3.9. ATMOSPHERIC HEAVY METAL DEPOSITION ALONG FOUR MAJOR HUNGARIAN RIVER VALLEYS

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3.9.1. INTRODUCTION

River valleys are the most populated areas of Hungary and the industrial centres are also located here. On the other hand these regions mean biotops for many plant and animal associations included protected species. Environmental pollution accidents and damages, as e.g. recent cyanide pollution in the north-eastern rivers (Febr. 2000), Szamos and Tisza may prove the importance of biomonitoring studies over large areas.

Bryophytes have been widely used as bioindicators of air contaminants for the past few decades, especially to estimate heavy metal, organic and radioactive pollution (Berg *et al.*, 1996; Markert ed., 1993; Knulst *et al.*, 1995). Numerous studies (Gydesen *et al.*, 1983; Herpin *et al.*, 1996; Markert *et al.*, 1996; Meenks *et al.*, 1991; Rühling *et al.*, 1987; Rühling ed., 1994; Steinnes *et al.*, 1994; Tuba *et al.*, 1994) have shown that surveys of the heavy metals by cryptogams are valuable, easy and cheap method to identify the possible emission sources and long range transport of pollutants. Mosses have no root system, so they can take up nutrients and chemical substances mainly from dust-fall and precipitation. They are good bioaccumulators because of their high capacity to retain many trace elements.

An international moss monitoring programme (Rühling *et al.*, 1987; Rühling ed., 1994) was initiated and conducted by Nordic Countries under the Nordic Council of Ministers in 1985 to characterize quantitatively and qualitatively the regional and atmospheric deposition pattern of heavy metals. In 1995-1996, about 30 European countries joint this project, considering methods of Scandinavian guidelines to map and to compare results among different areas.

In the Nordic countries there is a long-term survey, data from 1985 to 1995 show a general decline in concentrations of most metals, e.g. in the cadmium deposition with a reduction in 35 % in Denmark or in the lead deposition with a decrease about 30% in Sweden, and present that the deposition is dominated by long-range transport (Rühling *et al.*, 1987; Rühling ed., 1994; Gydesen *et al.*, 1983; Berg *et al.*, 1996; Steinnes *et al.*, 1994. The decrease in concentrations of metals is mainly due to stricter emission legislation, filter technique, closure of old polluting industrial plants and use of petrol without lead.

Our present study is the first attempt to provide data on pollution with heavy metals by moss analysis at a larger scale, along main river valleys *(see Fig.1.)* including the Danube which is 417 km long, Tisza with length of 597 km, Kőrös with 219 km and Rába with 192 km in Hungary.

3.9.2. MATERIALS AND METHODS

Samples of the moss species *Hypnum cupressiforme* were collected from 47 sites up to a distance of 15 km from rivers, from September to November, during a relatively dry autumn in 1997. This carpet-forming moss growing on stumps, barks, rocks, walls and soils is widespread in Hungary, and very useful for bioindication because heavy metal content analysis can be done months or later after the collection.

Procedure of sampling was performed according to the Scandinavian guidelines; the samples were taken mainly from forests, not exposed directly to precipitation. The sampling sites were at least 300 m far from main roads and built-up areas, and at least 100 m far from any roads and buildings. 5-10 subsamples were collected and mixed from each sample point (50 x 50 m). Each sample was analysed in three repetitions.

The green parts of mosses were cleaned carefully without washing and then dried at 70 °C. Samples of 0,2 g were digested with 2 cm^3 of cc. HNO_3 and 2 cm^3 of cc. H_2O_2 at 130°C under pressure in Teflon bombs for 45 min. Then it was filtered through Whatman No. 42 filter paper and brought to a volume of 10 ml with bi-distilled water. Cd, Cr, Cu, Ni, Pb, V and Zn concentrations were determined with ICP-AES measurement technique.

