

Aquatic mosses as sampling medium in geochemistry

Vodni mahovi kot vzorčno sredstvo v geokemiji

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Abstract: Results of author's research of aquatic mosses that grow in stream water as sampling medium for indicating geochemistry of the landscape are presented. Studied was their capability for indicating the chemical elements dissolved in water in comparison to stream sediment, as well as various aspects of their use. Their properties for detecting anomalous contents of elements were found in a number of cases superior to stream sediment as the usual geochemical sampling material. The water mosses have been confirmed as a valid sampling medium for geochemical mapping, exploration of mineral deposits and environmental monitoring.

Izveček: Prikazani so rezultati avtorjevih raziskav vodnih mahov, ki rastejo v površinskih vodnih tokovih, kot vzorčnega sredstva za ugotavljanje geokemične sestave pokrajine. Njihove zmožnosti indiciranja kemičnih prvin, raztopljenih v vodi, so bile proučevane v primerjavi z vodnim sedimentom. Presojani so bili različni vidiki njihove uporabe. V vrsti primerov so se izkazali vodni mahovi za uspešnejše sredstvo za odkrivanje anomalnih vsebnosti kemičnih prvin od vodnega sedimenta kot običajnega vzorčnega materiala. Raziskave so potrdile vodne mahove kot učinkovito vzorčno sredstvo za geokemično kartiranje, sledenje nahajališč mineralnih surovin in ugotavljanje stanja okolja.

Key words: geochemistry, water moss, geochemical mapping, mineral exploration, environmental monitoring

Ključne besede: geokemija, vodni mah, geokemično kartiranje, sledenje rudišč, ugotavljanje stanja okolja

INTRODUCTION

When the editor of the journal RMZ – Materials and Geoenvironment kindly asked me to write a paper typical of my research, I first thought of writing on selenium, or trace elements in coal, or statistical designs in geology. Then came to my mind the idea to summarize in the paper my research of aquatic bryophytes, i.e., the mosses that grow in water, and their properties as sampling me-

dium for indicating the geochemistry of the landscape. These studies were conducted mainly in the eighties of the past century, and some also in 2001. The results were presented at scientific meetings, but only a part of them, those regarding geochemical mapping, were published in more detail. Much of valuable results remained unpublished in the reports, either of the Geologic Depart-

ment of University in Ljubljana, or in reports of several Yugoslav-United States of America research projects on geochemical mapping of karst terrains. Let the summarized results of these studies show what of the achievements are valid to be used in the present and future geochemical work!

Geochemical significance of aquatic bryophytes

The geochemical interest for aquatic mosses as sampling media resides in their ability to absorb chemical elements that are dissolved in water in which they grow. It is assumed that the elemental contents in their tissues is proportional to the average concentration in water during their growth (SHACKLETTE ET ERDMAN, 1982). This makes water mosses an attractive indicator for the average soluble elements concentrations in water that are normally subject to large fluctuations. Besides, the contents in moss can be readily determined by the routine analytical methods, whereas correct determining of the low concentrations of many elements in water is problematic. In this sense the aquatic mosses were tested for geochemical prospecting by SHACKLETTE (1965) and SHACKLETTE ET ERDMAN (1982) in the USA, by SAETHER ET B RLVIKEN (1983) in Norway and STEENFELT in Greenland.

Chemical analysis of systematically sampled trees and shrubs for traces of ore metals was one of the first geochemical methods to be investigated (ROSE ET AL., 1979). In the early 1930s V.M. Goldschmidt, a pioneer in geochemistry, first made the suggestion that analysis of plant material might be an effective method of prospecting. Later, in the terminology of the Russian geochemist

Vernadsky, the method became known as the biogeochemical method. As for mosses, much later the Russians even coined the term bryogeochemistry, as a branch of the biogeochemistry (KVYATKOVSKY ET AL., 1982).

Geochemical prospecting for minerals consists of systematic measurement of chemical properties of natural materials: soil, vegetation, water sediment, etc. (ROSE ET AL., 1979). The purpose is discovering of abnormal chemical patterns, called anomalies, related to mineralization. Anomalies are much larger than the mineral deposits they surround, and therefore more likely to be detected than the deposits themselves. On the other hand, the contents of ore and accompanying elements in anomalies are lower, diminishing away from the deposit, an attaining at some distance from it the background contents typical for barren, nonmineralized materials. However, also the contents of elements that are slightly elevated above the background may lead to hidden orebodies.

The said concerns the mineralizations in rocks and anomalous contents in various surface materials. But very similar reasoning applies also to the anomalies caused by pollution in the environment. Instead of the natural mineralization there is the anthropogenic source of contamination that is surrounded by a halo of elevated elemental contents in various natural materials. Their intensity is decreasing away from the source. The goals of mineral prospecting and environmental control may differ. In the latter, the source of anomaly is often known, and of interest are the intensity and extent of contents of anomalous elements in the landscape as well as their harm to the environment.

Aquatic mosses have been long used for pollution monitoring in rivers (BENSON-EVANS ET WILLIAMS, 1976; BURTON ET PETERSON, 1979; CARTER ET PORTER, 1979; SAY ET AL., 1981; BROWN, 1984).

Short overview of our performed research

The use of aquatic mosses was brought to our attention by H.T. SHACKLETTE of the US Geological Survey beginning of the 1980's. In our research at the Geology Department in Ljubljana we first used them for uranium exploration in the Žirovski vrh uranium deposit area. First results were encouraging, and they were presented in 1982 at the AEG International meeting in Helsinki, but were not published in more detail.

In 1983 started the preparatory studies for elaboration of the future geochemical map of ancient Yugoslavia. A large part of its territory consists of karst that cannot be mapped by stream sediment, at that time regarded as the standard mapping medium, owing to lack of the regular surface drainage. We then proposed the idea of using soil and also aquatic moss samples for regional geochemical characterization of karstic territories. Several detailed studies were started in Slovenia and later extended along the entire Dinaric karst belt of Yugoslavia. At that time aquatic moss was already used as one of sampling materials for the geochemical mapping of northern Fennoscandia, the so-called Nordkalott Project (BŘLVIKEN ET AL., 1986). The results of our research were presented at the 1st International symposium on geochemistry and health in London, at the 31st International geological congress in Washington and at several local meetings, and published to some detail (PIRC ET MAKSIMOVIĆ, 1986; PIRC ET AL.,

1990). In the frame of this research also the performance of water moss for detecting lead and zinc mineralization in the Mežica Pb-Zn and some other deposits was assessed (JENŠTERLE, 1986; KOČEVAR, 1987), the relation of moss to stream sediment studied, and procedures of sampling and laboratory practices (LENARČIČ ET PIRC, 1987) of using moss for geochemical studies investigated. Much of results of these studies were never systematically summarized. More recently, in 2001, aquatic moss has been used in a pilot study parallel to river sediment for assessing the environmental impact of cities and industrial activity as reflected in the river drainage. These results were presented at a local meeting only, and are published here first.

Beside a number of results of the partial studies, in this paper also the background estimates for large numbers of chemical elements in aquatic moss from various terrains were carefully compiled, in most cases compared to drainage sediment and sometimes soil from same localities. These estimates will be of help to the researcher dealing with the aquatic mosses and other sampling materials.

MATERIALS AND METHODS

Sampling and preparation for analysis

Aquatic moss and stream sediment were sampled in water streams or springs and prepared for analysis (PIRC ET AL., 1991) essentially according to procedures described by SHACKLETTE (1965) and SHACKLETTE ET ERDMAN (1982) for moss, and McNEAL (1977) for sediment. The moss material of about 0.5 kg wet weight and sediment material of 1 kg weight were collected at the

sample site each from about 10 points in order to reduce the sampling variability. In general, at a site only the prevailing species of moss were collected. The population of aquatic mosses in water streams is surprisingly uniform. Since the chemical differences between species were found not important (SHACKLETTE ET ERDMAN, 1982; ERDMAN ET MODRESKI, 1984), the moss of various species collected at a sample site was analyzed as a single sample.

After collection, the mosses were thoroughly washed, in the field in stream water and in the laboratory in tap water, in order to remove sediment particles and tufa fixed on them, dried at 60 °C and ashed at 500 °C. The removal of particulate material, especially of tufa, was found a difficult task. Therefore special procedures for cleaning particulates after ashing were developed (LENARČIČ ET PIRC, 1987). The sediment was air-dried in the laboratory, quartered and sieved to -0.062 mm grain size for analysis.

Analysis

Samples were analyzed through years in a number of laboratories: by optical emission spectrography (OES) for 21 elements at the Chemical Institute Boris Kidrič, Ljubljana, the Geologic Institute Zagreb, the laboratory of the USGS in Denver, by atomic absorption spectrometry (AAS) mainly for Cd, Cu, Pb and Zn, and occasionally for other elements, at the Chemical Institute Boris Kidrič, Ljubljana, the Jožef Stefan Institute, Ljubljana, the Geologic Institute in Zagreb, the Laboratory of the USGS in Denver, by inductively coupled plasma spectrometry (ICP) for a wide range of elements at the USGS in Denver, and later, a wide array of

37 elements by ICP-MS, plasma spectrometry combined with mass spectrometry, at the ACME laboratories in Vancouver, Canada. U was determined by neutron activation analysis (NAA) at the Jožef Stefan Institute, Ljubljana and by fluorometry and spectrophotometry at the laboratory of the Žirovski vrh uranium mine, and later by ICP-MS at ACME. Hg was analyzed by flameless AAS. Determined were total contents of elements (AAS and ICP after four acid total extractions), except for a few elements (as As, Bi, Sb, Se, Te) for which aqua regia extraction was used.

The quality of analytical work was carefully controlled according to MIESCH (1967 a and b; 1976 a). The quality of determinations within batches was monitored by analyzing duplicate splits of randomly selected samples to estimate precision, and by analyzing geologic reference materials (ALLCOTT ET LAKIN, 1974; ABBEY, 1983; GOVINDARAJU, 1989) or applying various analytical methods or various laboratories for estimating the accuracy. Batches of samples with duplicates and geologic standards were submitted to laboratories in random sequences under neutral laboratory numbers (PIRC ET AL., 1991).

For every batch the determination ratio was recorded, i.e., the number of samples in which the constituent was validly determined versus the total number of analyzed samples. The quality of analytical determinations between various laboratories was monitored by parallel determinations in them. Agreements and discrepancies between various batches within batches were recorded, and unreliable determinations excluded from statistical calculations and interpretations.

