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## MULTIELEMENT ATMOSPHERIC DEPOSITION STUDY IN CROATIA USING MOSS BIOMONITORING, NAA, AAS AND GIS TECHNOLOGIES

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## INTRODUCTION

Air pollution is still a problem in most countries, not only because of environmental damage but also because it affects human health and represents a key economic problem. In the European Union the air quality strategy is based on physico-chemical measurements of ambient pollution concentrations and complementary modelling techniques as regulated by the Air Quality Framework Directive [1, 2] in order to establish air quality standards (limit and target values, respectively) for the major groups of air pollutants, and measurement programmes to monitor pollutant concentrations in the air. A daughter directive relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air [3] recommends that in addition to mandatory measurements of atmospheric pollutant concentrations, «the use of bioindicators may be considered where regional patterns of the impact on ecosystems are to be assessed». In fact, the regular use of epiphytic/epigeic plants (mainly mosses and lichens), so-called biomonitors, is already a well-established method for monitoring of atmospheric deposition of metals in Europe [4–8] not only scientifically, but even politically and economically.

Terrestrial mosses have several advantages as biomonitors when compared to higher plants: (1) they lack a developed root system, (2) variability of morphology through the growing season is small, (3) they lack cuticula, (4) they have a high surface-to-volume ratio, and

(5) a high cation exchange capacity [9, 10]. The bryophytes are evergreen and perennial plants, so it is easy to collect them at different times of the year and over large territories [11, 12]. It is assumed that mosses to a great extent absorb nutrients directly from the atmosphere. Procedures of sampling and chemical analysis of bryophytes are rather simple compared to the collection and analysis of precipitation samples, and comparisons have shown that concentrations of metals in moss in most cases reflect adequately the atmospheric deposition during the growth period of the moss [13, 14].

Since the first joint European moss survey in 1995 [5], a gradually increasing number of countries have joined this program. In the subsequent survey in 2000 [8] 28 countries participated including Hungary, Slovenia, and Austria, all neighboring countries to Croatia. Prior to the third joint European moss survey in 2005/2006 it was therefore decided to include Croatia among the participating countries. The purpose of this report is a presentation and discussion of the results obtained for mosses collected in Croatia in 2006. To the knowledge of the authors this is the first application in Croatia of biomonitoring atmospheric deposition of metals, except for a local study of mercury and some other elements from the petroleum industry undertaken in 1996–2004 using lichens [15].

## SELECTION OF MOSS SPECIES

Previous large-scale projects have successfully used the mosses *Hylocomium splendens*, *Pleurozium schre-*

*beri*, *Hypnum cupressiforme* and *Scleropodium purum* as recommended species [5, 11, 12]. All these species



*Hypnum cupressiforme*  
(location 2)

*Scleropodium touretii*  
(location 31)

*Camptothecium lutescens*  
(location 57)

Fig. 1. Most common moss species collected in the 2006 moss survey in Croatia

have similar physiognomy, as they grow in dense mats able to produce a high rate of bioaccumulation. However, since the above species are not widespread in arid areas of southern countries of Europe, it was necessary to find corresponding alternative moss species for monitoring studies in Croatia (see Fig. 1). Also, naturally growing moss is rarely present in urban areas, and sometimes it is very difficult to find and sample sufficient quantity of moss material for analysis, and one of the criteria for a choice of suitable biomonitor is the species abundance. The following moss genera, *Hylocomium*

*splendens*, *Hypnum cupressiforme*, *Brachythecium rutabulum* and *Homalothecium* were found suitable for assessing atmospheric deposition of key heavy metals and other elements in Croatia.

This combination of species has also already been used for biomonitoring purposes in some other European countries [16, 17] where other recommended species were not available. Interspecies comparisons showed that *Brachythecium rutabulum* and *Homalothecium* could be used along with *Hylocomium splendens*, *Pleurozium schreberi*, and *Hypnum cupressiforme*.

## EXPERIMENTAL

**Sampling.** Sampling was carried out according to the guidelines of the UNECE ICP Vegetation [18] and the selection of sampling sites was based on a modified EMEP network [19]. The resulting 94 sampling sites are shown on the map in Fig. 2. Sampling was carried out during the period July – August 2006.

A total of 94 moss samples were evenly collected over the territory of Croatia. Samples were collected at least 300 m from main roads, at least 100 m from local roads and at least 200 m from villages, in forest glades or on open heath to reduce through-fall effects from the forest canopy. In order to make the moss samples representative for a reasonably large area, each sample was composed of five to ten subsamples collected within an area of 50 × 50 m. Collected material was stored in paper bags. A separate set of disposable polyethylene gloves was used for collection of each sample. All collected moss samples were preliminary cleaned from extraneous material and transferred to the analytical laboratories.

The Republic of Croatia is a Central European and a Mediterranean country located between the Danube river basin in the north and the Adriatic Sea to the south.

Its geophysical location in Europe determines the environmental characteristics of the country, with the long coastal region, littoral highlands and the central plains. The general state of environment in Croatia is relatively good compared to the situation in EU industrial countries. This is mainly due to the low detrimental impact of the heavy industries due to their collapse in the 1990s.

It is also important to mention here the country benefits from a number of natural advantages and strengths such as: unique and relatively well preserved natural environment, high level of biodiversity, high stores of fresh water, etc.

The natural environment is a crucial asset in economic and social capital of Croatia, and a driver of economic development, given its pivotal role in tourism in Croatia.

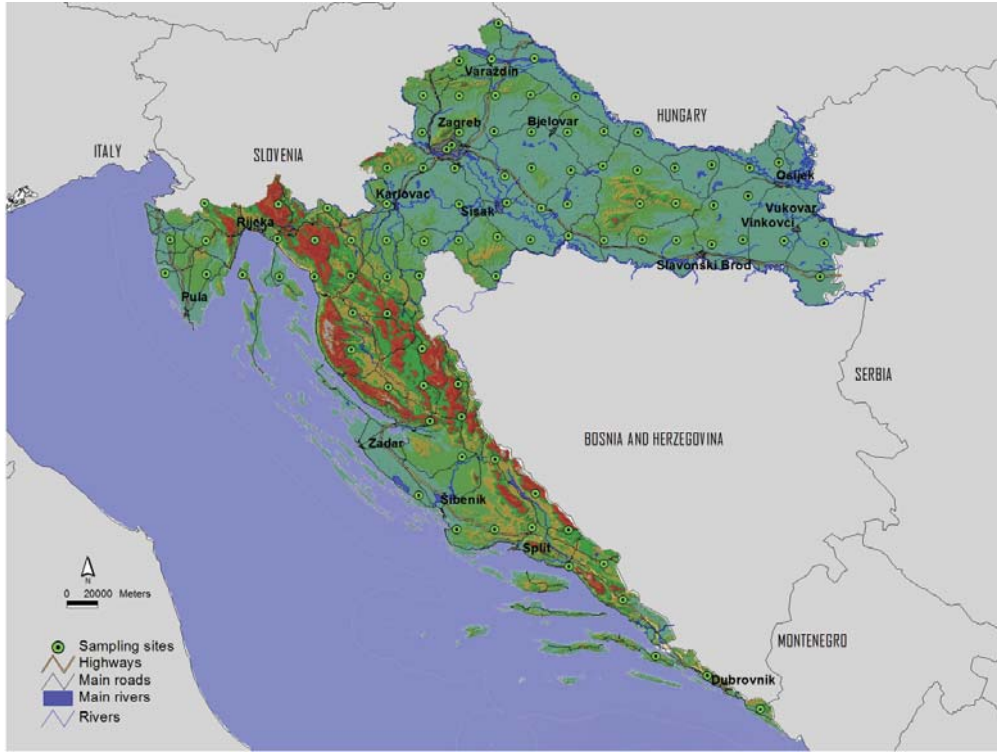


Fig. 2. Sampling sites

**Analysis. NAA.** The neutron activation analysis (NAA) was performed at the pulsed fast reactor IBR-2 at the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia. In the laboratory the samples were cleaned and air-dried to constant weight at 30–40 °C for 48 h. Green–brown moss shoots representing the last three years’ growth were subjected to analysis, as they correspond approximately to the deposition over the last three years.

