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Atmospheric Deposition of Trace Elements in Romania Studied by the Moss Biomonitoring Technique

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Abstract. The first systematic study in Romania of atmospheric pollution from heavy metals and other toxic elements based on moss analysis was undertaken as a Romanian–Russian–Norwegian collaboration, primarily in order to assess the general state of heavy metal pollution in Romania. An additional goal was to contribute to the European heavy metals in mosses survey, conducted under the auspices UNECE ICP Vegetation[1] which reports to the Working Group of Effects of the Long-range Transboundary Air Pollution Convention. Samples of the moss species *Hypnum cupressiforme*, *Hylocomium splendens* and *Brachytechium salebrosum* and *B. rutabulum* were collected during the period 1995–2001. A total of 40 elements were determined using NAA and AAS. The total concentrations of arsenic, cadmium, copper, nickel, vanadium and zinc are presented in the form of contour maps. Generally, the observed concentrations in Romania are markedly higher than those observed in most other countries of Europe using the moss technique.

Key words: atomic absorption spectrometry, heavy metal pollution, moss biomonitoring technique, neutron activation analysis, trace elements.

1. Introduction

Romania is a country with a number of useful energy and mineral resources, such as crude oil, natural gas, coal, ferrous and non-ferrous ores, gold, silver and bauxite ore deposits. The exploitation of these resources, however, has led to high levels of air, water and soil pollution. In spite of the fact that there are several national institutions in Romania responsible for environmental protection and monitoring,

[1] The United Nations Economic Commission for Europe International Co-operative Programme on Effects of Air Pollution on Natural Vegetation and Crops.

very limited information on the extent and distribution of pollution is available at the national level (Romanian Statistical Yearbook – 2001). Some investigations around local pollution sources (Donisa *et al.*, 2000; Culicov *et al.*, 2002) indicate that heavy metal pollution may be a substantial problem in some areas, but these studies do not provide detailed information on the situation on the national scale. A comprehensive review of heavy metal pollution from the atmosphere in Romania, however, using conventional sampling techniques would hardly be possible at present due to the lack of financial and human resources.

An alternative, simple and inexpensive method of investigating metal deposition from the atmosphere was suggested in the late 1960s by Swedish scientists (Rühling and Tyler, 1968, 1971) and further developed during the last 30 years in a majority of European countries. This moss biomonitoring technique was recently adopted by the United Nations Economic Commission for Europe (UNECE) as a method of investigating heavy metal deposition in Europe (Buse *et al.*, 2003). The first attempt to apply this technique in Romania was in 1991 but covered only a very limited area in the Banat region (Rühling, 1994). A second survey covering a much larger area in Eastern Carpathians (Lucaciu et al., 1999) was carried out in 1995. More recently sampling has been extended to other regions of the country.

The aim of the present paper is to give an overview of the Romanian moss survey activities from 1995 to 2001, and identify the main pollution sources in the investigated areas by applying principal component analysis and GIS technology. The results will form an excellent basis for local authorities to implement the necessary measures to reduce emissions to environmentally acceptable levels. Moreover, the responsible public health authorities will have a significantly improved basis for assessing possible risk to the population from previous and current emissions.

2. Material and Methods

2.1. STUDY AREAS AND SAMPLING

A total of 291 moss samples were collected in summer time during 1995–2001 in the Carpathian Mountains, Transilvanian plateau, and Prut river catchment at a 20×20 km grid square, and following internationally accepted guidelines (Rühling *et al.*, 1987; Table I and Figure 1). The large topographic variation in the area of investigation necessitated the collection of samples of different moss species. The majority of samples were *Hypnum cupressiforme* and *Hylocomium splendens.* In addition, a few samples of *Brachytechium salebrosum* and *Brachytechium rutabulum* were collected within the Prut river catchment (Mocanu *et al.*, 2001; Cucu-Man *et al.*, 2002). The investigated area covers more than 60% of Romania, including 11 of 12 National Parks (Figure 2) covering 3,21,885 km^2 and 63% of the localities where maximum permitted concentration values of air pollutants are exceeded on a yearly basis.

Table I. Moss samples collected in 1995–2001

Collection year	Nr. of samples	Sampling area	Moss species
1995	85	Oriental Carpathians	*Hylocomium splendens*
1998	75	Meridional and Occidental Carpathians	*Hylocomium splendens*
1999	69	Transylvanian Plateau	*Hypnum cupressiforme*
2000	43	South Romania	*Hypnum cupressiforme*
2001	21	Prut river catchment	*Hypnum cupressiforme* + *Brachytechium salebrosum* and *B. rutabulum*

Figure 1. Moss sampling sites in Romania. • Oriental Carpathians (1995); o Meridional and Occidental Carpathians (1998); + Transylvanian Plateau (1999); ▲ South Romania (2000); ∇ Prut river catchment (2001).