Sampling designs

Most of the regional sampling was performed according to statistical sample designs based on analysis of variance, as applied in geology first by OLSON ET POTTER (1954), later by KRUMBEIN ET SLACK (1965), and most extensively by MIESCH (1976 b) and co-workers from the US Geological Survey. The approach permits to divide the total variance among samples into variance components due to natural variability (between regions, areas, sample sites, various materials) and due to operation procedures (sampling and laboratory errors) (PIRC ET AL., 1991). An additional advantage of this method is the possibility of predicting the necessary sampling density and estimating the stability for the geochemical maps produced on the basis of the performed sampling (MIESCH, 1976 b; PIRC ET AL., 1991). Most of the estimates of elemental background values, laboratory precision estimates and comparisons between moss and stream abundances for this paper were obtained by the analysis of variance based sampling of large regions.

The sampling for mineral exploration and environment pollution was in general not based on statistical designs. It was performed according to principles of exploration geochemistry of the drainage system (ROSE ET AL., 1979). Samples were collected downstream of the supposed sources of the anomalous contents, belonging either to ore deposits or man produced pollution, in order to assess the response of the sample materials, and upstream of them, in order to assess the local background.

AQUATIC MOSS IN REGIONAL GEOCHEMISTRY

In the regional studies of carbonate rocks in the 1980s water moss was proposed and tested as sampling medium for geochemical mapping of karst territories. Its properties for regional sampling were established in comparison with stream or spring sediment and soil sampling. Owing to the lack of regular surface drainage in karst terrains, the moss and sediment were sampled mostly in karst springs. For comparison, also soil was sampled near the karst springs. Although the catchment areas of waters that take rise in karst springs are in general not well defined, the aquatic moss was found to be a satisfying sampling material for the geochemical characterization and broad scale geochemical mapping of the karstic terrains. The results were described in a considerable detail in the paper by PIRC ET AL. (1991). Here only some more important results will be listed.

The sampled population of aquatic bryophytes over the large extension of the Yugoslav Dinaric karst belt was found surprisingly uniform. The preponderant determined species are *Platyhypnidium* sp. (44 % of total), *Cratoneuron* sp. (38 %) and *Brachythecium* sp. (17 %). Results of the regional studies (PIRC ET AL., 1991) indicate that stable geochemical maps of carbonate terrains could be produced by the performed methodology with aquatic moss as sampling material for 9 out of 21 analyzed elements. Maps of B, Cr, Cu, Ni and Pb would reflect broad scale regional geochemical patterns, of La, Na, V and Zr semi-regional geochemical patterns; and maps of other 11 elements would show local variability. In comparison,

with sediment 11 stable maps could be produced and 12 with soil as sampling materials. Stable maps for other elements can be achieved by collecting more samples. Considering the fact that by the chemistry of aquatic moss, drainage sediment and soil various geochemical aspects of the landscape are characterized, the results confirm the validity of aquatic moss as sampling medium for geochemical mapping, comparable to the more utilized drainage sediment and soil.

One of the important results of regional studies was also the systematic estimation of the

background contents of 7 major and 14 trace elements in aquatic moss (on ash basis) on Middle and Upper Triassic carbonate terrains for the entire Dinaric karstic region, as listed in Table 1, and, in addition, in the publication by PIRC ET AL. (1991), the values of these elements separately for Slovenia, Croatia and Montenegro as well as for the 4 to 5 sampled areas within each of these republics (e.g., for Slovenia: the areas of Julian Alps, of Idrija, Inner Carniola, Lower Carniola and Sava region). In this frame the background was estimated also for drainage sediment and soil, sampled at the same localities (Table 1 and

Table 1. Chemical composition of background values for moss ash, stream sediment and soil in karstic Middle and Upper Triassic terrains of Slovenia, Croatia and Montenegro (modified after PIRC ET AL., 1990). Major elements in %, trace elements in µg/g. Analyzed by OES at Boris Kidrič Ljubljana and at RGF Zagreb. Numbers of samples: 65 for moss, 64 sediment and 78 for soil.

El	Moss ash		Sediment		Moss/sedim. ratio	Soil	
	Mean	Min-max	Mean	Min-max		Mean	Min-max
Al	3.25	0.3-11	4.81	0.8-10.5	0.73	5.85	0.08->10
Ca	10.14	2.5->10	7.15	0.9->10	1.4	3.96	0.1->10
Fe	1.44	0.1-8.5	4.45	0.5-10.5	0.32	3.49	0.2-9
Mg	6.96	2.0->10	4.06	0.6->10	1.7	2.89	0.4->10
Na	0.172	0.01-0.9	0.185	0.002-3.5	0.93	0.249	0.01-3
Ti	0.118	0.02-0.55	0.421	0.03-1.05	0.28	0.421	0.05-0.95
B	218	54-475	23	<10-315	9.5	35	<10-195
Ba	339	100->1000	156	<100-539	2.2	145	<100-370
Be	2.9	<3-20	2.1	<3-6	1.4	3.3	<3-10
Co	6.3	<3-55	4.9	<3-37	1.3	16	<3-52
Cr	29	<10-114	38	<3-800	0.76	68	<10-560
Cu	58	34-565	13	<3-62	4.5	19	4-85
Ga	5.8	<3-14	6.9	<3-30	0.84	10	<3-30
La	23	<10-140	40	10-110	0.57	44	<10-140
Mn	730	70-35,000	1510	90-9000	0.48	480	10-10,000
Ni	42	7-330	34	10-160	1.2	35	5-262
Pb	99	20-681	19	5-190	5.2	35	10-505
Sr	532	190->1000	123	<199- >1000	4.3	128	<100- >1000
V	107	50-250	89	23-245	1.2	96	14-265
Zn	760	355->700	45	<30-824	17	60	<30-297
Zr	149	<30-719	267	43->1000	0.56	385	43->1000
% Ash	8.7	6-14					

PIRC ET AL., 1991), which permits the comparison of the estimates between the three sampling materials. The data on relative enrichment or depletion in moss ash with respect to sediment reflect the degree of selective absorption of elements from water in tissues of the aquatic moss.

AQUATIC MOSS IN MINERAL EXPLORATION

Properties of aquatic bryophytes for detecting ore deposits were studied on a number of known mineral deposits in Slovenia in the 1980s. Most of the results appear in reports of the Institute of Geology of University in Ljubljana (PIRC, 1984, 1985; PIRC ET AL., 1987), and in diploma works (JENŠTERLE, 1986; and especially KOČEVAR, 1987). They will be summarized here in some detail.

The area of the Žirovski vrh uranium deposit

Aquatic moss and fines of stream sediment were sampled in 1982 and 1983 at 21 sample sites in 1st and 2nd order streams in the area

of the Žirovski vrh uranium deposit. The goal was the assessment of their performance as sampling media for uranium exploration in areas of ores hidden under barren cover. The terrain consists of barren Permo-Carboniferous dark grey slates, overlain by Middle Permian clastics. The main ore minerals, pitchblende and coffinite that occur disseminated in cement of grey sandstones of lower part of Middle Permian beds, were deposited during diagenesis. (DROVENIK ET AL., 1980). The production in the uranium deposit, discovered in 1960, was stopped after a short mining activity at the beginning of the 1990s.

The following species of aquatic bryophyta were determined at Žirovski vrh: *Platyhypnidium riparioides* at 12 sampling sites, *Brachythecium rivulare* at 7, *Brachythecium* sp. and *Thamnum allopecurum* each at 3 sites, *Scapania undulata*, *Mnium undulatum*, *Oxyrrhynchum speciosum*, *Plagiochilla aspleioides* and *Plagiothecium ruthei* at each 2, and *Bryum pseudo-triquetrum*, *Calliergonella cuspidata*, *Ctenidium molluscum*, *Mnium punctatum*,

Table 2. Uranium in aquatic moss on ash basis and associated drainage sediment at the Žirovski vrh uranium deposit area (data from PIRC, 1983, 1984) Analyzed by Boris Kidrič, Ljubljana by NAA.

Element in material	n	Contents, µg/g		Contrast of anomaly		Ratio moss/stream sediment	
		Mean	Min-max	Mean	Min-max	Mean	Min-max
Background samples							
moss	12	7.2	4.9-17.8	-	-	-	-
sediment	12	5.7	3.6-9.3	-	-	1.26	-
Mineralized samples							
moss	11	166	26.7-10,088	23	1.7-1400	-	-
sediment	11	54.8	10.4-80.5	9.6	1.8-14.1	24.1	2.4-184
Medians and ranges for % ash of background samples 19.2 (13.9 -31.3) and for mineralized samples 21.3 (11-27.7)							

Scapania nemorosa, *Sphagnum squarrosum*, and *Thuidium tamariscinum* each at a single sampling site. *Cratoneuron filicinum* and *Eurhynchium angustirette* appeared in traces only

Out of 23 sampled sites, 12 were found to belong to the local uranium background. For moss ash, the local background was estimated by the median (Me) of these samples at 7.2 µg/g U with the range from 4.9 µg/g U as

Table. 3. Chemical composition of aquatic moss on ash basis and stream or spring sediment fines from Mesozoic carbonate rocks at Mežica and Paleozoic clastic rocks at Žirovski vrh in Slovenia (modified after KOČEVAR, 1987). Determinations by IGCP, USGS, Denver, U by NAA, IJS, Ljubljana. Major elements and ash in %, trace elements µg/g.