The samples were not washed and not homogenized. Previous experience from the use of NAA in moss biomonitoring has shown that *Hylocomium splendens* samples of 0.3 g are sufficiently large to be used without homogenization [20].

The samples were pelletized before irradiation using simple press-forms. For short irradiation unwashed samples of about 0.3 g were heat-sealed in polyethylene bags.

For long irradiation samples of the same weight (about 0.3 g) were packed in aluminium cups. Characteristics of neutron flux density in the channels equipped with the pneumatic system are given in Table 1.

To determine short-lived isotopes samples were irradiated for 3 min. After irradiation two gamma-spectrometric measurements were performed; the first one for 5 min after 2–3 min of decay, and the second one for 20 min after 9–10 min of decay.

Long-lived isotopes were determined after irradiation for 100 h in the cadmium-screened channel 1. After irradiation samples were re-packed into clean containers and measured after 4–5 and 20–23 days for 45 min and for 3 h, respectively. Gamma spectra were registered as described elsewhere [22].

Table 2 lists selected peak energies for NAA and method of analysis. The gamma-spectra of the induced

Table 1. Flux parameters of irradiation positions [21]

Irradiation position	$\Phi_{th} \cdot 10^{12}, \text{cm}^{-2} \cdot \text{s}^{-1}$ $E = 0 - 0.55 \text{ eV}$	$\Phi_{epi} \cdot 10^{12}, \text{cm}^{-2} \cdot \text{s}^{-1}$ $E = 0.55 - 10^5 \text{ eV}$	$\Phi_{fast} \cdot 10^{12}, \text{cm}^{-2} \cdot \text{s}^{-1}$ $E = 10^5 - 25 \cdot 10^6 \text{ eV}$
Ch1 (Cd-screened)	0.023	3.3	4.2
Ch2	1.23	2.9	4.1

**Table 2. List of selected peak energies for NAA and method of analysis**

Element	Isotope	Half-life	Gamma peak (keV)	Method of analysis *
Na	<sup>24</sup> Na	14.7 h	2753.6	3
Al	<sup>28</sup> Al	2.2 min	1778.9	1
Cl	<sup>38</sup> Cl	37.2 min	2168.8	2
K	<sup>42</sup> K	12.4 h	1524.7	3
Ca	<sup>49</sup> Ca	8.7 min	3084.4	2
Sc	<sup>46</sup> Sc	83.8 d	889.2	4
Ti	<sup>51</sup> Ti	5.8 min	320.1	1
V	<sup>52</sup> V	3.8 min	1434.1	1
Cr	<sup>51</sup> Cr	27.7 d	320.1	4
Mn	<sup>56</sup> Mn	2.6 h	1810.7	2
Fe	<sup>59</sup> Fe	44.5 d	1099.2	4
Co	<sup>60</sup> Co	5.3 y	1173.1	4
Ni	<sup>58</sup> Co	70.9 d	810.8	4
Zn	<sup>65</sup> Zn	244.0 d	1116.0	4
As	<sup>76</sup> As	26.3 h	559.1	3
Se	<sup>75</sup> Se	119.8 d	264.7	4
Br	<sup>82</sup> Br	35.3 h	776.5	3
Rb	<sup>86</sup> Rb	18.7 d	1076.6	4
Sr	<sup>85</sup> Sr	64.8 d	514.0	4
Mo	<sup>99</sup> Mo	66.0 h	140.5	3
Sb	<sup>124</sup> Sb	60.2 d	1691.0	4
I	<sup>128</sup> I	25.0 min	442.9	2
Cs	<sup>134</sup> Cs	2.1 y	795.8	4
Ba	<sup>131</sup> Ba	11.8 d	496.8	4
La	<sup>140</sup> La	40.2 h	1596.5	3
Ce	<sup>141</sup> Ce	32.5 d	145.4	4
Nd	<sup>147</sup> Nd	10.98 d	531.04	4
Sm	<sup>152</sup> Eu	13.3 y	1407.5	4
Tb	<sup>160</sup> Tb	72.3 d	879.4	4
Dy	<sup>165</sup> Dy	2.33 h	94.7	2
Tm	<sup>170</sup> Tm	128.6 d	84.3	4
Yb	<sup>169</sup> Yb	32.0 d	198.0	4
Hf	<sup>181</sup> Hf	42.4 d	482.0	4
Ta	<sup>182</sup> Ta	114.4 d	1221.4	4
W	<sup>187</sup> W	23.9 h	685.8	3
Au	<sup>198</sup> Au	2.7 d	411.8	3
Th	<sup>233</sup> Pa	27.0 d	312.0	4
U	<sup>239</sup> Np	2.4 d	228.2	3

\*Method 1: conventional NAA, measured after 2–3 min of decay

Method 2: conventional NAA, measured after 9–10 min of decay

Method 3: epithermal NAA, measured after 4–5 days of decay

Method 4: epithermal NAA, measured after 20–23 days of decay

**Table 3. Optimal instrumental parameters for Pb determination by ZETAAS**

Wavelength, nm	283.3
Slit width, nm	0.5
Lamp current, mA	10
Calibration mode	Absorbance, peak area
Correction	Zeeman
Gas	Argon
Drying	
Temperature, °C	120
Ramp time, s	45
Hold time, s	10
Pyrolysis	
Temperature, °C	400
Ramp time, s	5
Hold time, s	15
Atomization	
Temperature, °C	2100
Ramp time, s	0
Hold time, s	2
Internal gas flow, ml · min <sup>-1</sup>	0
Cleaning	
Temperature, °C	2500
Ramp time, s	1
Hold time, s	2

activity were analyzed using software developed at the Frank Laboratory of Neutron Physics, JINR [23].

*AAS.* The environmentally important element Pb cannot be determined by INAA, and Hg is difficult at low concentration levels. These elements were therefore determined by atomic absorption spectrometry (AAS). Moss samples (0.5 g) were placed in a Teflon digestion vessels, 5 ml concentrated nitric acid and 2 ml H<sub>2</sub>O<sub>2</sub>

**Table 4. Optimal instrumental parameters for mercury determination by CV-AAS**

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Integration
Wavelength, nm	253.7
Slit width, nm	0.5
Integration time, s	3
Delay time, s	40
Replicates	3
Sample flow rate, ml · min <sup>-1</sup>	7
Reaction media	HCl-NaBH <sub>4</sub>
HCl flow rate, ml · min <sup>-1</sup>	1
NaBH <sub>4</sub> flow rate, ml · min <sup>-1</sup>	1

(30%, m/V) added, the vessels are capped closed, tightened and placed in the rotor of the microwave digestion system Milestone, Ethos Touch Control.

The digestion was carried out with the following digestion program: (1) temperature 180 °C, 5 min ramp time, 500 W and 20 bar; (2) temperature 180 °C, 5 min hold time, 500 W and 20 bar. Finally, the vessels were cooled, carefully opened, and digests quantitatively transferred to 10 ml calibrated flasks.