2.2. SAMPLE PREPARATION AND ANALYSIS

The upper three fully developed segments of each *Hylocomium splendens* specimen and corresponding green or green-brownish parts of the other moss species representing the last 2–3 years growth were cleaned from any extraneous material. No further homogenization of the samples was performed (Steinnes *et al.*, 1994). Moss samples were dried for 48 h at 40 °C to constant weight, and analysed

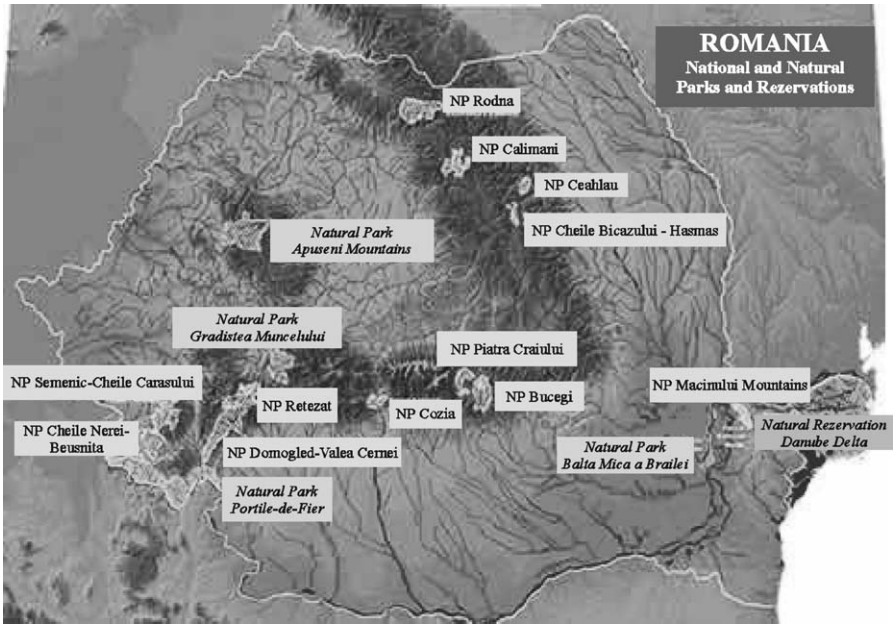

Figure 2. Location of National Parks and other protected regions in Romania.

by instrumental neutron activation analysis (NAA) and flame atomic absorption spectrometry (FAAS).

Conventional and epithermal NAA at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia (Frontasyeva and Pavlov, 2000), were used to determine concentrations of 37 elements.

In order to determine elements associated with long-lived radionuclides, samples of about 0.3 g were irradiated for 100 h in a cadmium-screened channel. Spectra of induced gamma activity were recorded after 4 and 16 days of cooling. Short irradiations for 5 min in a thermal channel allowed determination of Al, Ca, Cl, I, Mg, Mn, V. Gamma-ray spectra were recorded after 5 and 12 min after irradiation. Data processing was performed using software developed at FLNP JINR (Ostrovnaya et al., 1993; Ostrovnaya, 2000).

Copper, lead and cadmium concentrations for the 1995, 1998 and 2001 samples were determined by FAAS (Perkin Elmer AA-600) at the Norwegian University of Science and Technology, Trondheim. To determine Cd, Cu and Pb, moss samples of about 1 g were digested with 20 mL of concentrated nitric acid in a sample bottle on a hot plate at 80–85 °C for 18–20 h. After cooling to room temperature, the samples were filtered and demineralized water was added to a total volume of 50 mL. Calibration standards and blanks were included following the same procedure as samples. In 1999, Cu and Cd concentrations were determined by NAA.

2.3. QUALITY CONTROL

The quality control of NAA results was ensured by carrying out simultaneous analysis of the standard reference material (SRM) Lichen 336 IAEA (International Atomic Energy Agency), and the moss reference sample NORD DK-1 used for inter-laboratory calibration in the 1990 Nordic survey (Frontasyeva *et al.*, 1995). For long irradiation the two reference materials were packed together with 10–12 samples in each transport container. Certified values and NAA data of reference materials are given in Table II. The quality of the AAS data was checked by analysis of moss reference samples at regular intervals (Steinnes *et al.*, 1997).

2.4. DATA ANALYSIS

In order to generate the factors from correlation matrices, several computer runs with principal component analysis (PCA) were carried out for the overall set of moss data by means of the software STATISTICA 6.0. The factors obtained were subjected to orthogonal rotation by the varimax method. GIS-INTEGRO was used to generate the maps presenting the geographical distribution of the pollution patterns for several elements (Finkelshtein and Deev, 1999). The software used permits to create reliable maps only when the geographical distribution of the data is continuous (without white spots), therefore, the map of Pb could not be drawn.