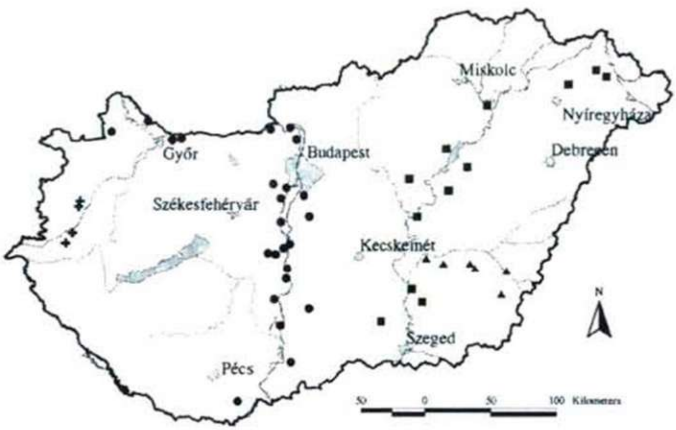

Fig. 1. Map of Hungary with sampling sites

3.9.3. Results and Discussion

The heavy metal concentrations data (Tables 1, 2 and Fig. 2) show that the highest values were measured at the rivers Danube and Tisza, close to industrial towns. The maximum concentrations were found at the sampling sites surrounding Budapest, Százhalombatta, Dunaújváros, Szolnok and Tiszaújváros. Effect of traffic compared to influence of industry is much milder as the sampling points were not close to the roads and contamination is rapidly reduced with distance (Tuba *et al.*, 1994).

Cadmium

Background average level for cadmium is 0.86 μg g^{-1} that is higher than the mean European values (0,2-0,7 μg g^{-1}) and similar to Russia (Rühling 1994). Main emission sources may be metal industry, mining and use of phosphate fertilizers in agriculture. The highest values are found along Danube around Budapest, Százhalombatta and Dunaújváros, and near the river Tisza (Tiszaújváros) due to industrial activities. There is also a high concentration of Cd in the village of Ásványráró (2,08 μg g^{-1}) that suggests that the cadmium may be transported to Hungary from the neighbouring regions (Slovakia and Austria) (Rühling ed., 1994).

Table 1 Concentrations of heavy metals in mosses taken near four river valleys (ig g^{-1} d.w.)

		Cd	Cr	Ni	V	Cu	Pb	Zn
DUNA	median	0,9	2,3	4,5	3,9	11,0	15,4	60,1
	mean	1,0	3,4	6,0	6,9	11,4	18,7	62,5
	min	0,3	0,9	2,1	1,5	6,7	5,4	32,1
	max	2,1	7,3	19,9	46,7	17,2	43,4	115,7
RÁBA	median	0,7	1,4	4,3	1,9	11,9	9,7	38,1
	mean	0,6	1,6	4,1	2,7	10,0	15,7	43,1
	min	0,3	0,9	3,1	1,0	6,6	5,4	32,7
	max	0,7	2,5	4,9	4,6	12,8	31,0	60,6
TISZA	median	0,8	1,7	3,0	1,9	10,4	14,1	45,7
	mean	1,0	3,2	5,6	11,8	10,1	15,8	56,5
	min	0,3	0,3	1,0	1,7	7,3	7,9	32,2
	max	2,1	14,0	30,4	86,0	15,2	35,6	128,2
KŐRÖS	median	0,6	2,7	4,1	2,7	11,0	14,7	48,9
	mean	0,6	2,4	4,6	2,9	11,2	16,7	55,0
	min	0,3	0,7	2,5	1,7	7,2	9,7	37,6
	max	0,7	4,3	7,8	4,8	16,0	25,6	82,9
AVERAGE	median	**0,7**	**2,4**	**4,4**	**2,8**	**11,0**	**15,5**	**51,9**
	mean	**0,8**	**3,1**	**6,7**	**11,4**	**11,0**	**17,8**	**58,2**
	min	**0,3**	**0,3**	**1,0**	**1,0**	**6,6**	**5,4**	**32,1**
	max	**2,1**	**14,0**	**30,4**	**86,0**	**17,2**	**43,4**	**128,2**

Chromium

The European baseline level for chromium in rural areas is around 1 μg g^{-1}(Rühling ed., 1994). Among investigated sites, environs of river Rába is the less polluted with range 0,93-2,07 μg g^{-1}. Higher concentrations are found around Budapest and in Dunaújváros (7.33 μg g^{-1}) by the rivers Danube because the local industry, especially iron and steel mills cause contamination. The river Kőrös and Tisza are more polluted than Rába, due to effects of industry of bordering country. The values were measured above 21 μg g^{-1} close to the frontier in Romania. A peak value was noted near industrial chemical centre of Tiszaújváros 13,98 μg g^{-1}.