Pb was determined by Zeeman electrothermal atomic absorption spectrometry (ZETAAS, Varian SpectrAA 640 Z), copper with flame atomic absorption spectrometry (FAAS, Thermo Solaar S4) and Hg by cold vapour atomic absorption spectrometry (CV-AAS) using a continuous flow vapour generation accessory (VGA-76, Varian) connected to an atomic absorption spectrometer (SpectrAA 55B, Varian).

Optimal instrumental conditions for Pb and Hg determination are given in Tables 3 and 4.

## QUALITY CONTROL

The QC of NAA results was ensured by simultaneous analysis of the examined samples and reference materials (RM) Lichen-336 IAEA (International Atomic Energy Agency) and NORD DK-1 (moss reference sample prepared for intercomparison in Scandinavia [24]). The NAA data and certified values of reference materials are given in Table 5. The QC of AAS determinations was performed by standard addition method and it was found that the recovery for the investigated elements

ranges between 98.5 to 101.2%. Besides the standard addition method, blank tests parallel to the decomposition of samples and preparation of sample solutions for analysis were also performed. The loss of Hg was checked by standard additions. The same sample was decomposed with and without addition of Hg. The added content of Hg was found in the solution obtained after microwave digestion.

**Table 5. NAA data and certified values of reference materials, mg/kg**

Element	DK-1 (determined)	DK-1 (certified)	Lichen-336 (determined)	Lichen-336 (certified)
Na	303 ± 25	315 ± 31	304 ± 26	320 ± 40
Mg	850 ± 150	910 ± 91	–	–
Al	830 ± 84	810 ± 81	720 ± 65	680 ± 109
Cl	328 ± 35	328 ± 33	1927 ± 288	1900 ± 304
K	3350 ± 165	3300 ± 297	1910 ± 90	1840 ± 202
Ca	1604 ± 180	1630 ± 40	–	–
Sc	0.16 ± 0.02	0.16 ± 0.02	0.176 ± 0.014	0.17 ± 0.20
V	4.12 ± 0.31	3.8 ± 0.3	1.38 ± 0.19	1.47 ± 0.22
Cr	1.94 ± 0.15	1.7 ± 0.4	1.10 ± 0.17	1.06 ± 0.17
Mn	143 ± 10	120 ± 10	69 ± 5.1	63 ± 7
Fe	575 ± 53	550 ± 50	430 ± 8.5	430 ± 51
Co	0.26 ± 0.01	0.23 ± 0.01	0.303 ± 0.070	0.29 ± 0.05
Ni	1.58 ± 0.33	1.8 ± 0.2	–	–
Cu	87 ± 2.5	85 ± 5	3.7 ± 0.5	3.6 ± 0.5
Zn	30.8 ± 4.0	29 ± 2	28.2 ± 2.3	30.4 ± 3.3
As	0.64 ± 0.02	0.64 ± 0.02	0.54 ± 0.71	0.63 ± 0.08
Se	0.43 ± 0.04	0.43 ± 0.04	0.22 ± 0.033	0.22 ± 0.04
Br	13.5 ± 0.94	12.8 ± 1.0	14.2 ± 2.3	12.9 ± 1.6
Rb	12.9 ± 0.86	12.6 ± 0.9	1.7 ± 0.17	1.76 ± 0.22
Sr	15.1 ± 3.0	10 ± 0.1	11.4 ± 0.55	9.3 ± 1.1
Zr	11.0 ± 1.2	11 ± 1.2	–	–
Mo	0.21 ± 0.02	0.2 ± 0.02	–	–
Ag	0.05 ± 0.004	0.05 ± 0.004	–	–
Cd	0.3 ± 0.11	0.3 ± 0.02	0.13 ± 0.015	0.117 ± 0.0006
Sb	0.347 ± 0.02	0.347 ± 0.02	0.078 ± 0.01	0.073 ± 0.0067
I	3.8 ± 0.07	3.8 ± 0.3	–	–
Cs	0.285 ± 0.02	0.30 ± 0.02	0.12 ± 0.024	0.110 ± 0.013
Ba	12.5 ± 0.12	12 ± 2	6.6 ± 0.7	6.4 ± 1.1
La	1.22 ± 0.34	1.22 ± 0.1	0.70 ± 0.06	0.66 ± 0.10
Ce	2.92 ± 0.53	2.92 ± 0.22	1.3 ± 0.25	1.28 ± 0.17
Sm	0.231 ± 0.05	0.231 ± 0.01	0.106 ± 0.06	0.106 ± 0.014
Eu	0.042 ± 0.01	0.042 ± 0.01	0.021 ± 0.003	0.023 ± 0.003
Tb	0.0218 ± 0.01	0.0216 ± 0.002	0.015 ± 0.002	0.014 ± 0.002
Hf	0.21 ± 0.06	0.21 ± 0.009	–	–
Ta	0.026 ± 0.005	0.026 ± 0.0036	–	–
W	0.73 ± 0.11	0.73 ± 0.21	–	–
Au	0.00074 ± 0.0014	0.00074 ± 0.00004	–	–
Th	0.16 ± 0.08	0.15 ± 0.0011	0.14 ± 0.01	0.14 ± 0.02
U	0.192 ± 0.02	0.192 ± 0.015	–	–

## MAPPING

The program GRINVEIW from the geographical information system software package GIS-INTEGRO with raster and vector graphics was used to generate raster-based pollution contour maps for the elements of

interest for the entire study area. The system is supplied with interfaces for all international standard GIS: ARC-info, MAP-info, etc.

## RESULTS AND DISCUSSION

The results of the descriptive statistical analysis of the elemental concentrations determined in the Croatian moss samples (min, max, mean and median) are given in Table 6. For comparison with a pristine area, corre-

sponding values from a selection of Norwegian moss data from 2005 [25], representing territories with minor influence from air pollution, are shown in the same table.