3. Results and Discussion

The results on samples collected over several years in different regions of Romania were unified in an integrated database because there was not much change in the emissions from main industries in Romania over those years (Romanian Statistical Yearbook 2001). An interspecies calibration study (*Hylocomium splendens* and *Hypnum cupressiforme*) was carried out in the framework of the 1995 campaign (unpublished data). The obtained results allowed the conclusion that these two species could be simultaneously used for monitoring purposes. The compatibility of *Hypnum cupressiforme* with *Brachytecium salebrasum* is discussed by Mocanu and Steinnes (2002). *Brachytecium rutabulum* was also found to be suitable for monitoring together with the above moss species (S. Cucu-Man, personal communication). For a majority of the 10 elements determined in European moss surveys (As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, V, Zn), the Romanian median values (Table III) are appreciably higher than in most other European regions (Romanian Statistical Yearbook – 2001; Rühling and Steinnes, 1998; Buse *et al.*, 2003). The calculated ratios of maximum to minimum concentration for each element per region show that the extension of the concentration range is not direct correlated with the maximum value in an investigated region. Practically no single point exists where all the main elements considered harmful to humans (Cr, Cu, Zn, As, Cd, Pb) are close to a national minimum value. This fact can perhaps be explained by

Table II. Certificate and experimental values for the used reference materials

Element	DK-1, (mg/kg)\ (Certified)	DK-1, (mg/kg) (Determined)	L-336, (mg/kg) (Certified)	L-336, (mg/kg) (Determined)
Na	315 ± 31	303 ± 25	320 ± 26	304 ± 26
Mg	910 ± 91	850 ± 150	610 ± 3	708 ± 101
Al	810 ± 81	830 ± 84	680 ± 3.4	720 ± 65
Cl	328 ± 33	328 ± 35	1920 ± 10	1927 ± 288
K	3300 ± 297	3350 ± 165	1840 ± 4	1910 ± 90
Ca	1630 ± 40	1604 ± 180	2600 ± 13	2810 ± 324
Sc	0.16 ± 0.02	0.16 ± 0.02	0.17 ± 0.01	0.18 ± 0.01
V	3.8 ± 0.3	4.1 ± 0.3	1.5 ± 0.4	1.4 ± 0.2
Cr	1.7 ± 0.4	1.9 ± 0.2	1.03 ± 0.08	1.10 ± 0.17
Mn	130 ± 10	143 ± 10	64 ± 3	69 ± 5
Fe	550 ± 50	575 ± 53	426 ± 1	430 ± 8
Co	0.23 ± 0.01	0.26 ± 0.01	0.287 ± 0.022	0.303 ± 0.070
Ni	1.80 ± 0.20	1.58 ± 0.33	–	–
Cu	85 ± 5.0	87 ± 2.5	3.55 ± 0.59	3.70 ± 0.50
Zn	29 ± 2	31 ± 4	31.6 ± 1.4	28.2 ± 2.3
As	0.64 ± 0.02	0.64 ± 0.02	0.639 ± 0.067	0.540 ± 0.071
Se	0.43 ± 0.04	0.43 ± 0.04	0.22 ± 0.01	0.22 ± 0.03
Br	12.4 ± 1	13.5 ± 1	12.9 ± 3.2	14.2 ± 2.3
Rb	12.8 ± 0.9	12.9 ± 0.9	1.72 ± 0.07	1.70 ± 0.17
Sr	10 ± 0.1	15 ± 3	9.2 ± 0.046	11.4 ± 0.550
Zr	11 ± 1.2	11 ± 1.2	–	–
Mo	0.20 ± 0.02	0.21 ± 0.02	–	–
Ag	0.05 ± 0.004	0.05 ± 0.004	–	–
Cd	0.3 ± 0.02	0.3 ± 0.11	0.117 ± 0.0006	0.13 ± 0.0150
Sb	0.35 ± 0.02	0.35 ± 0.02	0.073 ± 0.007	0.078 ± 0.010
I	3.8 ± 0.30	3.8 ± 0.07	–	–
Cs	0.29 ± 0.02	0.29 ± 0.03	0.11 ± 0.02	0.12 ± 0.02
Ba	12.0 ± 0.8	12.5 ± 0.8	6.4 ± 0.02	6.6 ± 0.70
La	1.22 ± 0.10	1.22 ± 0.34	0.66 ± 0.04	0.70 ± 0.06
Ce	2.92 ± 0.22	2.92 ± 0.53	1.27 ± 0.25	1.30 ± 0.25
Sm	0.231 ± 0.01	0.231 ± 0.05	0.106 ± 0.06	0.106 ± 0.06
Tb	0.0216 ± 0.002	0.0218 ± 0.010	0.014 ± 0.0010	0.015 ± 0.0006
Yb	0.054 ± 0.022	0.054 ± 0.020	0.037 ± 0.0018	0.042 ± 0.0026
Hf	0.21 ± 0.009	0.21 ± 0.060	–	–
Ta	0.026 ± 0.0036	0.026 ± 0.0050	–	–
W	0.73 ± 0.21	0.73 ± 0.11	–	–
Au	0.00074 ± 0.00004	0.00074 ± 0.00140	–	–
Pb	–	–	4.9 ± 0.96	5.0 ± 1.00
Th	0.15 ± 0.001	0.16 ± 0.080	0.14 ±0.0014	0.14 ± 0.0060
U	0.192 ± 0.015	0.192 ± 0.020	–	–