Nickel

The main emission sources of Ni are steel industry, oil and coal burning. In most of European countries the concentration varies between 2-4 μg g-1 in mosses, higher concentrations (10-20 μg g-1) are measured near to smelters and chemical company (Rühling ed., 1994). The Hungarian average level is about 4-6μg g-1, but there are some local emittors. Elevated concentrations were found at Esztergom (10,28 μg g-1), Bugyi (15,02 μg g-1), Dunaföldvár (9,34 μg g-1), Mezőberény (7,76 μg g-1), Gyoma (11,03 μg g-1) Százhalombatta (19,86 μg g-1) and Tiszaújváros (30,39 μg g-1). Only background contamination (~ 4μg g-1) could be detected at the river Rába. Pollution of Ni is also relatively low at the river Tisza apart from values of Tiszaújváros and Tiszafüred.

Vanadium

Vanadium is mainly originated from coil and oil burning. Deposition of V in Hungary does not reach a considerable amount and it is similar to values of West-European countries (4-6 μg g^{-1}) (Rühling ed., 1994). The concentrations of V show strong relationship with Ni levels, the most polluted areas are the same as we have already mentioned at Ni. There are only three industrial establishments representing potential pollution sources: an oil refinary and an oil-fuelled heat power station located in Százhalombatta (46,69 μg g^{-1}) (Tuba *et al.*, 1994) and a chemical company in Tiszaújváros 30,39 μg g^{-1}).

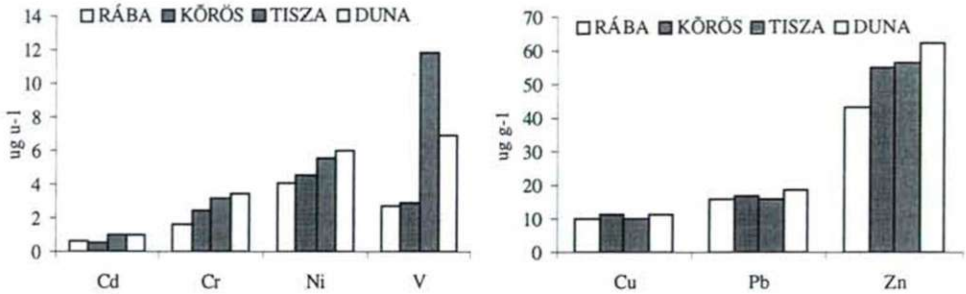

Fig. 2. Mean concentrations of heavy metals in mosses in the regions of four rivers (ig g^{-1} d.w.)

Copper

Copper can be originated from metal industry and from copper-containing fungicides used by agriculture. The background concentration of copper is about 10 μg g-1 in Hungary that is similar to European values (Rühling ed., 1994). Local effects could be not detected, however the input from bordering countries is remarkable. Eastern part of the country (at river Kőrös) is notably more contaminated than the others. (Timi°oara, Romania 126 μg g^{-1}).

Lead

The main sources of lead the combustion of leaded fuel, waste incineration and industry. As we measured background contamination of the country, our values are relatively low (10-20 μg g^{-1}) to compared with other countries (Rühling ed., 1994). Background levels near rivers Rába and Kőrös are the lowest. Higher concentration can be observed near towns, in the region Budapest (10-43 μg g^{-1}) due to a long-range transport of lead from extensive traffic.