**Table 6. Comparison of the results obtained in the present study with other Balkan countries and Norway, mg/kg**

	Croatia (present work)		Macedonia [17]		Northern Serbia [35]		Romania (Transilvania) [36]		Norway [25]	
No of samples	94		73		92		70		100	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Na	169	67-2332	419	118-8673	694	178-2440	902	192-4330	—	—
Mg	2120	676-12740	2377	674-7421	2780	1100-8130	2850	480-6840	1730	940-2370
Al	1350	398-21460	3736	825-17600	6800	1280-22090	5545	830-23000	200	67-820
Cl	170	64-2433	149	43-693	256	105-1030	370	160-1300	—	—
K	8085	2565-23720	8615	2861-18190	5090	2710-11750	7770	4770-19980	—	—
Ca	7623	2832-26740	5593	1207-23640	7720	2890-18120	5770	1250-23500	2820	1680-5490
Sc	0.36	0.10-5	0.81	0.12-6.79	1.31	0.27-4.13	0.94	0.21-6.13	0.052	0.009-0.220
Ti	105	23-1711	163	12-1365	71	11-297	—	—	23.5	12.4-66.4
V	3.1	0.91-32	6.9	1.79-43	11	2.85-39	8.7	1.95-32	0.92	0.39-5.1
Cr	2.8	0.76-33	7.47	2.33-122	6.51	1.14-22	13.8	2.72-51.9	0.55	0.10-4.2
Mn	106	20-1421	186	37-1475	217	30-2340	265	27-1470	256	22-750
Fe	1000	320-12140	2458	424-17380	3110	720-9230	3290	815-21340	209	77-1370
Co	0.45	0.06-5	1.09	0.24-13.6	8.24	1.42-39	1.41	0.32-7.0	0.202	0.065-0.654
Ni	2.7	0.66-18	2.4	0.09-24	6.73	1.96-26	5.4	0.6-32	1.14	0.12-6.6
Cu*	7.5	3.7-22.7	22	3-83	16.9	6.31-3140	21.5	2.21-2420	3.6	2.1-9.2
Zn	29	12-283	39	14-203	44	14-415	135	39-2950	26.5	7.9-173
As	0.37	0.10-6	0.80	0.12-8.0	3.35	0.46-61	2.2	0.59-45.1	0.093	0.020-0.505
Se	0.18	0.014-0.60	0.18	0.013-0.61	0.39	0.046-10	0.36	0.08-5.01	0.33	0.05-1.30
Br	2.5	0.38-5	2.16	0.06-7.7	5.75	1.83-18	8.6	2.03-20.9	4.5	1.4-20.3
Rb	13	2.8-57	10.9	5-47	13	3-47	15.0	5.8-135	7.7	1.3-51.5
Sr	21	4-125	31	11.8-136	22	6.8-95	37.4	1.8-290	15.8	3.6-43.3
Mo	0.16	0.05-1	0.19	0.03-1.12	0.85	0.12-23	0.65	0.13-10	0.135	0.065-0.70
Cd*	0.27	0.07-1.9	0.16	0.016-2.95	<0.4	<0.4-6.5	—	—	0.058	0.025-0.171
Sb	0.16	0.04-1.5	0.2	0.039-1.4	0.52	0.13-7	0.88	0.16-51	0.033	0.004-0.240
I	1.3	0.29-5	1.18	0.36-2.8	2.09	0.87-4	2.17	0.76-5.55	2.5	0.6-41.7
Cs	0.22	0.07-2.5	0.39	0.097-1.7	0.76	0.11-18.2	0.51	0.12-3.4	0.072	0.016-0.88
Ba	32	7-192	54	14-256	39	13-130	101	20-658	17.1	5.6-50.5



	Croatia (present work)		Macedonia [17]		Northern Serbia [35]		Romania (Transilvania) [36]		Norway [25]	
No of samples	94		73		92		70		100	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
La	1.1	0.29-18	2.32	0.50-22	4.66	1.09-13	2.4	0.4-15.2	0.189	0.045-2.56
Ce	2.3	0.57-34	5.60	0.83-42	9.2	1.84-28	6.1	0.9-42.5	0.342	0.095-4.61
Sm	0.2	0.05-2.6	0.46	0.07-3.4	—	—	0.59	0.01-2.51	0.33	0.05-1.34
Tb	0.023	0.004-0.4	0.06	0.01-0.56	0.11	0.02-0.36	0.07	0.01-0.42	0.003	<0.002-0.030
Hf	0.13	0.035-3	0.26	0.05-3.8	0.78	0.15-2.6	0.56	0.12-4.66	—	—
Ta	0.029	0.0069-0.46	0.09	0.013-0.79	0.11	0.024-0.29	0.10	0.01-0.66	0.01	<0.01-0.07
W	2.5	0.05-2.5	1.21	0.25-3.9	1.34	0.19-3.3	1.02	0.12-8.74	0.127	0.009-1.23
Au	0.0045	0.00017-0.05	0.0061	0.001-0.034	0.0041	0.00029-0.087	0.025	0.003-0.114	—	—
Hg*	0.064	0.007-0.301	0.056	0.018-0.264	0.386	0.01-2.69	—	—	0.046	0.026-0.166
Pb*	2.46	0.06-82.4	6.0	1.5-37.2	—	—	14.3	6.45-31.5	1.17	0.64-6.12
Th	0.25	0.068-4.7	0.67	0.12-7.6	0.82	0.18-2.4	0.81	0.21-4.16	0.033	0.004-0.240
U	0.10	0.026-1.5	0.21	0.03-1.45	0.32	0.08-1.03	0.28	0.04-1.36	0.015	0.001-0.138

\* Determined by AAS

Multivariate statistical analysis (factor analysis) was used to identify and characterize different pollution sources and to point out the most polluted areas. Factor analysis is a multivariate technique for reducing matrices of data to their lowest dimensionality by the use of

orthogonal factor space and transformations that yield predictions and/or recognizable factor [26]. Values of the six factors are given in Table 7. Factor scores representing the contributions of individual sampling sites to the relevant factor are given in Fig. 3.

**Table 7. Factor analysis of NAA and AAS data on moss samples from Croatia**

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Na	<b>0.891</b>	0.178	-0.091	0.272	-0.027	0.076	0.085
Mg	<b>0.817</b>	0.253	-0.160	0.321	0.024	0.149	0.106
Al	<b>0.954</b>	0.033	0.067	0.037	-0.121	0.113	0.005
Cl	0.144	0.251	0.015	<b>0.853</b>	-0.010	-0.018	-0.048
K	0.201	0.052	-0.254	<b>0.847</b>	0.116	0.051	0.076
Ca	0.151	<b>0.724</b>	0.346	0.094	0.059	-0.072	0.124
Sc	<b>0.959</b>	0.053	0.056	0.044	-0.071	0.129	0.011
Ti	<b>0.969</b>	0.010	0.038	0.067	-0.037	0.146	0.039
V	<b>0.888</b>	0.098	0.155	-0.048	-0.148	0.262	0.015
Cr	<b>0.920</b>	0.174	0.144	0.125	0.028	0.100	-0.057
Mn	0.291	-0.131	-0.032	0.115	<b>0.835</b>	0.142	-0.001
Fe	<b>0.932</b>	0.170	0.118	0.121	0.041	0.120	-0.037
Co	<b>0.935</b>	0.142	0.103	0.093	0.132	0.130	-0.048

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Ni	<b>0.867</b>	0.092	0.176	-0.007	-0.113	0.260	-0.008
Cu	0.127	-0.096	0.068	0.319	0.095	<b>0.638</b>	0.211
Zn	0.320	<b>0.827</b>	-0.129	0.227	0.057	0.062	0.006
As	0.701	<b>0.596</b>	0.069	0.173	-0.117	0.131	-0.054
Se	-0.011	0.190	<b>0.566</b>	-0.292	0.289	0.310	0.026
Br	0.431	0.087	<b>0.734</b>	0.021	0.073	0.123	-0.013
Rb	0.338	-0.055	-0.218	0.295	-0.080	0.102	<b>-0.635</b>
Sr	0.242	<b>0.375</b>	0.031	0.169	0.071	-0.188	<b>0.400</b>
Mo	0.198	<b>0.473</b>	0.116	-0.010	-0.323	0.399	0.051
Cd	-0.005	<b>0.819</b>	0.039	-0.028	-0.008	0.140	0.035
Sb	<b>0.542</b>	0.255	0.147	-0.014	-0.147	<b>0.520</b>	0.079
I	0.130	0.168	<b>0.783</b>	-0.251	-0.171	-0.047	-0.116
Cs	<b>0.855</b>	0.112	0.113	0.122	-0.103	0.115	-0.111
Ba	<b>0.724</b>	0.355	-0.056	0.198	0.317	0.049	0.117
La	<b>0.962</b>	0.045	0.122	0.036	0.176	-0.042	0.008
Ce	<b>0.969</b>	0.051	0.096	0.045	0.142	-0.050	0.022
Sm	<b>0.959</b>	0.111	0.097	0.043	0.096	-0.035	0.051
Tb	<b>0.955</b>	0.094	0.092	0.075	0.203	-0.029	0.018
Yb	<b>0.944</b>	0.119	0.109	0.093	0.215	-0.034	0.024
Hf	<b>0.965</b>	0.021	0.052	0.060	0.126	-0.054	0.029
Ta	<b>0.927</b>	0.111	0.035	0.025	0.270	-0.044	0.047
W	<b>0.538</b>	0.352	-0.110	0.035	<b>0.551</b>	-0.021	0.108
Au	0.252	-0.204	<b>0.590</b>	0.152	-0.418	-0.046	0.067
Hg	0.017	0.107	-0.004	-0.095	0.090	<b>0.615</b>	-0.083
Pb	0.096	0.065	-0.181	0.115	-0.050	0.177	<b>0.667</b>
Th	<b>0.975</b>	0.090	0.078	0.087	0.074	-0.012	-0.011
U	<b>0.963</b>	0.124	0.101	0.084	0.027	-0.028	0.024
<i>Expl.Var</i>	<i>19.720</i>	<i>3.424</i>	<i>2.396</i>	<i>2.281</i>	<i>1.916</i>	<i>1.762</i>	<i>1.188</i>
Prp.Totl	0.493	0.086	0.060	0.057	0.048	0.044	0.030