Table III. Descriptive statistics of experimental data. Concentrations are given in mg/kg

Year	1995				1998				1999				2000				2001			
Element	min	max	mean	median	min	max	mean	median	min	max	mean	median	min	max	mean	median	min	max	mean	median
Na*	0.12	5.3	0.78	0.54	0.18	3.7	1.2	0.84	0.19	4.33	1.0	0.89	0.28	2.1	0.93	0.83	0.22	0.98	0.44	0.36
Mg*	0.84	13	3.0	2.2	0.53	7.5	2.8	2.1	0.48	6.8	2.9	2.8	0.76	4.9	2.1	1.9	0.98	4.4	2.0	1.7
Al*	1.0	85	6.8	3.7	0.16	20	6.2	4.4	0.83	23	6.3	5.3	1.8	11	5.4	5.3	1.1	8.0	3.1	2.5
Cl*	0.24	2.2	0.77	0.73	0.17	1.0	0.33	0.29	0.16	1.3	0.43	0.37	0.18	0.39	0.28	0.28	0.19	0.58	0.34	0.29
K*	0.92	8.3	4.4	4.3	0.35	11	5.2	5.0	4.5	20	8.7	8.2	2.3	25	7.0	6.2	7.2	17	11	10
Ca*	1.7	22	6.1	4.9	1.6	22	5.0	4.8	1.2	23	6.6	5.9	2.9	10	5.3	4.9	4.2	13	8.0	7.7
Sc	0.12	3.7	0.85	0.57	0.080	1.5	0.39	0.32	0.21	6.1	1.4	0.94	0.23	0.95	0.54	0.55	0.16	1.5	0.48	0.35
V	2.0	54	9.8	6.3	3.3	29	11	8.8	1.9	32	9.8	8.5	3.6	16	8.0	7.8	2.3	18	7.0	4.9
Cr	0.41	30	5.1	2.6	1.6	15	6.4	5.5	2.7	52	16	14	3.7	34	12	12	1.3	13	5.4	4.6
Mn*	0.049	1.6	0.35	0.30	0.041	0.66	0.27	0.24	0.027	1.47	0.32	0.28	0.11	0.50	0.27	0.25	0.038	0.36	0.18	0.15
Fe*	0.47	14	3.0	1.9	0.84	11	3.6	2.6	0.82	21	4.4	3.3	0.85	5.2	2.4	2.3	0.62	5.8	1.9	1.3
Co	0.14	2.8	0.66	0.47	0.12	2.8	0.74	0.57	0.32	7.1	1.9	1.4	0.48	2.0	1.1	1.1	0.21	1.7	0.57	0.48
Ni	0.44	15	2.6	2.1	0.26	2.6	1.1	0.98	0.58	32	6.9	5.4	3.4	16	7.5	7.1	1.2	11	3.9	2.8
Cu*	0.006	0.23	0.018	0.011	0.002	0.080	0.014	0.010	0.018	2.4	0.20	0.73					0.005	0.023	0.011	0.011
Zn*	0.016	0.41	0.064	0.049	0.025	0.24	0.088	0.068	0.039	2.9	0.29	0.14	0.033	0.13	0.071	0.065	0.020	0.068	0.040	0.037
As	0.041	18	1.5	0.97	0.62	4.6	1.8	1.3	0.59	119	8.5	2.4	0.86	3.6	1.8	1.6	0.27	2.0	0.73	0.59
Se	0.090	1.5	0.41	0.34	0.17	1.2	0.60	0.56	0.075	5.0	0.71	0.37	0.029	0.52	0.21	0.20	0.034	0.40	0.16	0.15
Br	1.8	8.0	4.2	4.0	3.2	11	6.4	6.2	2.0	21	8.7	8.2	2.2	14	6.4	5.7	1.9	12	5.4	5.1
Rb	2.1	49	15	12	5.8	48	23	21	5.8	135	21	15	1.2	35	19	19	3.5	20	9.1	8.4
Sr	3.1	243	28	15	6.0	94	32	29	1.8	289	47	39	3.5	33	17	17	13	96	38	35

(Continued on next page)

Table III. (Continued)