El.	CARBONATE REGION (Area of Mežica)				CLASTIC REGION (Area of Žirovski vrh)			
	Moss ash n = 7		Stream sediment n = 7		Moss ash n = 4		Stream sediment n = 4	
	Mean	Min-max	Mean	Min-max	Mean	Min-max	Mean	Min-max
Al	4.5	1.2-9.6	3.1	1.2-8.1	7.3	3.1-8.3	6.8	6.3-7.7
Ca	16	11-28	17	1.9-22	9	5.9-21	0.93	0.17-4.1
Fe	2.5	0.6-4.9	1.5	0.89-4.1	3.4	1.9-4.3	3.35	2.8-4.4
K	2.9	1.4-3.9	0.7	0.4-2.2	2.5	1.3-6.2	1.8	1.7-2.2
Mg	4.1	1.9-6.9	8.8	1.4-10	1.9	1.3-3.1	0.93	0.43-2.5
Na	0.15	0.11-0.71	0.18	0.07-0.97	0.43	0.15-0.5	0.59	0.56-0.91
P	1.5	0.64-4.1	0.04	0.02-0.08	1.2	1.0-2.5	0.06	0.02-0.13
Ti	0.17	0.04-0.24	0.12	0.09-0.26	0.13	0.08-0.26	0.26	0.1-0.34
Ag	<4		<4		<4		<4	
As	<20		<20					
Ba	290	150-650	170	51-460	600	240-1400	530	450-630
Be	3	<2-5	<2	<2-2	3	<2-27	<2	<2-2
Cd	5	<4-12	<4		8	<4-10	<4	
Ce	55	<8-84	30	17-66	68	33-110	77	26-200
Co	15	6-27	8	6-17	55	12-95	14	12-17
Cr	60	31-100	33	20-91	81	65-100	79	60-84
Cu	73	56-120	11	8-28	150	80-190	23	14-30
Eu	<4		<4		<4		<4	
Ga	11	<8-24	<8	<8-18	20	<8-33	16	14-18
La	50	7-61	16	5-31	37	18-68	41	12-100
Li	40	17-86	33	12-70	79	34-150	81	55-98
Mn	1400	300-2900	390	190-790	8300	570-34000	720	490-930
Mo	<4		<4		<4		<4	
Nd	39	<8-54	16	<8-28	30	15-60	37	16-91
Ni	50	32-110	23	12-45	190	45-270	39	35-49
Pb	120	44-190	18	17-70	200	73-230	38	28-57
Sc	11	<4-43	6	<4-14	11	6-15	11	10-14
Sr	280	190-390	120	44-150	230	180-570	80	47-140
Th	<8	<8-14	<8	<8-9	10	<8-11	16	11-28
U*					7.2	4.9-17.8	5.7	3.6-9.3
V	80	36-190	48	25-110	72	50-110	86	77-95
Y	40	12-110	10	4-25	27	13-73	9	8-14
Yb	2	<2-6	<2	<2-8	<2	<2-4	<2	
Zn	835	350-2100	50	18-470	960	530-3300	97	92-120
% Ash	12	7-27			15	7-25		
U* - moss n=15, ss n=16								

minimum to 17.8 $\mu\text{g/g}$ U as maximum contents, and for stream sediment by Me of 5.7 $\mu\text{g/g}$ U (3.6–9.3 $\mu\text{g/g}$ U). On an average, the ratio of moss to stream sediment uranium background contents is 1.3 (Table 2).

At 11 anomalous sampling sites, the uranium contents in moss on ash basis ranged from 26.7 to 10,088 (!) $\mu\text{g/g}$ U with an average, expressed as median, of 166 $\mu\text{g/g}$ U. The values of the contrast of anomaly, defined as the ratio of anomalous contents with the background contents, ranged from 1.7 to 1400 (median of 23). The U contents in corresponding stream sediments range from 10.4 to 80.5 $\mu\text{g/g}$ U with the median of 54.8 $\mu\text{g/g}$ U, and the contrasts of anomaly from 1.8 to 14.1 (median of 9.6) for the stream sediment. The comparison between the moss (on ash basis) and stream sediment can be done by ratios of moss on ash basis to stream sediment contents at anomalous sites. These ratios ranged from 2.4 to 184, with the median value of 24.2.

It follows from these comparisons that moss is a very powerful sampling medium for detecting the investigated type of uranium mineralization, showing a much higher contrasts of anomalies than the corresponding stream sediment. It is also more sensitive to the presence of anomalous uranium, this being shown by high ratios of uranium in moss versus uranium in stream sediment (as for our study, on an average, about 24 times higher U in moss on ash basis than in stream sediment).

The Žirovski vrh study and that of carbonate terrains at Mežica (KOČEVAR, 1987) permitted to establish the estimates of background

contents in moss on ash basis and in associated fines of stream sediment for a number of elements. They are listed in Table 3.

The area of the Mežica Pb-Zn deposit

The lead and zinc ore is of the Alpine type hosted in carbonate rocks. The ore is in Middle Triassic carbonate rocks and was initially deposited during sedimentation and later partly reworked. Mineral association is very simple. Of economic importance were galena and sphalerite that contained some cadmium and germanium. Wulfenite is found in some parts of the deposit. Metallic lead was produced, zinc and molybdenum concentrate. The mine was in production for 300 years and is now closed (DROVENIK ET AL., 1980).

Four anomalous sites were sampled several times, No 834, 836 (PIRC, 1985) and 1024, 1025 (KOČEVAR, 1987). The results for aquatic moss on ash basis (Me 18 and range 7–29 % ash) and associated stream sediment are listed in Table 4. For cadmium at Mežica the average contrast of anomaly is 36 and its maximum value 43 in moss ash, and an average of 23 and maximum of 29 in sediment. The mean ratio of contents in moss ash to sediment is 22. The average contrast of anomaly for molybdenum was found to be 45 and its maximum value 85 in water moss ash in contrast to mean of 22 and maximum value 30 for associated sediment. The mean ratio of contents in moss ash to sediment is 5.7. The moss is indicated to be a more appropriate sampling medium than the sediment for Cd and Mo in the studied environment.

Table 4. Ore elements in aquatic moss on ash basis and associated drainage sediment at the Mežica lead and zinc deposit area (data from PIRC, 1984, 1985; JENŠTERLE, 1986; KOČEVAR, 1987) Analyzed at Boris Kidrič, Ljubljana by AAS.

Element in material	Contents, µg/g		Contrast of anomaly		Ratio moss/stream sediment	
	Mean	Min-max	Mean	Min-max	Mean	Min-max
Cd, moss	181	146-216	36	29-43		
Cd, s.s.	9.2	7-11.5	23	17-29	22	13-31
Mo, moss	77	10-145	45	6-85		
Mo, s.s.	13.5	9-18	22	15-30	5.7	0.55-16
Pb, moss	5595	1437-53,099	47	12-442		
Pb, s.s.	982	679-1617	55	38-90	8.6	0.9-51
Zn, moss	26,713	1588-45,465	32	1.9-54		
Zn, s.s.	1763	475-2,233	35	9.5-45	7	3.3-20
Ash, %	18	7-20				
Considered background values for moss ash: 5 µg/g Cd, 120 µg/g Pb, 835 µg/g Zn (Tab. 3), 1.7 µg/g Mo (Tab. 7), for drainage sediment: 0.4 µg/g Cd (PIRC & ŠAJN, 1997), 18 µg/g Pb, 50 µg/g Zn, 0.6 µg/g Mo (Tab. 7)						

In the Mežica carbonate area, for lead the contrast of anomaly has an average of 47 with a maximum of 442 in moss, and 55 with 90 as maximum, respectively, in sediment. The average Pb in moss ash versus sediment ratio is 8.6. For zinc an average of 32 and the nabar and some elementary mercury were mined. It was in production for five centuries, and according to the mined metal, Idrija was the world second largest producer. Ores were emplaced during the Middle Triassic igneous-tectonic activity into Upper Paleozoic and Lower and Middle Triassic sedimentary rocks. Since ore does not contain admixtures, the produced mercury is very pure (DROVENIK ET AL., 1980).

The sample sites were selected in the most polluted areas, upstream the river to assess the local background, and 10 km downstream to estimate the downstream dilution (KOČEVAR, 1987). The upstream sample turned out to be highly polluted, so the background estimates from the literature were used for calculating the anomaly contrasts. These are enormous, as seen from the Table 5. The estimated mean contrast of anomaly is 2900, with a maximum of over 34,800 in dry weight moss and a mean of 765 with the maximum value of 1110 in stream sediment. The average ratio of Hg in dry weight moss to sediment is 3.6, with a maximum of above 10. The moss indicates better the mercury dispersion at Idrija than the sediment. The results also give evidence of the extremely high pollution of Idrija in the 1980s.

Table 5. Mercury in dry weight aquatic moss and associated drainage sediment in the Idrija mercury deposit area (data from PIRC, 1986; KOČEVAR, 1987) Analyzed by AAS in Boris Kidrič, Ljubljana and RGF Zagreb.

Sample	Locality			
	Moss species	Hg, µg/g	Contrast of anomaly	Moss/sediment ratio
2053	Divje jezero at Idrija, 2 km upstream of Idrija			
	moss – <i>Brachythecium rivulare</i>	130	4330	-
	stream sediment	25	278	5.2
2051	Idrija, brook Pront, area of the mine			
	moss – <i>Brachythecium rivulare</i>	44	1470	-
	stream sediment	43	478	1
2052	Idrija, 2 km downstream of treatment plant			
	moss not determined	1045	34,830	-
	stream sediment (lab. Zagreb)	100	1,110	10.4
	stream sediment (lab. Ljubljana)	525	5,830	2
2055	Idrija, 2 km downstream of treatment plant			
	moss – <i>Cinclidotus fontinaloides</i>	4.3	143	-
	sediment not analyzed	-	-	-
Considered background value for moss dry substance 0.03 µg/g Hg (FIEDLER & RÖSLER, 1993), for stream sediment 0.09 µg/g Hg (PIRC & ŠAJN, 1997).				

Other mineral deposits in Slovenia

Aquatic moss was sampled also at some abandoned metallic mines in Slovenia (KOČEVAR, 1987). Lead ore deposits are common in the Sava Folds, where the ore veins cut the Permo-Carboniferous clastic beds. Mineral association is very rich; but main ore minerals are galena, some sphalerite and in places barite. Sampled were the Knape, Maljek and Pleše deposits; in the latter, the ore occurs also in Trassic dolomite. In ore veins in Carboniferous beds of the Trojane antimony deposit antimonite is the main ore mineral. In the Škofje deposit copper ore occurs in the upper part of Middle Permian grey sandstones. The ore minerals chalcopryrite, bornite and chalcosite were deposited

in pores of sandstone during diagenesis (DROVENIK ET AL., 1980).

The sampling (Tab. 6) in general confirmed the results of the Mežica study concerning Pb and Zn. The performances of aquatic moss and sediment appear to be about equal. At a single sample site for antimony at Trojane, the contrast of anomaly is 719 for moss versus 164 for sediment, and the ratio moss ash to sediment is above 9. The moss appears to be superior to the associated drainage sediment. For copper at Škofje, the established average contrast of anomaly is 14 (and maximum 19) for moss and 10 (maximum 11) for drainage sediment, and the ratio moss ash versus sediment is 3.7.

Table 6. Ore elements in aquatic moss on ash basis and associated drainage sediment in areas of various metallic deposits in Slovenia (Modified after KOČEVAR, 1987). Analyzed by AAS at Boris Kidrič, Ljubljana.