Zinc

Zinc contamination is related with metal industries and use of pesticides in the agriculture. Zn level in European countries usually is less than 40 μg g^{-1} (Rühling ed., 1994), the average values in Hungary are between 30-50 μg g^{-1}. The background contamination of Zn is the highest by Danube, input from Austria and Slovakia could be well detected at the Upper Danube (60-116 μg g^{-1}). Locally increased Zn levels were also found near to central part of river, but a purification can be definitely observed at the Lower Danube (32-47 μg g^{-1}). Peak concentrations were found close to the capital (Érd 116 μg g^{-1}) and at Tiszaújváros (128 μg g^{-1}).

Table 2 Sampling sites and concentrations of heavy metals measured in collected mosses (μg g^{-1} dry weight)

	Duna	Cd	Cr	Ni	V	Cu	Pb	Zn
1	Ásványráró	2,1	2,3	5,7	9,0	9,8	13,9	50,0
2	Mosonszentmiklós	0,4	1,8	3,2	2,0	11,0	7,5	81,2
3	Gönyü	0,6	1,4	4,9	1,9	12,8	5,4	60,6
4	Nagyszentjános	0,5	2,1	3,0	2,5	6,7	13,0	36,4
5	Esztergom	1,6	5,9	10,3	9,8	10,2	11,7	87,9
6	Visegrád	1,7	7,0	7,1	12,3	13,6	27,0	75,9
7	Leányfalu	1,1	3,4	4,1	4,9	11,0	21,7	65,0
8	Pusztazámor	0,8	4,8	8,7	12,8	15,3	43,4	61,5
9	Érd	0,9	5,7	9,9	11,7	17,2	17,4	115,7
10	Alsónémedi	0,9	3,4	4,9	5,2	11,9	22,9	59,6
11	Bugyi	1,5	6,1	15,0	6,8	15,8	28,5	105,0
12	Szalkszentmárton	1,2	2,3	2,4	2,5	9,0	7,9	54,3
13	Százhalombatta	1,9	6,0	19,9	46,7	13,9	37,9	73,2
14	Adony	1,0	3,9	5,1	4,8	14,8	42,3	49,3
15	Mezőfalva	1,4	1,9	2,5	3,0	9,5	21,0	40,7
16	Dunaújváros	1,8	7,3	8,6	7,4	13,4	27,9	94,0
17	Baracs	0,9	2,3	3,8	2,3	10,3	11,2	57,1
18	Dunaföldvár	1,3	6,8	9,3	6,1	14,0	14,1	63,6
19	Bölcske	0,7	1,4	2,1	2,2	8,1	9,0	61,0
20	Paks	0,9	0,9	2,6	3,1	11,3	22,4	37,0
21	Kalocsa	0,6	1,0	2,2	1,5	6,7	6,7	47,2
22	Dombori	0,5	1,0	2,5	2,9	8,7	7,4	46,2
23	Baja	0,3	1,8	2,9	2,5	10,5	13,1	32,1
24	Pócsa	0,5	1,9	3,3	2,4	8,3	16,8	45,2
	Tisza	**Cd**	**Cr**	**Ni**	**V**	**Cu**	**Pb**	**Zn**
1	Vásárosnamény	0,5	2,4	3,7	2,0	7,6	14,8	43,1
2	Kisvárda	0,6	3,0	4,3	3,3	10,6	21,6	80,3
3	Nyírbogdány	0,3	1,2	1,8	1,8	11,0	35,6	46,1
4	Tiszaújváros	1,9	14,0	30,4	86,0	15,2	18,9	128,2
5	Poroszló	1,2	3,0	4,3	14,2	12,2	13,3	74,3
6	Tiszafüred	1,9	7,5	8,6	23,2	10,3	13,2	67,5
7	Jászkisér	0,9	1,6	4,0	1,8	8,6	14,2	45,4
8	Kunhegyes	0,3	1,5	2,4	2,0	11,7	14,0	34,5
9	Szolnok	2,1	0,4	1,9	1,8	8,2	15,1	55,4
10	Szentes	0,7	0,3	1,0	1,7	7,4	8,3	36,8
11	Derekegyháza	0,8	1,0	2,3	1,8	7,3	12,5	33,8
12	Kistelek	0,7	1,8	2,4	1,7	11,3	7,9	32,2
	Rába	**Cd**	**Cr**	**Ni**	**V**	**Cu**	**Pb**	**Zn**
1	Körmend	0,7	1,2	3,4	1,9	6,6	9,7	32,7
2	Vasvár	0,7	2,5	4,3	4,6	11,9	31,0	50,3
3	Sárvár	0,3	0,9	3,1	1,0	6,6	7,9	33,7
4	Vág	0,7	2,1	4,6	4,2	12,1	24,5	38,1
5	Gönyü	0,6	1,4	4,9	1,9	12,8	5,4	60,6
	Kőrös	**Cd**	**Cr**	**Ni**	**V**	**Cu**	**Pb**	**Zn**
1	Gyula	0,6	3,0	4,2	3,2	14,3	15,7	82,9
2	Doboz	0,3	2,6	4,0	2,3	7,6	13,6	37,6
3	Mezőberény	0,6	4,3	7,8	4,8	13,2	23,4	52,5
4	Gyoma	0,6	0,7	3,0	1,7	7,2	9,7	72,6
5	Szarvas	0,7	1,1	2,5	1,8	8,8	12,2	45,3
6	Öcsöd	0,5	2,7	5,8	4,0	16,0	25,6	39,2