Year	1995				1998				1999				2000				2001			
Element	min	max	mean	median	min	max	mean	median	min	max	mean	median	min	max	mean	median	min	max	mean	median
Zr	4.1	269	37	21	14	484	102	82	5.2	797	71	40	5.3	29	15	12	23	207	70	55
Mo	0.031	1.6	0.30	0.21	0.36	4.2	1.8	1.7	0.13	15	1.5	0.71	0.010	1.1	0.35	0.29	0.19	1.3	0.66	0.62
Ag	0.013	2.0	0.12	0.072	0.017	0.85	0.26	0.21	0.032	4.5	0.70	0.14	0.021	0.35	0.13	0.12	0.015	0.095	0.058	0.068
Cd	0.30	8.4	0.93	0.60	0.21	5.1	1.4	1.3	0.22	55	4.0	2.0					0.26	1.0	0.51	0.46
Sb	0.011	54	1.8	0.34	0.15	2.0	0.72	0.52	0.16	51	4.7	0.92	0.47	1.2	0.68	0.65	0.086	0.45	0.17	0.14
I	0.47	7.4	1.8	1.6	0.90	14	2.3	2.0	0.76	5.6	2.3	2.2	0.36	2.5	1.1	0.92	0.82	3.9	1.9	1.8
Cs	0.019	2.5	0.47	0.34	0.13	1.9	0.65	0.55	0.12	3.4	0.66	0.52	0.19	1.2	0.55	0.46	0.11	0.76	0.26	0.20
Ba	12	519	67	41	22	182	82	75	20	658	116	100	27	143	75	73	39	135	74	66
La	0.16	21	3.5	2.3	0.095	9.3	3.0	2.4	0.36	15	3.3	2.3	1.3	9.8	4.2	3.6	0.77	5.9	2.2	1.5
Ce	0.68	32	7.3	5.5	1.2	19	6.4	5.1	0.93	43	9.6	6.1	2.5	18	7.5	6.0	2.4	22	8.1	6.9
Sm	0.057	3.1	0.51	0.33	0.032	1.8	0.56	0.38	0.008	2.5	0.55	0.41	0.24	1.8	0.68	0.59	0.11	0.86	0.28	0.18
Tb	0.007	0.39	0.078	0.043	0.019	0.41	0.11	0.086	0.006	0.42	0.11	0.070	0.021	0.11	0.054	0.051	0.017	0.13	0.048	0.036
Yb	0.016	1.5	0.22	0.12	0.054	0.85	0.30	0.21	0.033	1.5	0.33	0.23	0.040	0.22	0.10	0.10	0.050	0.42	0.16	0.13
Hf	0.054	3.3	0.50	0.29	0.35	6.4	1.9	1.3	0.12	4.7	0.80	0.59	0.090	0.74	0.37	0.32	0.19	1.6	0.53	0.43
Ta	0.011	4.1	0.15	0.057	0.038	0.51	0.18	0.14	0.018	0.66	0.15	0.096	0.020	0.13	0.070	0.060	0.020	0.16	0.056	0.042
W	0.052	7.1	0.98	0.64	0.085	1.7	0.39	0.33	0.12	8.7	1.7	1.0	0.070	0.45	0.16	0.13	0.070	0.43	0.18	0.15
Au	0.002	0.26	0.023	0.019	0.001	0.10	0.008	0.005	0.003	0.14	0.034	0.026	0.002	0.025	0.010	0.009	0.002	0.036	0.006	0.003
Pb	13	231	37	27	6.2	157	34	30									6.5	32	14	14
Th	0.064	4.7	0.72	0.38	0.20	3.1	1.0	0.83	0.21	4.2	1.2	0.82	0.16	5.3	0.94	0.72	0.14	1.2	0.41	0.32
U	0.010	0.98	0.25	0.17	0.053	0.71	0.26	0.21	0.050	1.4	0.36	0.29	0.091	0.57	0.22	0.19	0.047	0.44	0.14	0.12

*Concentrations are given in g/kg.

the topographical diversity of the region covered by the sampling net in different years – from plains (2000 and 2001) to highlands (1999) and mountains (1995 and 1998). Due to this variety of relief it is practically impossible to select a general background level for Romania.

3.1. PRINCIPAL COMPONENT ANALYSIS

The factor loadings and explained variances from the optimum run established are given in Table IV. A total of 82.6% of the variance is explained by seven factors. Among them, several factors are suspected to have a wind-blown dust contribution (Steinnes, 1995). Only the second factor which includes elements associated to non-ferrous mining and metallurgy (Zn, As, Se, Mo, Ag, Sb, Au) has a clear anthropogenic pattern.

Aluminum is the third most abundant element in the lithosphere and the most abundant of the presently studied elements. Most naturally occurring aluminum compounds are sparingly soluble and bioavailable; therefore, relatively small quantities of aluminum are found in most biological samples unless contaminated with soil (dust) (Pais *et al.*, 1997). A normalizing procedure of element content in each sample to the corresponding Al content in the sample was applied to reduce the influence of the predominant crust component. For that purpose, ratios of X_n/Al_n were calculated, where X_a is concentration of element X in sample number n and Al_n is Al concentration in sample number n. Subsequently new runs with principal component analysis were carried out and the number of factors decreased from 7 to 4 (Table V).

The first factor is a "mineral dust" factor related to anthropogenic activities producing particulates, such as ore transport and deposit of tailings. This factor is loaded with Tb, Yb, Hf, Sm, Ce, Fe, Mg, V, La, Zr, Sc, U, Mn, Co, Cr, Ca, Ba.