The six factors are interpreted as follows:

**Factor 1** has particularly high values of Na, Mg, Al, Sc, Ti, V, Cr, Fe, Co, Ni, Cs, Ba, Hf, Ta, Th, U, and REE (rare-earth elements). Most of these elements are typical of crustal material, and probably this component at least partly reflects the contamination of moss samples with soil particles. However, high values for elements such as V, Cr, Co, and Ni and the fact that the factor scores are highest in/around Zagreb (sites 4, 5, 93B) and Sisak and Kutina (34, 35) indicate that Factor 1 is a general pollution factor. Contributions could be, e.g., from fly-ash

particles produced by high-temperature processes such as coal burning, which may have a major element composition similar to crustal material, and from burning of heavy fuel oils, where V and Ni are characteristic components. The geographical distribution of Factor 1 is shown in Fig. 4. The corresponding distribution map of U is also shown as a representative of an element of assumed geogenic origin.

**Factor 2**, with high factor loadings particularly for Zn, As, and Cd, looks like a typical pollution component associated with a point source. The geographical distri-

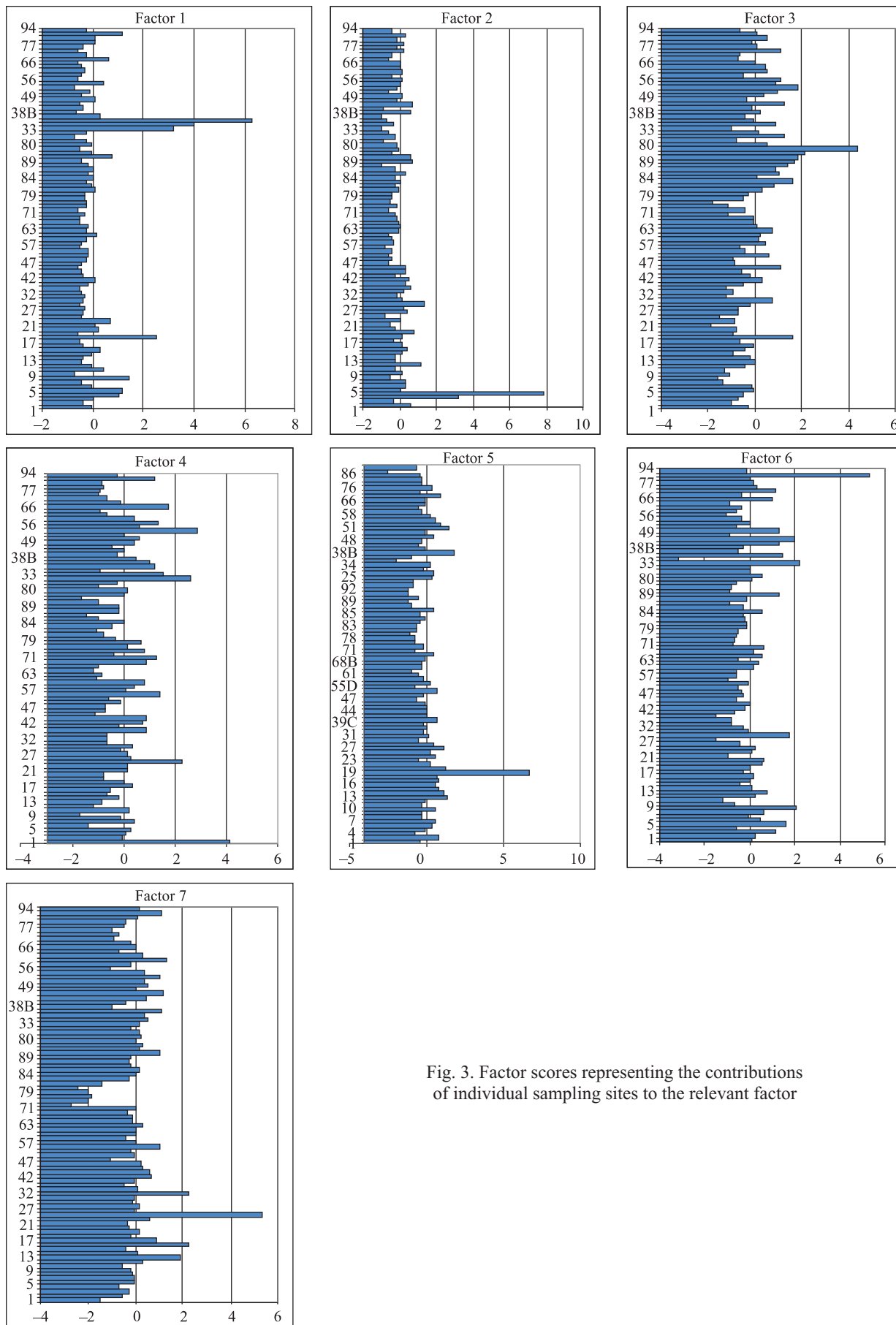


Fig. 3. Factor scores representing the contributions of individual sampling sites to the relevant factor