Element in material	Contents, µg/g		Contrast of anomaly		Ratio moss/stream sediment	
	Mean	Min-max	Mean	Min-max	Mean	Min-max
Knape, clastic terrains, moss not determined, 14 % ash						
Site 2039						
Zn, moss	2,100	-	2.2	-	-	-
Zn, s.s.	470	-	4.8	-	4.5	-
Maljek (Litija) clastic terrains, moss <i>Cratoneuron filicinum</i>, 10 % ash						
Site 2049						
Pb, moss	990	-	4.9	-	-	-
Pb, s.s.	210	-	5.5	-	4.7	-
Ba, moss	1,600	-	2.7	-	-	-
Ba, s.s.	670	-	1.3	-	2.4	-
Pleše, clastic terrains, moss <i>Cratoneuron filicinum</i>, 17 % ash						
Site 2044						
Pb, moss, ICP	1,050	-	5.2	-	-	-
Pb, moss, AAS	1,353	-	6.8	-	-	-
Zn, moss ICP	2,800	-	2.9	-	-	-
Zn, moss AAS	2,333	-	2.4	-	-	-
Trojane antimony deposit, moss <i>Brachythecium rivulare</i>, 7 % and 15 % ash						
Site 2047						
Sb, moss	769	-	700	-	-	-
Sb, s.s.	82	-	205	-	9.4	-
As, moss	40	-	3.6	-	-	-
As, s.s.	30	-	4.2	-	1.3	-
Zn, moss	3,300	-	3.4	-	-	-
Zn, s.s.	120	-	1.2	-	27.5	-
Site 2048						
Sb, moss	468	-	425	-	-	-
Škofje copper deposit, 13 % and 12 % ash						
Site 2040	moss – <i>Brachythecium rivulare</i>					
Cu, moss (n = 3)	2,100	1,372-2,868	14	9.1-19	-	-
Cu, s.s. (n = 3)	240	166-252	10	7.2-11	8.7	8.3-11.4
Site 2065	moss – <i>Brachythecium sp.</i>					
Cu, moss	1,370	-	9.1	-	-	-
Cu, s.s.	367	-	16	-	3.7	-
Considered background values for moss ash: 600 µg/g Ba, 8 µg/g Cd, 55 µg/g Co, 150 µg/g Cu, 200 µg/g Pb, 960 µg/g Zn (Tab. 3), 11 µg/g As, 1.1 µg/g Sb (Tab. 7), for drainage sediment: 530 µg/g Ba, 14 µg/g Co, 23 µg/g Cu, 38 µg/g Pb, 97 µg/g Zn (Tab. 3), 7 µg/g As, 0.4 µg/g Cd, 0.4 µg/g Sb (PIRC & ŠAJN, 1997).						

In conclusion, as based upon the values of contrast of anomaly, the aquatic moss appears to be a valuable sampling material for geochemical prospecting of mercury, uranium, antimony, cadmium, molybdenum and copper, superior to total digested drainage sediment, and also for zinc and lead for which the contrasts of anomaly are about equal in moss and in sediment. This conclusion is based upon the values of contrasts of anomaly estimated in the studies for moss and sediment (Tables 2 and 4 to 6).

Here should be mentioned also the very high observed contents of Cd, Cu, Hg, Mo, Pb, Sb, Zn and U in the aquatic mosses. The maximum values of contrast of anomaly are in descending order 34 830 for Hg, 1400 U, 700 Sb, 442 Pb, 85 Mo, 54 Zn, 43 Cd and 19 for Cu. With respect to the ability of plants to concentrate chemical elements in their tissue, KOVALEVSKII (1979) considers Hg a high barrier element, Zn high to medium, Cu and Pb medium to low, and U a low barrier element (The barrier in his terminology is the maximum content of element which a plant is capable of absorbing in the tissues). Our research confirms his classification, except for uranium, which at Žirovski vrh behaves in aquatic moss as an outstanding high barrier element.

By considering the percent ash, the dry matter contents of these maximum aquatic moss samples are 0.004 % Cd, 0.027 % Cu, 0.105 % Hg, 0.0026 % Mo, 0.065 % Pb, 0.0054 % Sb, 0.108 % Zn and 0.08 % U, as calculated by KOČEVAR (1987) and the present author.

AQUATIC MOSSES FOR DETECTING THE ENVIRONMENT POLLUTION

An earlier study of uranium in drainage

In the Žirovski vrh area, also a short study for estimating the environmental impact of uranium mineralization and mining in rivers Brebovščica, Poljanščica and Sora by using the aquatic moss was performed (KOČEVAR, 1987). She found in moss sampled at 2 km downstream of the mine in river Brebovščica that drains the mine area about 30- times higher contents on ash basis than the local background she estimated at 8 µg/g U. However, the moss in river Poljanščica 1.5 km downstream of confluence of Brebovščica, and the one in Poljanščica at Škofja Loka, about 20 km downstream, displayed just the background contents. Interesting to note that uranium content of moss in Poljanščica upstream of confluence with polluted Brebovščica showed higher than background uranium. She concluded that the Žirovski vrh mine does not pollute with uranium the river Poljanščica – at least according to the results of her moss study (KOČEVAR, 1987).

Background estimates for aquatic moss and drainage sediment

KOČEVAR (1987) sampled also moss in rivers. Her results for moss and those for river sediment as based on ICP determinations in 1986 permitted the compilation of background values for rivers. The data of the pilot study for assessing the river pollution caused by towns that was started by the present author in 2001 served for estimation of background values for moss and sediment in rivers in 2001 based on the ICP-MS de-

Table 7. Background estimates for moss ash of three Slovenian rivers in 1986 and 2001 and for stream sediment. Major elements in %, trace elements µg/g.

El.	3 Rivers 1986				3 Rivers 2001			
	Moss ash		S.S. mean	Ratio moss/s.s.	Moss ash		S.S. mean	Ratio moss/s.s.
	Mean	Min-max			Mean	Min-max		
Al	7.5	3.1-9.9	5	1.5	2.40	1.81-2.46	0.74	3.2
Ca	10	9-13	9	1.1	13.36	9.35-17.70	14.6	0.91
Fe	3.7	1.9-4.2	2.4	1.5	1.35	0.96-1.84	1.86	0.72
K	2.5	1.3-3.4	1.25	2	2.85	2.71-3.86	0.08	36
Mg	2.3	1.3-3.1	4.8	0.5	1.96	1.92-5.56	2.1	0.93
Na	0.38	0.16-0.65	0.4	1	0.263	0.214-0.306	0.009	29
P	1.7	1.2-2.7	0.05	34	3.122	0.698-3.185	0.049	64
Ti	0.19	0.09-0.2	0.2	1	0.065	0.064-0.079	0.03	2.1
Ag	-	-	-	-	0.136	0.121-34.594	<0.5	>0.27
As	<20	<20-20	<20	1	10.9	7.8-11.4	5	2.2
B	-	-	-	-	-	-	3	-
Ba	570	240-610	350	1.6	215	108-217	53	4
Be	3	<2-5	<2	>1.5	1	<1-1	-	-
Bi	-	-	-	-	0.30	0.14-0.30	<0.5	>0.6
Cd	4	<4-5	<4	>1	0.92	0.81-1.23	0.3	3.1
Ce	59	33-62	54	1.1	n.d.	-	-	-
Co	16	12-33	11	1.4	29.7	10.6-36.4	9	3.3
Cr	87	66-1200	56	1.5	33	26-34	21	1.6
Cs	-	-	-	-	1.6	1.6-2.1	-	-
Cu	250	150-300	17	15	85.4	36.63-89.27	25	3.4
Ga	19	8-24	10	1.9	-	-	2	-
Hf	-	-	-	-	0.17	0.08-0.30	-	-
Hg	-	-	-	-	-	-	0.075	-
La	34	18-35	28	1.2	16	11-17	7	2.3
Li	65	34-67	57	1.1	-	-	-	-
Mn	1300	570-2500	695	1.9	6535	1055-12015	338	19
Mo	-	-	-	-	1.74	1.44-1.88	0.6	2.9
Nb	-	-	-	-	1.47	1.27-1.60	-	-
Nd	26	15-34	26	1	-	-	-	-
Ni	62	45-140	31	2	44.9	21.4-122.4	23	2
Pb	160	73-320	24	6.7	60.66	28.20-60.81	23	2.6
S	n.d.	-	-	-	0.96	0.40-1.23	0.09	11
Sb	-	-	-	-	1.07	0.96-1.67	<0.5	>2
Sc	15	6-19	8	1.9	7.4	4.4-9	1.4	5.3
Sn	-	-	-	-	2.3	1.7-2.4	-	-
Sr	270	230-340	100	2.7	226	218-246	66	3.4
Ta	-	-	-	-	0.1	-	-	-
Tl	-	-	-	-	<1	-	-	-
Th	8	<8-16	10	0.8	4.4	3.5-4.8	2	2.2
U*	8.2	2.5-22.4	1	8	1.4	1.2-1.8	1	1.4
V	67	50-100	67	1	39	33-43	13	3
W	-	-	-	-	0.6	0.5-1.0	<1	>0.6
Y	30	13-50	10	3	-	-	-	-
Yb	2	<2-4	<2	>1	-	-	-	-
Zn	1300	539-1400	73	18	399.4	311.3-443.7	72	5.5
Zr	-	-	-	-	8.8	2.7-10.5	-	-
% ash	11	8-14	-	-	17.4	15.3-29.4	-	-

Aquatic moss in rivers in 1986 (Sava, Cerkljarska, Medija, analyzed by ICP at USGS, Denver (data in KOČEVAR, 1987), and in rivers in 2001 (Sava, Sora, Voglajna), data of this study.
Stream sediment: for 1986, the average of carbonate and clastic terrains estimates (Tab. 3), for 2001, median of 8 rivers upstream of towns (Drava, Koperščica, Tržiška Bistrica, Kamniška Bistrica, Ljubljana, Sava, Sora, Voglajna). All determination for 2001 by ICP and ICP -MS at ACME, Vancouver.

terminations. They are listed as preliminary estimates of background values for moss on ash basis and associated stream sediment in Table 7. For the two data sets also the mean background moss to sediment ratios were calculated and listed.

The estimated background values are of varying quality. At least one third of them might be assessed as very good, and the additional third of them satisfying. But also some of the remaining third, those of low quality, can help in providing the first orientation.