The second factor contains all the easily mobile elements (Cl, Na, Cs, Se, Br, K, I, Th, Mo, Rb, Ca). This seems to indicate an element supply to the moss from soil solution, occurring in periods when the soil surface is saturated with water (snowmelt, etc), and facilitated by the fact that it is no "protective" litter/humus layer between moss and the mineral soil. The occurrence of Th in this factor though is somewhat surprising.

Factor 3 is obviously pollution–related (non-ferrous metal smelting) and contains Sb, Zn, As and Ag.

The fourth factor shows an association of W with Ni, the explanation of which is not straight-forward.

3.2. NATIONAL PARKS

A total of 20 samples (denoted NP samples in the subsequent text) were collected not farther than 15 km from these protected areas. Figure 3 is a selection of 10 elements indicating the minimum and maximum values in the whole set of samples

Table IV. Factor loadings for the overall data set

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Na	**0.76**	0.07	0.02	−0.13	0.29	0.16	0.03
Mg	**0.80**	−0.03	−0.01	0.27	0.08	0.27	0.07
Al	**0.67**	−0.02	0.01	0.18	0.07	0.09	−0.04
Cl	−0.00	0.03	−0.10	**0.82**	−0.08	0.22	0.04
K	0.02	0.13	0.52	−0.29	0.03	0.45	0.11
Ca	0.18	0.15	−0.03	0.15	0.06	**0.77**	0.04
Sc	0.57	0.22	**0.61**	0.24	0.27	−0.02	−0.01
V	**0.83**	0.01	−0.01	0.17	0.15	0.15	0.11
Cr	0.42	0.19	**0.65**	−0.12	0.25	0.13	0.09
Mn	0.32	0.06	0.16	0.50	0.14	−0.16	0.17
Fe	**0.71**	0.36	0.25	0.03	0.46	0.04	0.03
Co	0.49	0.39	**0.66**	−0.02	0.22	−0.04	0.05
Ni	0.18	0.09	**0.79**	0.05	0.17	−0.07	−0.02
Zn	−0.03	**0.78**	0.20	−0.00	0.27	0.14	−0.09
As	0.09	**0.91**	0.00	−0.06	−0.09	0.07	0.05
Se	0.17	**0.80**	0.09	0.05	0.40	−0.05	0.08
Br	0.07	0.04	0.50	−0.24	0.12	0.04	**0.64**
Rb	0.39	0.25	0.21	0.06	**0.62**	−0.32	0.06
Sr	0.17	0.22	0.21	0.07	**0.66**	0.42	0.01
Zr	0.40	0.26	−0.01	−0.09	**0.78**	−0.01	0.12
Mo	0.15	**0.85**	−0.20	−0.22	0.06	0.02	0.22
Ag	0.05	**0.77**	0.28	0.01	0.27	−0.06	0.04
Sb	−0.08	**0.78**	0.11	0.07	0.20	0.05	−0.12
I	0.08	0.06	−0.01	0.24	0.07	0.04	**0.84**
Cs	**0.66**	0.13	0.31	0.09	0.44	−0.18	0.08
Ba	0.39	0.11	0.42	0.03	**0.64**	0.13	0.05
La	**0.82**	−0.06	0.34	0.00	−0.02	0.04	−0.08
Ce	**0.76**	−0.01	0.46	0.04	0.09	−0.09	0.02
Sm	**0.89**	−0.09	0.24	−0.02	−0.01	0.01	−0.00
Tb	**0.84**	0.13	0.19	−0.01	0.39	−0.09	0.06
Yb	**0.79**	0.17	0.23	0.04	0.41	−0.04	0.06
Hf	**0.67**	0.11	−0.22	−0.23	0.52	−0.05	0.17
Ta	0.37	0.01	−0.01	−0.08	0.15	−0.23	0.04
W	0.38	0.05	0.53	0.12	−0.24	−0.03	0.12
Au	−0.05	**0.66**	0.12	0.24	−0.21	0.10	0.02
Th	**0.85**	0.09	0.28	−0.10	0.13	0.02	0.06
U	**0.87**	0.11	0.34	0.05	0.01	0.01	0.11
Eigenvalue	14.59	4.84	2.35	1.96	1.45	1.31	1.20
(%)	39.44	13.07	6.36	5.29	3.91	3.55	3.24