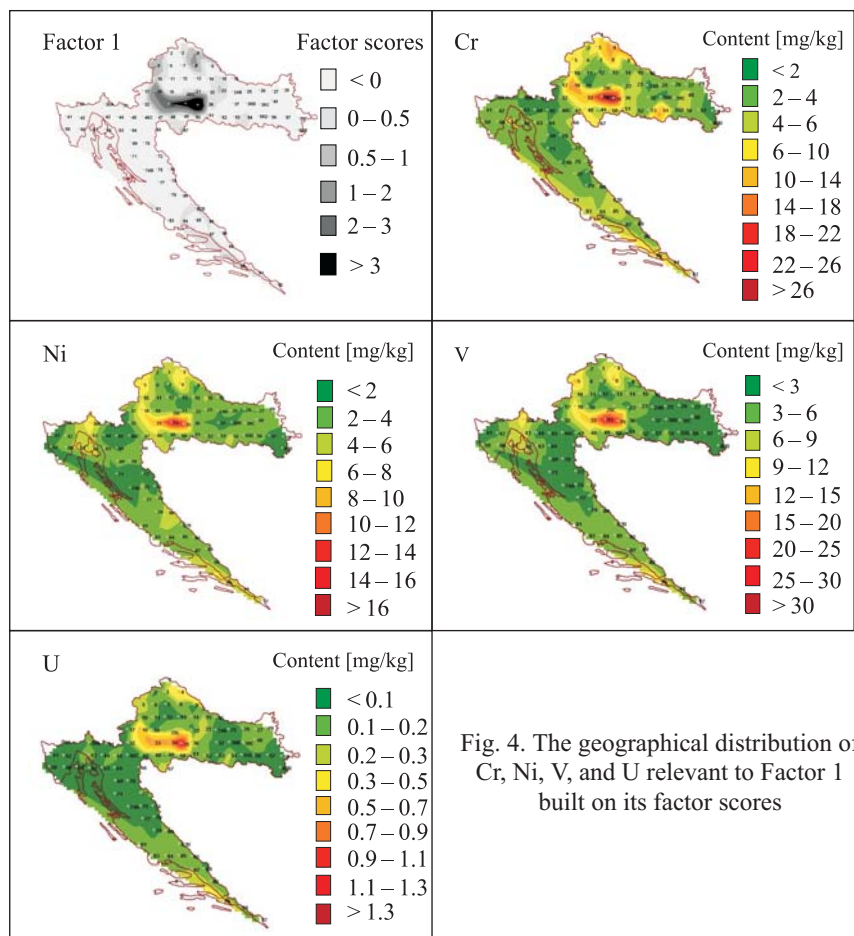


Fig. 4. The geographical distribution of Cr, Ni, V, and U relevant to Factor 1 built on its factor scores

bution of Factor 2 is shown in Fig. 5, along with the corresponding distribution maps for the above elements. High factor scores are evident at sites 3 and 4 to the north-east of the town Varazdin, which has steel industry. However, the fact that the impact of Factor 2 is significantly higher at site 4, which is more distant from

Varazdin, focuses the attention on possible transboundary transport from Hungary. One candidate source is glass industry in the town Nagykanisza, situated about 50 km east of the Croatian border. The fact that site 4 is also high in Pb, a characteristic pollutant from glass industries, supports this hypothesis.

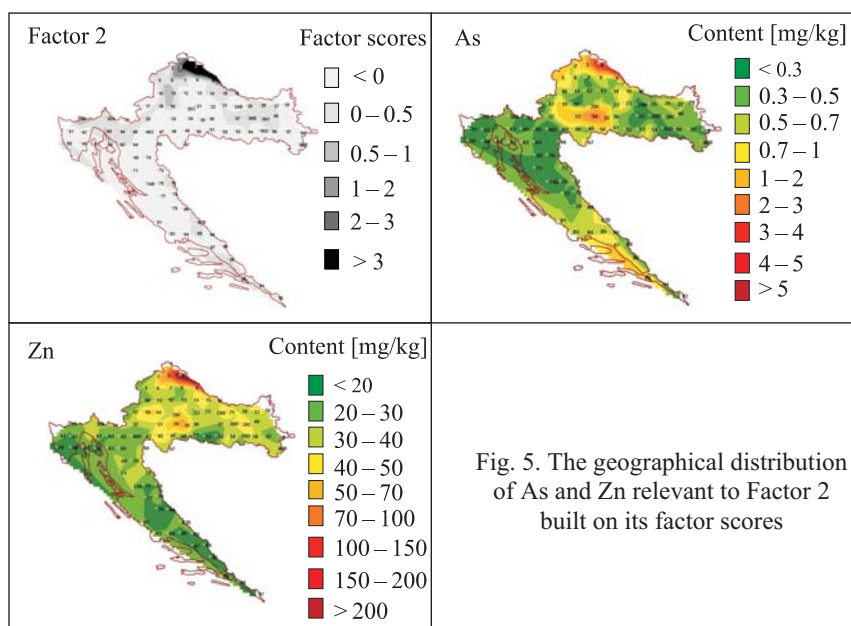


Fig. 5. The geographical distribution of As and Zn relevant to Factor 2 built on its factor scores

**Factor 3** has high loadings for Br and I. The geographical distribution of Factor 3 is shown in Fig. 6, along with the corresponding distribution maps of I and Br. The highest factor scores are found at sites 91 and 92, but also sites 83B, 85, 88, 89, and 90 show relatively high scores. These sites are all located along the Adriatic coast, where the industrial activity is moderate. This indicates that Factor 3 represents a natural process, i.e., the release of these elements as volatile organo-halogens by marine organisms [27] and subsequent deposition on land [28, 29]. The observed association of Se with this factor is as might be expected, since this element is also subject to emission in volatile organic form by marine

organisms [30], and thus present at higher concentrations, e.g., in moss [4, 20] and surface soil [31] near the ocean than farther inland. In the case of Br high loadings also at sites inland (5, 18, 34) indicate contribution from anthropogenic sources such as oil industry.

**Factor 4**, with high factor loadings for Cl and K, and **Factor 5**, with high loadings for Mn, are probably not pollution-related, but connected to the normal nutrient uptake of the moss [32].

**Factor 6**, with high loadings for Cu, Sb, and Hg, appears like a typical pollution factor. The geographical distribution of Factor 6 is shown in Fig. 7, along with distribution maps for Cu and Sb. The highest factor

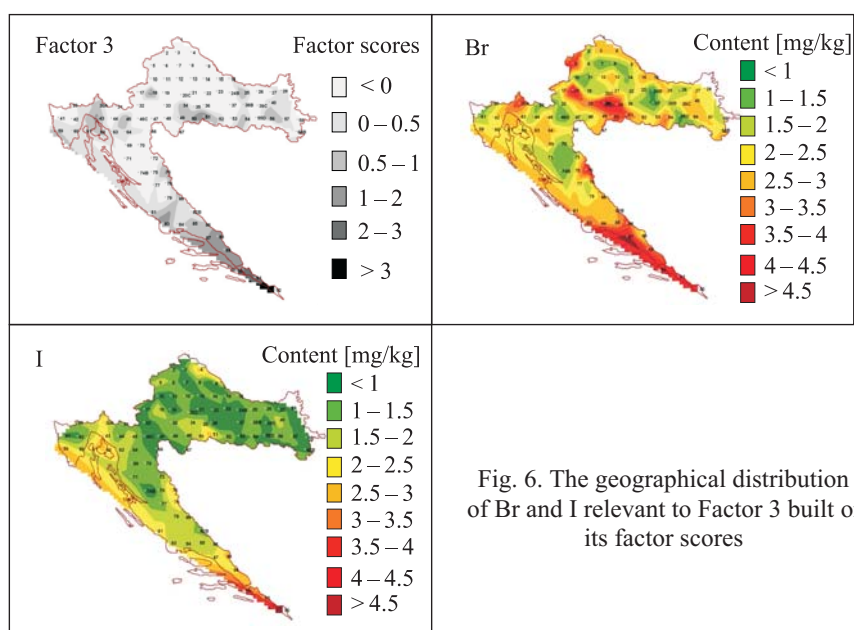


Fig. 6. The geographical distribution of Br and I relevant to Factor 3 built on its factor scores