Pollution caused by urban agglomerations in rivers, pilot study of towns in 2001

The basic idea for this investigating of the pollution was to determine in the samples as many elements as possible in order to obtain the first indication, the fingerprint of its multielemental pattern. The aquatic moss and river sediment were sampled at two sites, one upstream and the other downstream of each town. Owing to the small numbers of samples, the resulting considerations are on the semiquantitative level

The results are compiled in Tables 8 to 10 for the towns of Jesenice, Celje and Ljubljana. Jesenice with a population of 20,000 souls is an old iron mining and ironmaking center, Celje of 40,000 inhabitants is an important industrial town (zinc smelting and ironmaking in the past, and chemical industry, production of titanium oxide, among others), and Ljubljana, the capital of Republic Slovenia, a population of 270,000 inhabitants, the prevalingly light industry and two coal firing heating-power stations.

In the tables the contents for 22 elements are listed for each anomalous site representing the sample collected downstream of the town, and the barren site of sample collected upstream of town, for both moss on ash basis and total digested sediment. Contrasts of anomaly calculated from anomalous contents and background values from Table 7 are listed first. They indicate the anomalous contents with respect to general background. Since our interest was in the contribution of towns to river pollution, the local contrasts of anomaly (LCA) are more indicative of the pollution brought into the river. They were calculated as ratios of the anomalous to barren sample contents. By CLA the sense of the anomaly – positive (above 1), nonexistent (around 1) or negative (below 1), and its strength – high, medium, low are described. As by the elemental contents in moss chiefly the soluble part of element characteristic of the river water is indicated, and by the contents in river sediment chiefly (but not entirely) its component in the fine particulates of the sediment, the contrasts of local anomaly provide the estimates of the corresponding components of elemental pollution, of its dissolved and particulate components. The moss to sediment ratios in the last column of Tables 8 to 10 give the idea of the degree of concentration of element in the moss ash with respect to corresponding sediment.

The following discussion based on absolute contents of elements, on contrasts of local anomaly (CLA) and on moss/sediment ratios is semi-quantitative since these values are mostly derived from single determinations of single samples. The error of procedure (i.e. of sampling and analysis) is consequently large. Therefore the results in the

Table 8. Jesenice, characteristic geochemical pattern of urban pollution in aquatic moss and stream sediment samples of river Sava in 2001. Contents of major elements in %, trace elements in µg/g. Analyzed by IGCP-MS at ACME, Vancouver, Canada.

El.	Contents				Contrast of anomaly		Local contrast of anomaly		Moss/S.S. ratio
	Moss		S.S.						
	Anom.	Barr.	Anom.	Barr.	Moss	S.S	Moss	S.S.	
Elements typical for plant tissue									
P	1.02	0.70	0.06	0.017	0.33	1.1	0.79	1.7	18
K	2.15	2.71	0.07	0.04	0.75	0.87	0.79	1.7	54
Na	0.15	0.21	0.015	0.016	0.57	1.7	0.70	1	9.9
Elements of higher contrast of local anomaly for moss than for sediment									
Cu	3778	36	28	7	44	1.1	103	4	135
Pb	841	38	48	10	14	2.1	22	4.8	17
Sn	29.5	1.7	n.d.	n.d.	13	n.d.	17	n.d.	n.d.
Ag	1.2	0.15	1.1	<0.5	8.8	>2.2	7.9	>2.2	1.1
Ni	77	11	19	11	1.7	0.8	3.6	1.7	4.0
Elements of higher contrast of local anomaly for sediment than for moss									
Ba	161	108	100	16	0.75	1.9	1.5	6.2	1.6
Hg	n.d.	n.d.	0.625	0.035	n.d.	8.3	n.d.	4	n.d.
Zn	683	311	141	34	1.7	1.0	2.2	4	5.0
As	2.4	10.9	9	3	1.1	1.8	1.1	3	1.4
Co	11.1	10.6	7	3	0.37	0.78	1.0	2.3	1.6
Mn	1567	1055	339	147	0.19	0.47	1.4	2.3	4.6
Sb	1.78	0.96	9	<5	1.7	>1.8	1.8	>2.0	2.0
Elements of equal contrasts of local anomaly for moss and sediment									
S	1.06	0.40	625	56	1.1	2.7	2.6	3	1.7
Mo	3.75	1.88	1.8	0.7	2.1	3.0	2.0	2.6	2.1
Cr	44	26	17	9	1.3	0.81	1.7	1.9	2.6
Elements of feeble or no contrast in anomalous site									
Cd	127	123	0.4	0.3	1.4	3	1.0	1.3	3.2
U	2.4	1.8	1	1	1.7	1.8	1.3	1	2.4
Ti	0.70	0.064	0.002	0.003	1.1	0.7	1.1	0.67	35
Elements preferentially accumulated in moss ash versus stream sediment									
Cu	3778	36	28	7	44	1.1	103	4	135
Ti	0.70	0.064	0.002	0.003	1.1	0.7	1.1	0.67	35
Pb	814	38	48	10	14	2.1	22	4.8	17
Zn	683	311	141	34	1.7	1.0	2.2	4.0	5.0
Mn	1567	1055	339	147	0.19	0.47	1.4	2.3	4.6
Ni	77	11	19	11	1.7	0.8	3.6	1.7	4.0
V	50	43	13	7	1.3	1.0	1.2	1.8	3.8
Cd	127	123	0.4	0.3	1.4	3	1.0	1.3	3.2
Cr	44	26	17	9	1.3	0.81	1.7	1.9	2.6
U	2.4	1.8	1	1	1.7	1.8	1.3	1	2.4
Mo	3.75	1.88	1.8	0.7	2.1	3.0	2.0	2.6	2.1
S	1.06	0.40	625	56	1.1	2.7	2.6	3	1.7
Co	11.1	10.6	7	3	0.37	0.78	1.0	2.3	1.6
Ba	161	108	100	16	0.75	1.9	1.5	6.2	1.6
As	2.4	10.9	9	3	1.1	1.8	1.1	3	1.4
Elements not or not properly analyzed in moss and/or sediment									
Sn	29.5	1.7	n.d.	n.d.	13	n.d.	17	n.d.	n.d.
Hg	n.d.	n.d.	0.625	0.035	n.d.	8.3	n.d.	4	n.d.
U	2.4	1.8	1	1	1.7	1.8	1.3	1	2.4
Barren sample collected upstream, anomalous downstream of town. Background values from data for 2001 in Tab. 7. Ash: barren sample 29.4 %, anomalous s ample 18.4 %.									

following text should be regarded as indications that should be verified by later work.

The common characteristics for all three towns are very high concentrations of bioessential elements P, K and Na in ashed moss versus sediment. Moss to sediment ratio is 17 to 37 for P, 9 to 54 for K and 3.4 to 13 for Na. The phenomenon is associated with living processes of plant growth and will not be discussed further. The elemental patterns of other elements, however, differ a lot among the three towns.

The town of Jesenice

The pollution of Jesenice is the highest in the moss ash, i.e., occurring in soluble form, by Cu, Pb, Sn and Ag, as indicated by high values of CLA 193, 22, 17 and 7.9), followed by Ag and Ni (CLA >2.2 and 3.6); a part of these elements is associated with particulates (CLA for sediment from 4 for Cu to 1.7 for Ni, while for Sn it was not determined). Pollution prevalent in sediment, as particulates, is indicated for Ba, Zn, As, Co, Mn and Sb (CLA 6.2, 4, 3, 2.3, 2.3 and >2.0). About equal are responses in moss and sediment for S, Mo, Fe and Cr (CLA moderate and low, 2.6 to 1.7 in ash and 3 to 1.9 in sediment). Contrast of Cd, U and Ti are feeble, absent or negative (CLA around 1, 1-1.3 for moss and 0.67 to 1.8 for sediment).

For the Jesenice pollution, ashed moss to sediment elemental ratios for the anomaly are the highest for Cu, Ti and Pb (values 135, 35 and 17, followed by Zn, Mn, Ni, V, Cr, U and Mo (values ranging from 5 for Zn to 2.1 for Mo).

In short, in the drainage downstream of Jesenice occur very highly anomalous Cu

and highly anomalous Pb and Sn in river moss, moderately anomalous Ag in moss and Ba in sediment, and low anomalous Hg, Zn, As, Co, Mn, Sb prevailing in sediment, Ag and Ni in moss, and S, Mo, Fe and Cr in both materials. Very high moss to sediment elemental ratio is for Cu, high for Ti and P, moderate for Zn, and low (4.6 to 1.4) for Mn, Ni, V, Cd, Cr, U, Mo, S, Co, Ba, As.

The town of Celje

The river pollution of the metallurgical and industrial town of Celje (Tab. 9) is characterized by an elemental pattern characteristic for zinc smelting, iron works, production of titanium oxide, and chemical industry. The highest pollution detected in moss ash is for Zn, Sb and As with CLA values of 223, 17 and 14; accompanied by high CLA values of 70, >7.7 and 9 in sediment. This indicates the presence in drainage of these elements typical for zinc smelting in either soluble or particulate forms. Moderate CLA determined for Ni, Sn and U (3.9, 3.3 and 2.2) indicate their partly solute state in river water, paralleled for Ni by elevated presence also in particulates. Sn and U were not determined in sediment.

Highly anomalous in sediment are Hg (CLA 70, but not analyzed in moss) and Ba (22 times the local background, and hardly elevated in moss ash). Cu, Mn and Ti are moderately anomalous in sediment (CLA 6.1 to 4.1), with somewhat lower CLA values for moss ash (2.3, 3.7, 2.7), indicating presence in solute and solid forms. Ti introduced by TiO_2 production apparently does only moderately influence the drainage geochemistry, CLA being 2.7 for moss and 4.1 for sediment.

Table 9. Celje, characteristic geochemical pattern of urban pollution in aquatic moss and stream sediment samples of river Voglajna in 2001. Contents of major elements in %, trace elements in µg/g. Analyzed by IGCP-MS at ACME, Vancouver, Canada.