Table V. Factor loadings for the overall data set normalized to Al content

	Factor 1	Factor 2	Factor 3	Factor 4
Na/Al	0.19	**0.86**	0.25	0.20
Mg/Al	**0.85**	0.49	0.06	0.01
Cl/Al	0.30	**0.92**	0.12	0.09
K/Al	0.35	**0.81**	0.20	0.17
Ca/Al	**0.62**	**0.66**	0.15	0.09
Sc/Al	**0.74**	0.09	0.43	0.33
V/Al	**0.81**	0.56	0.07	0.00
Cr/Al	**0.63**	0.50	0.28	0.37
Mn/Al	**0.70**	0.57	0.11	0.06
Fe/Al	**0.87**	0.34	0.30	0.13
Co/Al	**0.66**	0.38	0.44	0.39
Ni/Al	0.25	0.20	0.34	**0.61**
Zn/Al	0.28	0.21	**0.84**	0.04
As/Al	0.12	0.29	**0.75**	0.02
Se/Al	0.32	**0.84**	0.36	0.07
Br/Al	0.39	**0.84**	0.13	0.23
Rb/Al	0.59	**0.73**	0.20	0.10
Sr/Al	0.33	0.55	0.32	0.14
Zr/Al	**0.76**	0.27	0.33	0.02
Mo/Al	0.57	**0.74**	0.26	0.00
Ag/Al	0.11	0.23	**0.72**	0.34
Sb/Al	0.06	0.10	**0.89**	−0.03
I/Al	0.50	**0.80**	0.11	0.07
Cs/Al	0.41	**0.86**	0.15	0.10
Ba/Al	**0.62**	0.59	0.23	0.24
La/Al	**0.80**	0.36	0.05	0.22
Ce/Al	**0.87**	0.32	0.10	0.25
Sm/Al	**0.90**	0.30	0.01	0.18
Tb/Al	**0.94**	0.18	0.17	0.07
Yb/Al	**0.91**	0.31	0.21	0.11
Hf/Al	**0.91**	0.35	0.12	−0.02
Ta/Al	0.45	0.17	0.03	0.03
W/Al	0.11	0.18	−0.01	**0.82**
Au/Al	0.09	0.59	0.44	0.28
Th/Al	0.59	**0.75**	0.17	0.11
U/Al	**0.73**	0.57	0.15	0.27
Eigenvalue	23.56	3.07	2.41	1.28
(%)	65.46	8.54	6.71	3.56

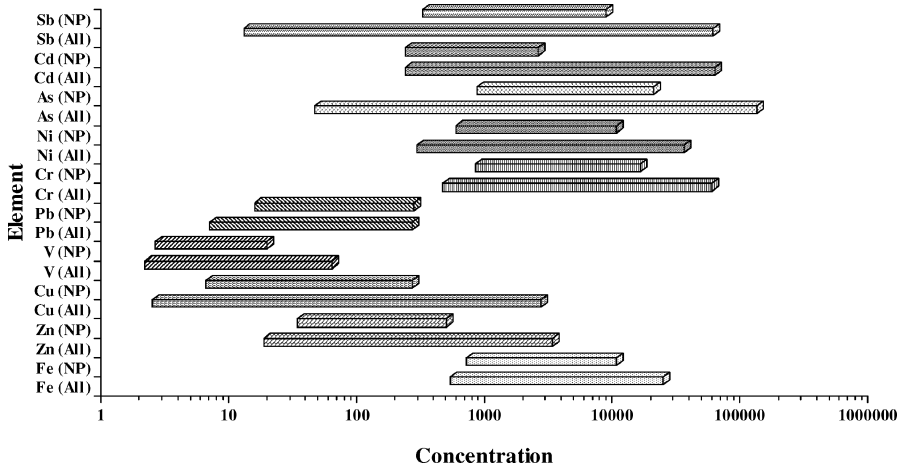

Figure 3. Minimum and maximum element content in the whole data set and in National Park (NP) samples, respectively. Concentrations are in mg/kg for Fe, Zn, Cu, V and Pb and in μg/kg for Cr, Ni, As, Cd, Sb.

(All) and corresponding values for the samples around National Parks (NP). This shows that whereas a majority of NP minimum values are close to the national minimums (for Cd these values coincide), some elements are subject to significant air pollution even in these supposedly pristine areas (eg. for Pb, NP maximum is equal to national maximum). It is obvious that Romanian National Parks suffer a sever influence form local pollution sources that surround them, especially for elements such as Pb, As, Sb and Fe.

Median values observed for Romanian National Parks are comparable with those reported for Polish Holy Cross Mountains National Park (Migaszewski *et al.*, 2002), and several times higher than those reported for Wolinski National Park in 1995 (Kowalska, 2003).