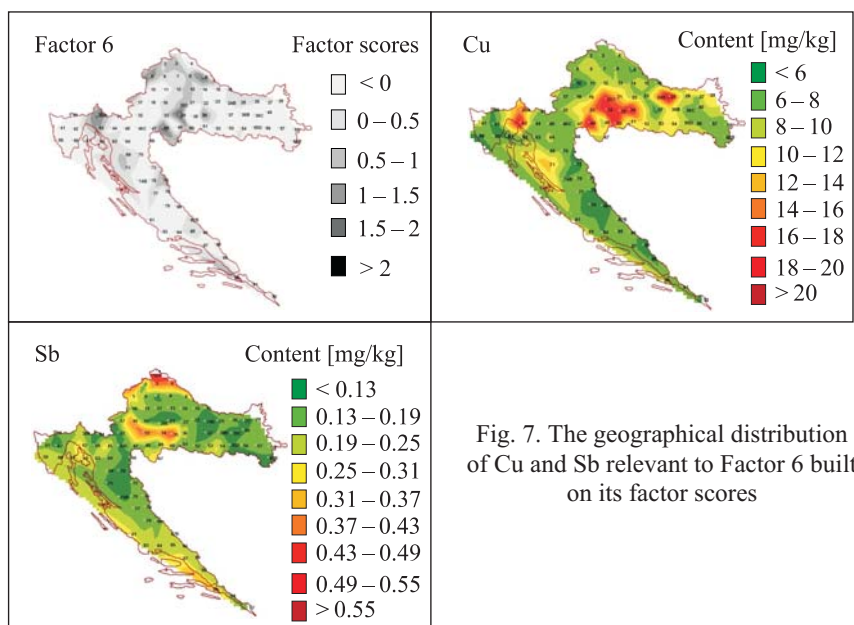


Fig. 7. The geographical distribution of Cu and Sb relevant to Factor 6 built on its factor scores

score is observed at site 93B located in the center of Zagreb, but moderate to high values are also observed at sites 5, 9, 30A, 34, and 48. Cu and Sb are known to be emitted from automobile traffic [33], and we may ascribe Factor 6 to this source.

**Factor 7**, with relatively high positive loading for Pb, is strongly dominated by a high Pb value at site 21 located east of the center of Zagreb, the source of which is not known.

Some of the elements of priority in the European moss survey [34] call for specific comments:

**Arsenic** in general shows low to moderate values in the moss. The highest value is evident at site 4, and may be due to the same source responsible for high values of Zn, Cd, and Pb at this site. The geographical distribution of As is shown in Fig. 5.

**Cadmium** follows Factor 2 with highest levels at sites 3 and 4, see above.

**Chromium** follows Factor 1 with the highest values at sites 33, 34, and 35, near Sisak and Kutina. The geographical distribution of Cr is shown in Fig. 4.

**Copper** shows highest values at sites 20, 67, 70, 72, 75, and 92, and is associated with Factor 6. These sites are scattered and not particularly associated with any known point sources. This supports the above hypothe-

sis that Factor 6 may be related to automobile traffic. The geographical distribution of Cu is shown in Fig. 7.

**Lead** shows much higher values at sites 14 and 21 than at any other sites, and forms a separate Factor 7. The sources of this lead are not clear.

**Mercury** is generally low (< 0.2 ppm) but is associated with Factor 6, ascribed above to automobile traffic.

**Nickel** does not show any marked maximum anywhere, but is present at concentrations significantly above average at 5–6 sites spread over the country, and may be associated with burning of heavy fuel oil for heating and electricity production, or metal industry. In the factor analysis this metal is associated with Factor 1, and its distribution map is shown in Fig. 4.

**Vanadium.** The same comments as for Ni apply to this element. The two metals show sufficient co-variation to support the conclusion that combustion of heavy fuel oil is a significant factor, as also indicated from the distribution of V shown in Fig. 4.

**Zinc** is associated with Factor 2, and shows the highest concentrations at site 4, followed by site 3. Elsewhere the level is fairly constant and probably near the natural background in the moss. This supports the assumption made above concerning the main source of the Factor 2 elements. The geographical distribution of Zn is shown in Fig. 5.

## CONCLUSIONS

As evident from the median values in Table 6 it is clear that Croatia is considerably polluted compared to many other countries in Europe. Still the situation in Croatia with respect to metal deposition is markedly better than in some of its neighboring countries, in particular with relation to the presence of strong point sources. Some parts of the country appear to be relatively pristine with respect to metal deposition. This in particular concerns most of the Adriatic coast, which is so important for Croatia as a very popular area for tourism.

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## REFERENCES

1. European Union, 1996. Council Directive 96/62/EC of 27 September 1996 on Ambient Air Quality Assessment and Management. Official Journal of the European Communities, 21.11.1996, L 296/55–63.

2. European Union, 2008. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008

on Ambient Air Quality and Cleaner Air for Europe. Official Journal of the European Union, 11.06.2008, L152/1–44.

3. European Union, 2004. Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 Relating to Arsenic, Cadmium, Mercury, Nickel

and Polycyclic Aromatic Hydrocarbons in Ambient Air. Official Journal of the European Union, 26.01.2005, L 23/3–16.

4. *Steinnes E., Rambaek J. P., Hanssen J. E.* Large-Scale Multi-Element Survey of Atmospheric Deposition Using Naturally Growing Moss as Biomonitor // *Chemosphere*. 1992. V. 35. P. 735–752.

5. *Rühling Å., Steinnes E., Berg T.* Atmospheric Heavy Metal Deposition in Northern Europe 1995 // *Nord* 1996:37. Nordic Council of Ministers. Copenhagen, 1996. 46 p.

6. *Freitas M. C. et al.* Nuclear Analytical Techniques in Atmospheric Trace Element Studies in Portugal // *Trace Elements/Their Distribution and Effects in the Environment* / Eds. B. Markert and K. Friese. Amsterdam, Tokyo, N. Y.: Elsevier, 2000. P.187–213.

7. *Wolterbeek H. T.* Biomonitoring of Trace Element Air Pollution: Principles, Possibilities and Perspectives // *Environmental Pollution*. 2002. V. 120. P. 11–21.

8. *Harmens H. et al.* Heavy Metal Concentrations in European Mosses: 2000/2001 Survey // *J. Atmospheric Chemistry*. 2004. V. 49. P. 425–436.

9. *Gjengedal E., Steinnes E.* Uptake of Metal Ions in Moss from Artificial Precipitation // *Environmental Monitoring and Assessment*. 1990. V. 14. P. 77–87.

10. *Bargagli R., Brown D. H., Nelli L.* Biomonitoring with Moss: Procedures for Correcting for Soil Contamination // *Environmental Pollution*. 1995. V. 89. P. 169–175.

11. *Rühling Å. et al.* Survey of Atmospheric Heavy Metal Deposition in the Nordic Countries in 1985. Monitored by Moss Analyses. 1987. *NORD*; 21. P. 1–44.

12. *Rühling Å. et al.* Atmospheric Heavy Metal Deposition in Northern Europe 1990. Report Nord 1992:12. Nordic Council of Ministers. Copenhagen, 1992. 41 p.

13. *Berg T., Røyset O., Steinnes E.* Moss (*Hylocomium splendens*) Used as Biomonitor of Atmospheric Trace Element Deposition: Estimation of Uptake Efficiencies // *Atmospheric Environment*. 1995. V. 29. P. 353–360.

14. *Berg T., Steinnes E.* Use of Mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as Biomonitors of Heavy Metal Deposition: From Relative to Absolute Values // *Environmental Pollution*. 1997. V. 98. P. 61–71.

15. *Horvat M. et al.* Mercury and Other Elements in Lichens at INA-Naftaplin Gas Treatment Plant, Molve, Croatia // *J. Environmental Monitoring*. 2000. V. 2. P. 139–144.

16. *Sucharova J., Suchara I.* Current Multi-Element Distribution in Forest Epigeic Moss in the Czech Republic — a Survey of the Czech National Biomonitoring Programme 2000 // *Chemosphere*. 2004. V. 57. P. 1389–1398.