El.	Contents				Contrast of anomaly		Local contrast of anomaly		Moss/S.S. Ratio
	Moss		S.S.						
	Anom.	Barr.	Anom.	Barr.	Moss	S.S.	Moss	S.S.	
Elements typical for plant tissue									
P	2.52	3.18	0.145	0.091	0.81	2.9	0.79	1.5	17
K	3.94	3.86	0.42	0.12	1.4	1.75	1.0	3.5	9.3
Na	0.514	0.263	0.149	0.012	1.9	16	1.9	12	3.4
Elements of higher contrast of local anomaly for moss than for sediment									
Zn	88762	399	6946	104	222	96	223	70	13
Sb	18.2	1.07	3.8	<0.5	17	>3.6	17	>7.7	4.6
As	108	7.8	45	5	9.9	9	14	9	2.4
Ni	220	44.9	91	223	4.9	3.9	4.9	3.9	2.4
Sn	7.6	2.3	n.d.	n.d.	3.3	n.d.	3.3	n.d.	n.d.
U	2.6	1.2	1	1	1.8	1	2.2	1	2.6
Elements of higher contrast of local anomaly for sediment than for moss									
Hg	n.d.	n.d.	0.776	0.075	n.d.	10	n.d.	70	n.d.
Ba	433	2.15	1166	53	2.0	22	2	22	0.37
Cu	213	89.3	122	20	2.5	4.9	2.3	6.1	1.7
Mn	46070	12556	1480	257	5.5	2.2	3.7	6.1	29
Ti	0.217	0.079	0.053	0.013	3.3	18	2.7	4.1	4.0
Elements of equal contrasts of local anomaly for moss and sediment									
Cd	4.89	0.81	22	0.3	53	13	60	73	2.2
Co	231	29.7	68	7	7.8	7.5	7.8	9.8	3.4
Pb	359	60.8	191	28	5.9	8.3	5.9	6.8	1.9
Ni	220	44.9	91	223	4.9	3.9	4.9	3.9	2.4
Mo	7.10	1.74	2.33	0.6	4.1	3.7	4.1	3.9	3.0
Cr	94	33	53	21	2.8	2.5	2.8	2.5	1.8
V	86	39	31	19	2.2	2.4	2.2	1.6	2.8
Pollutants from upstream									
Ag	12.29	34.59	3.4	2.0	90	>6.8	0.35	1.7	3.6
Elements of feeble or no contrast in anomalous site									
S	1.05	1.23	0.27	0.19	1.1	3.0	0.85	1.4	3.9
Elements preferentially accumulated in moss ash versus stream sediment									
Mn	46070	12556	1480	257	5.5	2.2	3.7	6.1	29
Zn	88762	399	6946	104	222	96	223	70	13
Sb	18.2	1.07	3.8	<0.5	17	>3.6	17	>7.7	4.6
Ti	0.217	0.079	0.053	0.013	3.3	18	2.7	4.1	4.0
S	1.05	1.23	0.27	0.19	1.1	3.0	0.85	1.4	3.9
Ag	12.29	34.59	3.4	2.0	90	>6.8	0.35	1.7	3.6
Co	231	29.7	68	7	7.8	7.5	7.8	9.8	3.4
Mo	7.10	1.74	2.33	0.6	4.1	3.7	4.1	3.9	3.0
V	86	39	31	19	2.2	2.4	2.2	1.6	2.8
U	2.6	1.2	1	1	1.8	1	2.2	1	2.6
As	108	7.8	45	5	9.9	9	14	9	2.4
Ni	220	44.9	91	223	4.9	3.9	4.9	3.9	2.4
Cd	4.89	0.81	22	0.3	53	13	60	73	2.2
Elements not or not properly analyzed in moss and/or sediment									
Sn	7.6	2.3	n.d.	n.d.	3.3	n.d.	3.3	n.d.	n.d.
Hg	n.d.	n.d.	0.776	0.075	n.d.	10	n.d.	70	n.d.
U	2.6	1.2	1	1	1.8	n.d.	2.2	n.d.	2.6
Barren sample collected upstream, anomalous downstream of town. Background values from data for 2001 in Tab. 7. Ash: barren sample 17.4 %, anomalous sample 29.9 %.									

For a number of elements high CLA was determined both in moss and sediment. The very high contrast of anomaly is indicated for Cd, consequence of zinc smelting, in both sediment (73) and moss ash (60). Co and Pb display CLA values in the approximate range 5 to 10 in both media, followed by Ni, Mo, Cr and V with the CLA range from about 2 to 5. Feeble contrast, around 1, is displayed for S in both moss and sediment. A special case is Ag; the pollution source appears to be located upstream of the barren sample site upstream of Celje, in the Hudinja river, the confluent of Voglajna. Its contents in water across Celje keep diminishing, as shown by CLA smaller than unity (0.35) in moss ash. The reverse is true for the sediment with CLA of 1.7, indicating that very high concentrations in river water only with delay get fixed in the sediment.

Highest moss ash to sediment elemental ratios are for Mn (29) and Zn (13) followed by Sb, Ti, S, Ag, Co, Mo, V, U, As Ni and Cd (from 4.6 down to 2.2). Ratios were not calculated for Sn and Hg owing to lack of determinations in the other sample material, and in U owing to unreliable analytics of the sediment.

To resume for Celje, very high pollution by Zn, Cd, Hg, As and Ba, moderate by Sb, Co, Pb, Cu and Mn, and low by Ni, Ti, Mo, Cr and V. High Ag pollution comes from upstream Celje. Very high contrasts of anomaly in both river moss and sediment appear for Zn and Cd, for Ba and Hg in sediment, high contrasts for Sb and As in moss. Moderately anomalous are Cu and Mn in sediment. and Co, Pb in both media. Of low contrasts are Sn, U, Ti, Ni, Mo, Cr and V.

The town of Ljubljana

The pollution by the residential town of Ljubljana with not much industry follows a different pattern and also contrasts of anomalies are appreciably lower. The local anomalies could not be determined owing to lack of the barren moss sample upstream of town. For it, the background values for rivers in 2001 were used (Table 7). Results obtained are therefore less reliable.

The elements with higher contrasts of anomaly are Ag, Mn, Cr, Co, Ni, Sn and U, and corresponding values of contrast of anomaly of 34, 4.4, 3.7, 3.6, 2.9, 2.8 and 2.6. Only Ag and Co show appreciable contrasts of anomaly in sediment (7.6 and 1.8, Mn), Cr and Ni are not anomalous in sediment, and for Sn and U contrasts were not determined. It follows that the Ag and Co pollution appears in appreciable amounts in water and sediment, that of Mn, Cr and Ni essentially in water, and that of Sn and U in water, while data for sediment are lacking.

Pollution higher in sediment than in water moss appears for Ba, Cu, Pb, Hg, Mo and Sb, the contrasts of anomaly ranging from 6.2 for Ba to >3.2 for Sb. For these elements except for Hg (no data for moss) also appreciable anomalous contents are indicated in moss, i.e. they are enriched in river water, the CA for moss ranging from 3.1 for Cu to 1.5 for Ba. About equal contrasts for Zn, 4 in moss and 4.5 in sediment, indicate its anomalous contents being dissolved in river water and present also in the river sediment. Low or no anomaly is indicated for S, V, As, Ti and Cd, the CA varying in the range from 0.83 (Ti in sediment) to 1.5 for both media.

Table 10. Ljubljana, characteristic geochemical pattern of urban pollution in aquatic moss and stream sediment samples of river Ljubljanica in 2001. Contents of major elements in %, trace elements in µg/g. Analyzed by IGCP-MS at ACME, Vancouver, Canada.

El.	Contents				Contrast of anomaly		Local contrast of anomaly		Moss/S.S. ratio
	Moss		S.S.						
	Anom.	Barr.	Anom.	Barr.	Moss	S.S	Moss	S.S.	
Elements typical for plant tissue									
P	4.03	bkg	0.11	0.07	1.3	2.2	1.4	n.d.	37
K	3.95	>>	0.08	0.08	1.4	1.0	1.4	n.d.	49
Na	0.176	>>	0.013	0.009	0.67	1.4	0.67	1.4	13
Elements of higher contrast of local anomaly for moss than for sediment									
Ag	4.70	bkg	6.1	0.8	34	>12	34*	7.6	0.7
Mn	36681	>>	264	338	4.4	0.37	4.4	0.78	139
Cr	121	>>	79	111	3.7	3.8	3.7	0.71	1.5
Co	106	>>	13	7	3.6	1.4	3.6	1.8	9.1
Ni	130	>>	35	31	2.9	1.5	2.9	1.1	3.7
Sn	6.3	>>	n.d.	n.d.	2.7	n.d.	2.7	n.d.	n.d.
U	3.6	>>	1	1	2.6	n.d.	2.6	n.d.	3.6
Elements of higher contrast of local anomaly for sediment than for moss									
Ba	226	>>	109	82	0.75	1.9	1.5	6.2	1.6
Cu	257	>>	100	19	3.1	4.0	3.1	5.3	2.7
Pb	161	bkg	113	23	2.6	4.9	2.7	4.9	1.4
Hg	n.d.	n.d.	1.272	0.123	n.d.	17	n.d.	4.5	n.d.
Mo	4.02	>>	2.0	0.6	2.3	3.3	2.3	3.3	2.0
Sb	2.09	>>	1.6	>0.5	1.9	>1.5	1.9	>3.2	1.3
Elements of equal contrasts of local anomaly for moss and sediment									
Zn	1503	bkg	506	128	3.8	7.0	4.0	4.5	3.0
S	1.15	>>	0.38	0.25	1.2	4.2	1.2	1.5	3.8
Cd	3.06	>>	1.0	0.6	1.4	3	1.0	1.3	3.2
Elements of feeble or no contrast in anomalous site									
S	1.15	>>	0.38	0.25	1.2	4.2	1.2	1.5	3.8
V	58	bkg	23	24	1.5	1.8	1.5	1	8.5
As	14.4	>>	7	5	1.3	1.4	1.3	1.2	2.0
Cd	3.06	>>	1.0	0.6	1.4	3	1.0	1.3	3.2
Elements preferentially accumulated in moss ash versus stream sediment									
Mn	36681	>>	264	338	4.4	0.37	4.4	0.78	139
Ti	0.054	bkg	0.004	0.004	0.83	1.3	0.83	n.d.	13
Co	106	bkg	13	7	3.6	1.4	3.6	1.8	9.1
V	58	bkg	23	24	1.5	1.8	1.5	1	8.5
S	1.15	>>	0.38	0.25	1.2	4.2	1.2	1.5	3.8
Ni	130	>>	35	31	2.9	1.5	2.9	1.1	3.7
U	3.6	>>	1	1	2.6	n.d.	2.6	n.d.	3.6
Cd	3.06	>>	1.0	0.6	1.4	3	1.0	1.3	3.2
Zn	1503	bkg	506	128	3.8	7.0	4.0	4.5	3.0
Cu	257	>>	100	19	3.1	4.0	3.1	5.3	2.7
As	14.4	>>	7	5	1.3	1.4	1.3	1.2	2.0
Mo	4.02	>>	2.0	0.6	2.3	3.3	2.3	3.3	2.0
Elements not or not properly analyzed in moss and/or sediment									
Sn	6.3	>>	n.d.	n.d.	2.7	n.d.	2.7	n.d.	n.d.
Hg	n.d.	n.d.	1.272	0.123	n.d.	17	n.d.	4.5	n.d.
Ti	0.054	bkg	0.004	0.004	0.83	1.3	0.83	n.d.	13
U	3.6	>>	1	1	2.6	n.d.	2.6	n.d.	3.6
Barren sample collected upstream, anomalous downstream of town. Background values from data for 2001 in Tab. 7. Ash: barren sample 17.4 %, anomalous sample 14.7 %.									