3.9.4. Conclusion

Effects of the major pollution sources located in river valleys and influence of the long-distance transport from bordering countries could be well detected on base of moss analysis. The local emittors are steel, metal and chemical industry, oil refinery and heat power plants, the burning of coil and oil, cement production and transport. Peak concentrations along four major river valleys were measured in the region of Budapest, near Százhalombatta, Dunaújváros, Tiszaújváros, Tiszafüred and Gyoma. The Hungarian background concentrations of Cd, Cr, Cu and Zn are mildly elevated on an international scale (Rühling 1994).

The level of Ni is increased compared to other countries, but it is mainly due to input from industry of neighbouring countries (Rühling 1994). The values of Pb and V were found similar to European average (Rühling 1994).

Among the investigated river valleys, the most polluted one is the Danube, especially higher values of Cr, Ni and Zn were measured by upper and central region. The valley of the Rába is less contamined by Cr and Pb, but levels of Ni and Cu are elevated. Cd and Pb concentration are mildly increased at surroundings of river Tisza, local sources and Romanian input seems to be significant in cases of Ni and V. The area of river Kőrös is less polluted by Cd, but average values of Cr, Ni and V are elevated.

The present survey of heavy metal deposition reflects a mildly increased pollution in Hungary in 1997 compared to European values of 1995 (Rühling 1994). Our presented data serve a reference data base for the future to follow-up any changes and trends of the background heavy metal pollution due to atmospheric deposition.

3.9.5. Summary

The atmosphere is an important pathway for transport and deposition of the pollutants to both aquatic and terrestrial ecosystems. Hungary, due to its geographical situation in the Carpathian Basin can be regarded as a deposit area of the contaminants. There is a significant anthropogenic impact from neighbouring countries, adding to it an important internal emission, especially from the industrial centers located mainly near rivers. As a great part of population lives in the rivers valleys, and these regions are biotops for many rare species, there is a demand to estimate the state of their surroundings.

The aim of this paper is to characterize the atmospheric deposition of *Cd, Cr, Cu, Ni, Pb, V* and *Zn* in largest Hungarian river valleys (*Duna = Danube, Tisza, Kőrös, Rába*) to present days. Our studies join an international mapping project (*Atmospheric Heavy Metal Deposition in Europe)* (Rühling *et al.*, 1987; Rühling ed., 1994) following their standardized methods. Samples of moss *Hypnum cupressiforme* were collected at a total of 47 sampling points near the rivers during the autumn of 1997 and were analysed by atomic emission spectrometry with inductively coupled plasma *(ICP-AES)*. Results prove that major pollution sources are the industrial towns *(Százhalombatta, Dunaújváros, Tiszaújváros)*, and mean concentrations of heavy metals are higher than in most European countries, particularly in cases of cadmium and chromium. There also is significant input of nickel by atmospheric transport from bordering countries. The values of Cu, Pb, V and Zn were measured similar to European levels.

3.9.6. Acknowledgements

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