17. *Barandovski L. et al.* Atmospheric Deposition of Trace Element Pollutants in Macedonia Studied by the Moss Biomonitoring Technique // *Environmental Monitoring and Assessment*. 2008. V. 138. P. 107–118. <http://dx.doi.org/10.1007/s10661-007-9747-6>

18. International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops: Heavy Metals in European Mosses: 2005/2006 Survey. Monitoring Manual. 2005. <http://icpvegetation.ceh.ac.uk/publications.htm>

19. <http://www.emep.int/grid/index.html>

20. *Steinnes E. et al.* Atmospheric Deposition of Trace Elements in Norway: Temporal and Spatial Trends Studied by Moss Analysis // *Water, Air, and Soil Pollution*. 1994. V. 74. P. 121–140.

21. *Frontasyeva M. V., Pavlov S. S.* Analytical Investigations at the IBR-2 Reactor in Dubna. JINR Preprint E14-2000-177. Dubna, 2000.

22. *Steinnes E., Frontasyeva M. V.* Epithermal Analysis of Mosses Used to Monitor Heavy Metal Deposition around an Iron Smelter Complex // *The Analyst*. 1995. V. 120. P. 1437–1440.

23. *Ostrovnaya T. M. et al.* Software for NAA on the Basis of Relative and Absolute Methods Using Nuclear Data Base // *Activation Analysis in Environmental Protection*. Dubna, 1993. P. 319–326.

24. *Frontasyeva M. V. et al.* Intercomparison of Moss Reference Material by Different Multielement Techniques // *J. Radioanalytical and Nuclear Chemistry*. 1995. V. 192. P. 371–379.

25. *Steinnes E. et al.* Atmospheric Deposition of Heavy Metals in Norway. Nation-Wide Survey in 2005. State Program for Pollution Monitoring. Report 980/2007. Norwegian State Pollution Control Authority. Oslo, 2007. 36 p. (In Norwegian).

26. *Garson D.* Factor Analysis. PA 765: Quantitative Research in Public Administration North Carolina State University. <http://www2.chass.ncsu.edu/garson/pa765/index.htm>

27. *Yoshida S., Muramatsu Y.* Determination of Organic, Inorganic, and Particulate Iodine in the Coastal Atmosphere of Japan // *J. Radioanalytical and Nuclear Chemistry – Articles*. 1995. V. 196. P. 295–302.

28. *Låg J., Steinnes E.* Regional Distribution of Halogens in Norwegian Forest Soils // *Geoderma*. 1976. V. 16. P. 317–325.

29. *Steinnes E., Frontasyeva M. V.* Marine Gradients of Halogens in Soil Studied by Epithermal Neutron Activation Analysis // *J. Radioanalytical and Nuclear Chemistry*. 2002. V. 253. P. 173–177.

30. *Cooke T. D., Bruland K. W.* Aquatic Chemistry of Selenium: Evidence of Biomethylation // *Environmental Science and Technology*. 1987. V. 21. P. 1214–1219.

31. *Låg J., Steinnes E.* Soil Selenium in Relation to Precipitation // *Ambio*. 1974. V. 3. P. 237–238.

32. *Steinnes E.* A Critical Evaluation of the Use of Naturally Growing Moss to Monitor the Deposition of Atmospheric Metals // *Science of the Total Environment*. 1995. V. 160/161. P. 243–249.

33. *Gomez D. R. et al.* Antimony: A Traffic-Related Element in the Atmosphere of Buenos Aires, Argentina // *J. Environmental Monitoring*. 2005. V. 7. P. 1162–1168.

34. *European Atlas: Spatial and Temporal Trends in Heavy Metal Accumulation in Mosses in Europe (1990–2005)*. UNECE ICP Vegetation / Eds. H. Harmens, D. Norris and participants of the moss survey. Centre for Ecology & Hydrology, Univ. of Wales Bangor, UK, July 2008. P. 51.

35. *Frontasyeva M. V. et al.* Atmospheric Deposition of Heavy Metals in Northern Serbia and Bosnia-Herzegov-

ina Studied by Moss Biomonitoring, Neutron Activation Analysis and GIS Technology // *J. Radioanalytical and Nuclear Chemistry*. 2004. V. 259, No. 1. P. 141–147.

36. *Stan O. et al.* New Results from Air Pollution Studies in Romania // *Proc. of NATO ARW «Man-Made Radionuclides and Heavy Metals in Environment»* / Eds. M. V. Frontasyeva, P. Vater and V. P. Perelygin. NATO Sci. Series. Kluwer Acad. Publ., 2001. IV Earth and Environmental Sciences. V. 5. P. 179–190.

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Изучение многоэлементных атмосферных выпадений в Хорватии с использованием мхов-биомониторов, НАА, ААС и ГИС-технологий

Впервые метод мхов-биомониторов и два взаимодополняющих аналитических метода: нейтронный активационный анализ (НАА) и атомная абсорбционная спектрометрия (ААС) — были применены для изучения многоэлементных атмосферных выпадений в Республике Хорватии. Образцы мхов-биомониторов были собраны летом 2006 г. с 98 площадок пробоотбора, равномерно распределенных на всей территории страны. Сбор образцов проводился в соответствии с протоколом международной конвенции по дальнему переносу атмосферных поллютантов (LRTAP) и правилами пробоотбора Европейской программы по биомониторингу атмосферных выпадений тяжелых металлов. Нейтронный активационный анализ с использованием тепловых и резонансных нейтронов позволил определить концентрации 41 элемента, включая такие важные тяжелые металлы, как Pb, Cd, Hg и Cu, которые были определены с помощью ААС. Метод главных компонент (факторный анализ с VARIMAX вращением) был использован для дифференциации главным образом элементов антропогенного происхождения от элементов, имеющих в основном природное происхождение. С помощью ГИС-технологий были построены географические карты распределений элементов на изучаемой территории. Для большинства элементов значения медиан концентраций по Хорватии согласуются с соответствующими значениями для всей Европы. Было показано, что Адриатическое побережье Хорватии может рассматриваться как экологически чистая территория. Настоящее исследование было предпринято с целью достоверной оценки качества воздуха во всей Хорватии, получения информации, необходимой для лучшей идентификации источников загрязнения и совершенствования оценки рисков для окружающей среды и здоровья населения Хорватии, ассоциируемых с токсичными металлами.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ, в Институте прикладной экологии (Oikon Ltd.) в Загребе (Хорватия) и в Институте химии Университета им. Св. Кирилла и Мефодия в Скопье (Македония).

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Spiric Z. et al.

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Multielement Atmospheric Deposition Study in Croatia Using Moss Biomonitoring, NAA, AAS and GIS Technologies

For the first time the moss biomonitoring technique and two complementary analytical techniques — neutron activation analysis (NAA) and atomic absorption spectrometry (AAS) — were applied to study multielement atmospheric deposition in the Republic of Croatia. Moss samples were collected during the summer 2006 from 98 sites evenly distributed over the country. Sampling was performed in accordance with the LRTAP Convention — ICP Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. Conventional and epithermal neutron activation analyses made it possible to determine concentrations of 41 elements including key heavy metals such as Pb, Cd, Hg, and Cu determined by AAS. Principal component analysis (factor analysis with VARIMAX rotation) was applied to distinguish elements mainly of anthropogenic origin from those predominantly originating from natural sources. Geographical distribution maps of the elements over the sampled territory were constructed using GIS technology. The median values for Croatia are consistent with the corresponding values for all Europe for most elements. It was shown that the Adriatic coastline of Croatia may be considered as an environmentally pristine area. This study was conducted for providing reliable assessment of air quality throughout Croatia and producing information needed for better identification of pollution sources and improving the potential for assessing environmental and health risks in Croatia associated with toxic metals.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, at Oikon Ltd. — Institute for Applied Ecology, Zagreb (Croatia) and Institute of Chemistry, Sts. Cyril and Methodius University, Skopje (Macedonia).

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