High moss ash to sediment anomalous elemental ratios are indicated for Mn (139) and Ti (13), moderate for Co (9.1) and V (8.5), and low (in the range from 3.9 to 2.0) for S, Ni, U, Cd, Zn, Cu, As and Mo. The anomalous ratio values for the elements from Ni to Mo, however, are lower than the background values for this moss ash to sediment ratio (compare data from Table 8).

In short, typical for Ljubljana are higher anomalous values in moss than in sediment for Ag, Mn, Cr, Co, Ni, high for Sn and U without data for sediment, and higher for sediment than moss for Ba, Cu, Pb, Mo, Sb, and high for Hg without data in moss, and high values in both media for Zn. Very high moss to sediment anomalous ratio is for Mn, high for Ti, moderate for Co and V, and low for S, Ni, U, Cd, Zn, Cu, As and Mo.

By a qualitative (and tentative) evaluation of the magnitudes of anomalies of the three investigated towns, about 65 percent of anomalies appear in moss and 35 in sediment for the studied 18 elements. As for towns, about 70 percent of pollution is indicated for Celje (60 percent of the total in moss and 80 percent in sediment), 20 percent for Jesenice (30 percent of total in moss and 10 percent in sediment) and 10 percent only for Ljubljana (10 percent of total in moss and 10 percent in sediment). These rough, possibly little correct estimates may give an idea of the state of the rivers flowing through these three towns, and the environmental impact they have on the drainage.

GENERAL DISCUSSION

The reported work is a contribution to the assessment of the part aquatic mosses may play in the study of dispersion of chemical elements in the supergene zone. They are an indicator of the elements mobilized by natural and anthropogenic processes into the environment in the soluble form in natural waters. These elements may be more conveniently detected in mosses than in the waters in which their contents are highly variable and at low concentrations not easily determined by analytical methods. In this sense they may assist in the study of establishing the geochemical cycles of matter, and matter in general, in the supergene zone, and especially the anthropogenic part of it. The understanding of these migration processes is inevitable for planning the sustainable management of the environment.

The civilization is mobilizing by its large-scale activities a broad array of substances of wide diversity, varying stability and little known harm to the biosphere, in forms hitherto unknown to the nature, and widely dispersing them in the environment. In the task of recording and understanding these processes, also aquatic mosses might be useful owing to their capacity to characterize by their chemical composition the mean composition of the dissolved matter in natural waters, that is difficult to correctly assess by water analyses owing to large fluctuations and often very low concentrations that are not easily determined by chemical analysis.

On the basis of the reported research we might conceive their use as indicator materials for signaling the presence of any chemical element that is present in anomalous concentrations in natural waters with much less sampling and analytical effort than by analyzing the waters themselves. The pilot multielemental analysis of aquatic mosses can provide a fingerprint, the first insight into the complex composition of the water, and of the pollution in general. In continuation, the information on the array of anomalous elements can be investigated by additional means – by analyses of waters and other materials in order to determine the speciation, to quantify the fluxes and paths, and detect the sources.

CONCLUSIONS AND RECOMMENDATIONS

In the studies reported in the paper the value of aquatic moss sampling for detecting average concentrations of elements that occur dissolved in the waters of the natural drainage systems is confirmed. The displayed results support the use of aquatic moss as a sampling material in mineral exploration, environmental control and regional geochemistry.

The basis of studies is the property of water mosses to absorb chemical elements dissolved in water in which they grow. It is assumed that the elemental contents in their tissues is proportional to the average concentration in water during their growth. Contents in mosses ashed at 500 °C were compared to contents in fines of drainage sediment, which is the usual sampling medium in geochemistry. The water moss indicates

the average concentration in water, and the sediment the contents fixed in or on the solid particles. The main criterion was the concept of contrast of anomaly, which is defined as the ratio of contents in the studied sample to the contents of background.

Results of extensive regional studies (PIRC ET AL., 1991) indicate that stable broad scale geochemical maps of carbonate terrains could be produced by the performed methodology with aquatic moss as sampling material. The performance is comparable to maps produced with drainage sediment and soil. Background contents of 7 major and 14 trace elements in aquatic moss in comparison with drainage sediment and soil for the entire Dinaric Triassic karstic region of ancient Yugoslavia, were established (Table 1). Estimates for individual republics and sampling areas within them appear in the work above.

Background estimates for aquatic moss and drainage sediment in the Mežica Triassic carbonate terrains and in Žirovski vrh Paleozoic clastic terrains for 8 major and 25 trace elements (Table 3) result from studies performed in Slovenia in the 1980's. Background estimates for aquatic moss and sediment in Slovenian rivers were calculated on 1986 data for 8 major and 23 trace elements, and on 2001 data for 8 major and 34 trace elements (Table 7). The estimated background values are of varying quality.

The results of studies of using aquatic moss for geochemical prospecting, performed in the 1980s, were established primarily on the ground of contrast of anomaly that indicates the sensibility of detecting anomalous con-

tents. For uranium in aquatic moss at Žirovski vrh (Table 2), the mean established contrast of anomaly is 23, and its maximum value 1400 for moss versus 9.6 (maximum 14) for drainage sediment. The average ratio of uranium contents in moss ash versus sediment is 24. The aquatic moss appears to be much more sensitive prospecting medium than the drainage sediment.

The performance of aquatic moss for prospecting other mineralizations was studied by KOČEVAR (1987). In the Mežica carbonate terrains, for cadmium the established mean contrast of anomaly is 36 (maximum value 43) in moss, and 23 (maximum 29) in sediment, and the ratio moss ash to sediment is 22. The molybdenum average contrast of anomaly in moss ash is 45 with 85 as its maximum value, and in sediment 22 with a maximum of 30; the average Mo moss to sediment ratio in 5.7. The moss is indicated to be a more appropriate sampling medium than the sediment. For lead the established contrast of anomaly amounts to 47 (with a maximum of 442) in moss ash and to 55 (with 90 as maximum) in sediment. The average Pb moss ash to sediment ratio is 8.6. For zinc the average contrast of anomaly is 32 (maximum of 54) in moss ash and 35 (with maximum of 45) in sediment. The average moss ash to sediment ratio for Zn is 7. Similar indications for lead and zinc result also from samples at Knape, Maljek and Pleše deposits (Table 6).

At the Idrija mercury deposit the estimated mean contrast of anomaly is 2900, with a maximum of over 34,800 in dry weight moss and a mean of 765 with the maximum value of 1110 in stream sediment. The average ra-

tio of Hg in dry weight moss to sediment is 3.6, with a maximum of above 10 (Table 5). At a single sample site for antimony at Trojane, the contrast of anomaly is 719 for moss versus 164 for sediment, and the ratio moss ash to sediment is above 9. For copper at Škofje, the established average contrast of anomaly is 14 (and maximum 19) for moss and 10 (maximum 11) for drainage sediment, and the ratio moss ash versus total sediment (Table 6).

As based upon the values of contrast of anomaly, the aquatic moss appears to be a valuable sampling material for geochemical prospecting of mercury, uranium, antimony, cadmium, molybdenum and copper, superior to total digested drainage sediment, and also for zinc and lead for which its performance is about equal to the sediment..

The very high observed maximum contents of Cd, Cu, Hg, Mo, Pb, Sb, Zn and U in the aquatic mosses indicate for these elements very high absorption barriers in Kovalevskii's terminology. In aquatic moss evidently also U behaves as a high-barrier element

By considering the percent ash, the dry matter contents in the maximum aquatic moss samples are 0.004 % Cd, 0.027 % Cu, 0.105 % Hg, 0.0026 % Mo, 0.065 % Pb, 0.0054 % Sb, 0.108 % Zn and 0.08 % U.

An environmental study of uranium in aquatic moss sampled in Brebovščica and Poljanščica in rivers in 1986 indicates the U pollution of the Žirovski vrh uranium mine did not affect noticeably the Poljanščica river (KOČEVAR, 1987).

The pilot study of the state of rivers flowing across the towns of Jesenice, Celje and Ljubljana in 2001 resulted in detecting of very distinct geochemical patterns in aquatic moss and drainage sediment, according to the prevailing economic activities in them. In the three studied cases, very high concentrations of bioessential elements P, K and Na in ash moss versus sediment were established, which is a characteristic of plant material.

For the Jesenice pollution of the Sava river very highly anomalous Cu and highly anomalous Pb and Sn in river moss, moderately anomalous Ag in moss and Ba in sediment, and low anomalous values of Hg, Zn, As, Co, Mn, Sb prevailing in sediment, Ag and Ni in moss, and S, Mo, Fe and Cr in both materials were indicated. Very high moss to sediment elemental ratio is for Cu, high for Ti and Pb, and moderate for Zn, and low for Mn, Ni, V, Cd, Cr, U, Mo, S, Co, Ba, As. The indicated pattern is characteristic for iron metallurgy.

For the Celje pollution of the Voglajna river, very high Zn, Cd, Hg, As and Ba, moderate Sb, Co, Pb, Cu and Mn, and low Ni, Ti, Mo, Cr and V were indicated. High Ag pollution comes from upstream Celje. Very high contrasts of anomaly in both river moss and sediment appear for Zn and Cd, for Ba and Hg in sediment, high contrasts for Sb and As in moss. Moderately anomalous are Cu and Mn in sediment and Co, Pb in both media. Of low contrasts are Sn, U, Ti, Ni, Mo, Cr and V. The indicated pattern is typical for Zn smelting, iron metallurgy and chemical industry.

The Ljubljana pollution of the Ljubljanica river is characterized by indicated higher anomalous values in moss than in sediment for Ag, Mn, Cr, Co, Ni, high for Sn and U without data for sediment, and higher for sediment than moss for Ba, Cu, Pb, Mo, Sb, and high for Hg without data in moss, and high values in both media for Zn. Very high moss to sediment anomalous ratio is for Mn, high for Ti, moderate for Co and V, and low for S, Ni, U, Cd, Zn, Cu, As and Mo.

Roughly estimated by magnitudes of the anomalies, about 70 percent of total pollution is indicated for Celje (60 percent of the total in moss and 80 percent in sediment), 20 percent for Jesenice (30 percent of total in moss and 10 percent in sediment) and 10 percent only for Ljubljana (10 percent of total in moss and 10 percent in sediment).