3.3. EXTENT OF POLLUTION PATTERNS

Geographical distribution of the pollution patterns for several elements is presented in Figure 4. Several emission sources for As, Cd, Cu, Zn and Pb can be distinguished. The most important one is the Baia Mare center, known for its traditional Cu, Pb and Zn smelting, Au and Ag processing and surrounded by numerous complex ore mines. The Barcau basin is polluted by lignite mining in Chiesd, Sarmasag, Ip, Borumiaca, Popesti, Voievozi and Varviz-Varzari. Other areas in the Western Carpathians highly polluted with As, Cd, Cu and Pb are those influenced by a non-ferrous smelter (Cu, Pb and Zn) in Baia de Aries and Cu smelters at Zlatna and Rosia Poieni. Similarly high values for these metals in the north and north-western part of Eastern Carpathians may be explained by several mines in Fundu Moldovei,

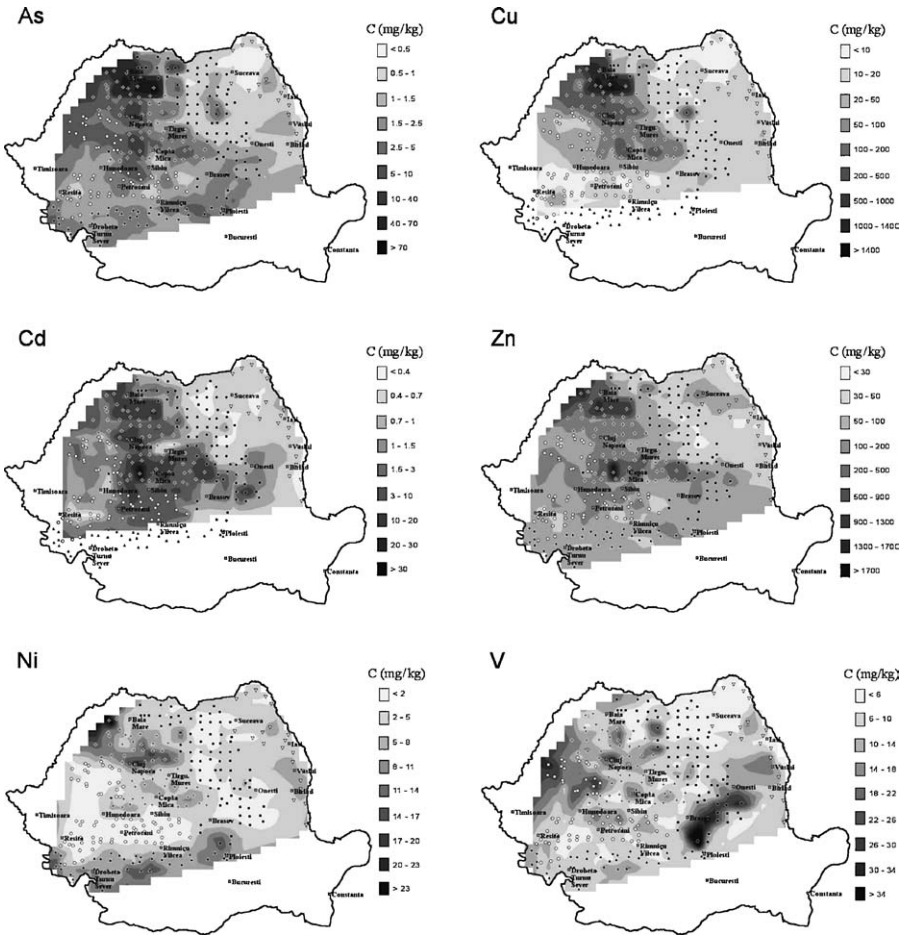

Figure 4. Geographical distribution of the pollution patterns for several elements. C = concentration of element.

Crucea, Lesu Ursului and Tarnita. Coal-fired power plants in Mintia Deva, Calan and Hunedoara, a H_2SO_4 plant in Copsa Mica, and chemical plants in Turda, Ocna Mures and Tarnaveni also provide contributions to As and Cd pollution. The iron and steel works in Resita, Otelu Rosu, Nadrag, Calan and Hunedoara are responsible for Ni emissions to those areas. Elevated levels of Ni were also found in the Petrosani and Motru-Rovinari coal basins and in the Tirgu Jiu region, presumably from coal burning. An additional source of airborne Ni is the thermal power station in Rogojelu (situated down from Targu Jiu). The high emissions of Ni from Valea Prahovei and Buzau regions correlate strongly with those of V and are obviously related to local oil refineries. The highest levels of vanadium were found in the Ploiesti, Valea Prahovei and Buzau oil regions, with an old tradition in oil exploration and processing.

4. Conclusions

The most important results obtained in this study are as follows:

- Identification of areas with contamination levels to be considered for the evaluation of environmental risk;
- Establishment of a nearly complete national sampling network for a future monitoring program;
- Creation of a database for continued studies at regular time intervals;
- Covering one more "white area" on the map of atmospheric deposition of heavy metals in Europe (Buse *et al.*, 2003; Rühling and Steinnes, 1998).

The levels of heavy metal deposition in several Romanian regions observed in this work are among the highest in Europe. Even areas within and close to national parks appear to be significantly polluted with heavy metals. The average life expectancy in Romania for humans is among the lowest in Europe: 66.56 years for men and 73.17 years for women. The serious air pollution situation is likely to be one of the factors responsible for these unfortunate health conditions. During the period after 1989, and especially during the last three years, extensive measures have been taken in order to improve the environmental conditions in Romania. The results from the present work however show that there is still a long way to go.

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