originating from scattered dust eroded from heaps at the uranium scattered dust spread from heaps at the uranium pits abandoned since 1992. Table 3 gives the absolute deposition values for uranium.