The future research should concentrate upon:

- (1) providing more data on anomalous elemental contents in aquatic mosses in various natural and anthropogenic circumstances,
- (2) studying next to aquatic bryophytes and drainage sediment additional sampling materials, at least waters, suspended matter in it, various digestions of drainage sediment, heavy mineral concentrates etc.,
- (3) attempts to calibrate the signals of anomalous elements in moss with their concentrations in water, which could permit to quantify the elemental fluxes in the drainage and describing the corresponding parts of geochemical cycles. The understanding of these migration processes is necessary for planning the sustainable management of the environment.

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Vodni mahovi kot vzorčno sredstvo v geokemiji

Povzetek: V članku so kratko predstavljene dvajsetletne raziskave vodnih mahov v površinskih vodnih tokovih kot vzorčnega sredstva za ugotavljanje geokemične sestave pokrajine. Velik del rezultatov je bil delno objavljen, tisti iz leta 2001 pa še sploh ne. V raziskavah je bila ocenjevana lastnost mahov, da absorbirajo kemične prvine, raztopljene v vodi, v kateri rastejo. Pri tem naj bi bila vsebnost v njihovem tkivu sorazmerna s povprečno koncentracijo prvine v vodi za časa njihove rasti. Vsebnosti v mahu (upepeljenem pri 500 °C) smo primerjali z vodnim sedimentom, ki je običajno vzorčno sredstvo v geokemičnih raziskavah. Privzema se, da vodni mah indicira predvsem povprečni delež prvine v vodni raztopini, sediment pa predvsem delež, ki je vezan v trdnih delcih ali na njih. Poglavitno ocenjevalno orodje je bil koncept kontrasta anomalije, ki je opredeljen kot razmerje med vsebnostjo kemične prvine v anomalnem vzorcu in vsebnostjo ozadja. Rezultati raziskav, opisanih v članku, vsestransko potrjujejo uporabnost vodnega mahu za odkrivanje vsebnosti kemičnih prvin, raztopljenih v naravnih vodah. Mah se je izkazal za dobro vzorčno sredstvo za regionalno geokemično kartiranje, sledenje nahajališč mineralnih surovin in ugotavljanje stanja okolja.

Regionalne geokemične študije, opravljene s statističnimi vzročnimi načrti na temelju analize variance, so podrobno opisane v delu PIRC ET AL. (1991). Pokazale so, da je mogoče z vzorčenjem vodnega mahu na karbonatnih ozemljih izdelovati stabilne regionalne geokemične karte, primerljive s kartami na temelju vodnega mulja in tal. Izračunane so bile vrednosti ozadja 7 glavnih in 14 slednih prvin v vodnem mahu v primerjavi z muljem in tlemi za vse triasno kraško ozemlje dinarskega pasu nekdanje Jugoslavije (tabela 1). Ocene manjših območij so v zgoraj omenjenem delu.

Ocene ozadja 8 glavnih in 25 slednih prvin v mahu in potočnem mulju triasnega karbonatnega območja Mežice in paleozojskega klastičnega območja Žirovskega vrha (tab. 3) sledijo iz razskav v Sloveniji v osemdesetih letih. Izračunane so bile tudi ocene ozadja vodnega mahu in mulja v slovenskih rekah, iz leta 1968 za 8 glavnih in 23 slednih prvin in iz leta 2001 za 8 glavnih in 34 slednih prvin (tabela 7).

V raziskavah uporabe vzorčnih sredstev za geokemično prospekcijsko na območju Žirovskega vrha v zgodnjih osemdesetih letih (tabela 2) je bilo ugotovljeno povprečje (povsod v članku je mera povprečja mediana) kontrasta anomalije U 23 in največja vrednost 1400 v mahu v primerjavi s povprečjem 9,6 in maksimumom 14 v potočnem mulju. Povprečno razmerje vsebnosti urana v pepelu mahu glede na mulj je 24. Vodni mah se je izkazal za občutljivejše prospekcijsko vzorčno sredstvo od potočnega mulja. Vlogo vodnega mahu v prospekcijski drugih nahajališč je obdelovala KOČEVAR (1987). S karbonatnega območja Mežice so ocene Cd, Mo, Pb in Zn (tabela 4). Ugotovljeno povprečje kontrasta anomalije Cd v pepelu mahu je 36 in maksimum 43 in v ustreznem mulju 23 ob maksimumu 29, razmerje pepela mahu do mulja je pa 22. Za Mo je povprečje v pepelu mahu 45 ob maksimumu 85 in v mulju 22 ob maksimumu 30, in povprečno

razmerje vsebnosti 5,7. Za Pb je v mahu povprečje 47 z maksimumom 442, v mulju 55 z maksimumom 90. Povprečno razmerje vsebnosti Pb v pepelu mahu s sedimentom je 8,6. Povprečje kontrasta anomalije cinka v pepelu mahu je 32 z ugotovljenim maksimumom 54 in v mulju povprečje 35 ob najvišji vrednosti 45. Razmerje pepel mahu do sedimenta je 7. V raziskovanih okoliščinah je vodni mah je občutljivejši indikator Cd in Mo od mulja in približno enako občutljiv indikator Pb in Zn kakor mulj.

Na področju Idrije je izkazal vodni mah znatno višje kontraste anomalije Hg (maksimum skoraj 35.000!) od mulja (tabela 5). Na edini vzorčni točki z območja antimonovega rudišča Trojane (tab 6) je bil ugotovljeni kontrast anomalije Sb v pepelu mahu 719 v primerjavi z vrednostjo 164 v mulju, ob razmerju pepel mahu do mulja nad 9. Na območju bakrovega nahajališča Škofje pri Cerknem (tabela 6) je bil ugotovljen povprečni kontrast anomalije Cu 14 ob maksimumu 19 v pepelu mahu in povprečje 10 z maksimumom 11 v mulju.

Glede na vrednosti kontrasta anomalije se je torej vodni mah izkazal za uporabno vzorčno sredstvo za geokemično prospekcijsko proučevanih nahajališč živega srebra, urana, antimona, kadmija, molibdena in bakra, občutljivejše od totalno analiziranega vodnega sedimenta, pa tudi cinka in svinca, pri katerih so bile ugotovljeni kontrasti približno enaki v obeh sredstvih.

Ugotovljene zelo visoke maksimalne vsebnosti Cd, Cu, Hg, Mo, Pb, Sb, Zn in U v vodnih mahovih pričajo o tem, da je absorpcijska bariera v smislu Kovalskega teh kemičnih prvin v vodnih mahovih visoka. Tudi uran se očitno vede v vodnem mahu kot visoko barierna prvina. Ob upoštevanju odstotka pepela so vsebnosti v suhi snovi preiskovanih maksimalno anomalnih vzorcev vodnega mahu 0,004 % Cd, 0,027 % Cu, 0,105 % Hg, 0,0026 % Mo, 0,065 % Pb, 0,0054 % Sb, 0,108 % Zn in 0,08 % U.

Okoljska študija urana v vodnem mahu na območju rudnika Žirovski vrh leta 1986 kaže, da močno onesnaženje U v Brebovščici dolvodno od rudnika bistveno ni prizadelo Poljanske Sore, v katero se izliva (KOČEVAR, 1987).

Orientacijska raziskava stanja rek skozi mesta Jesenice, Celje in Ljubljana leta 2001 je nakazala zelo različne geokemične vzorce onesnaženja v vodnem mahu in rečnem sedimentu, pač v odvisnosti od poglobitnih industrijskih dejavnosti v njih. Skupno za vse reke so zelo visoko anomalne vsebnosti bioesencialnih prvin P, K in Na v pepelu mahu z ozirom na zelo nizke v sedimentu. To je značilnost rastlinske snovi.

V Savi dolvodno od Jesenic (tabela 8) so bili ugotovljeni zelo visoko anomalni Cu, visoko anomalna Pb in Sn v vodnem mahu, zmerno anomalna Ag v mahu in Ba v sedimentu, in nizko anomalni Hg, Zn, As, Co, Mn, Sb pretežno v sedimentu, Ag in Ni v mahu in S, Mo, Fe in Cr v obeh sredstvih. Indicirani vzorec onesnaženja je očitno značilen za železovo metalurgijo.

V Voglajni dolvodno od Celja (tabela 9) so bili določeni zelo visoko anomalni Zn, Cd, Hg, As and Ba, zmerni Sb, Co, Pb, Cu in Mn, in nizki Ni, Ti, Mo, Cr in V; visoko onesnaženje z Ag prihaja gorvodno od Celja. Zelo visoki kontrasti anomalije Zn in Cd so v vodnem mahu in sedimentu in Ba ter Hg v sedimentu, visoki kontrasti Sb in As so v mahu. Zmerno anomalni so Cu in Mn v sedimentu in Co ter Pb v obeh sredstvih. Nizke kontraste kažejo Sn, U, Ti, Ni, Mo, Cr in V. Vzorec onesnaženja je tipičen za vpliv nekdanje cinkarne, Štorskke železarne in kemične industrije.

V Ljubljani dolvodno od prestolnice (tabela 10) so nakazane višje anomalne vsebnosti Ag, Mn, Cr, Co, Ni v vodnem mahu kakor v sedimentu, in visoke Sn in U (U brez določitev v sedimentu) v mahu, in višje vsebnosti Ba, Cu, Pb, Mo, Sb v sedimentu kakor v mahu, ter visoke Hg (brez podatkov za mah) v sedimentu. Visok kontrast anomalije Zn je v obeh medijih.

Z grobo primerjavo velikosti kontrastov zelo približno ocenjujemo, da je nekako 70 odstotkov indiciranega onesnaženja s preiskovanimi kemičnimi prvinami v Celju (60 odstotkov celotnega v mahu in 8 v sedimentu), 20 odstotkov na Jesenicah (30 odstotkov v mahu in 10 v sedimentu) in samo 10 odstotkov v Ljubljani (10 odstotkov celote v mahu in 10 v sedimentu).

Prihodnje raziskave naj bi zagotovile več podatkov iz različnih okolij, razen vodnega mahun in sedimenta (z delnimi razklopi) naj bi pritegnili še druga sredstva kot vodo, suspendirano snov v njej in izpirke. Cilj je boljše razumevanje elementnih ciklov in tokov snovi, geogenih in antropogenih. Rezultati bodo prispevali k boljše utemeljenemu načrtovanju sonaravnega razvoja okolja.