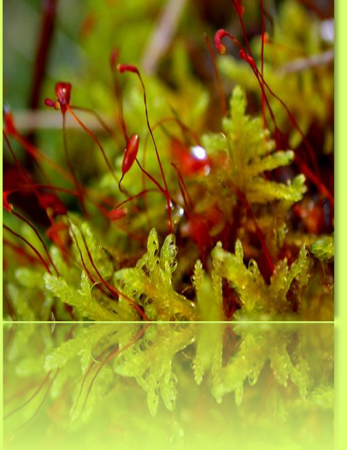

Moss biomonitoring of air pollution with heavy metals in zinc and lead mine environ

Biljana Balabanova[1], Trajče Stafilov[2], Katerina Bačeva[2], Robert Šajn[3]

[1]Faculty of Agriculture, Goce Delčev University, POB 201, 2000 Štip, Macedonia
[2]Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia
[3]Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia

INTRODUCTION

The environmental fate of heavy metals absorbed onto dust particles are of growing concern in addressing environmental issues for mine and processing plants environs [1]**. Bio-monitoring with moss species was conducted in potential polluted area with presence of lead/zinc mine, where continuously dust distribution occurs. The main aim of this study was to determinate narrower areas with high content of certain heavy metals, and potential long-distant distribution.**

EXPERIMENTAL

MOSS SPECIES

Hypnum cupressiforme (Hedw.)

Campothecium lutescens (De Not.)

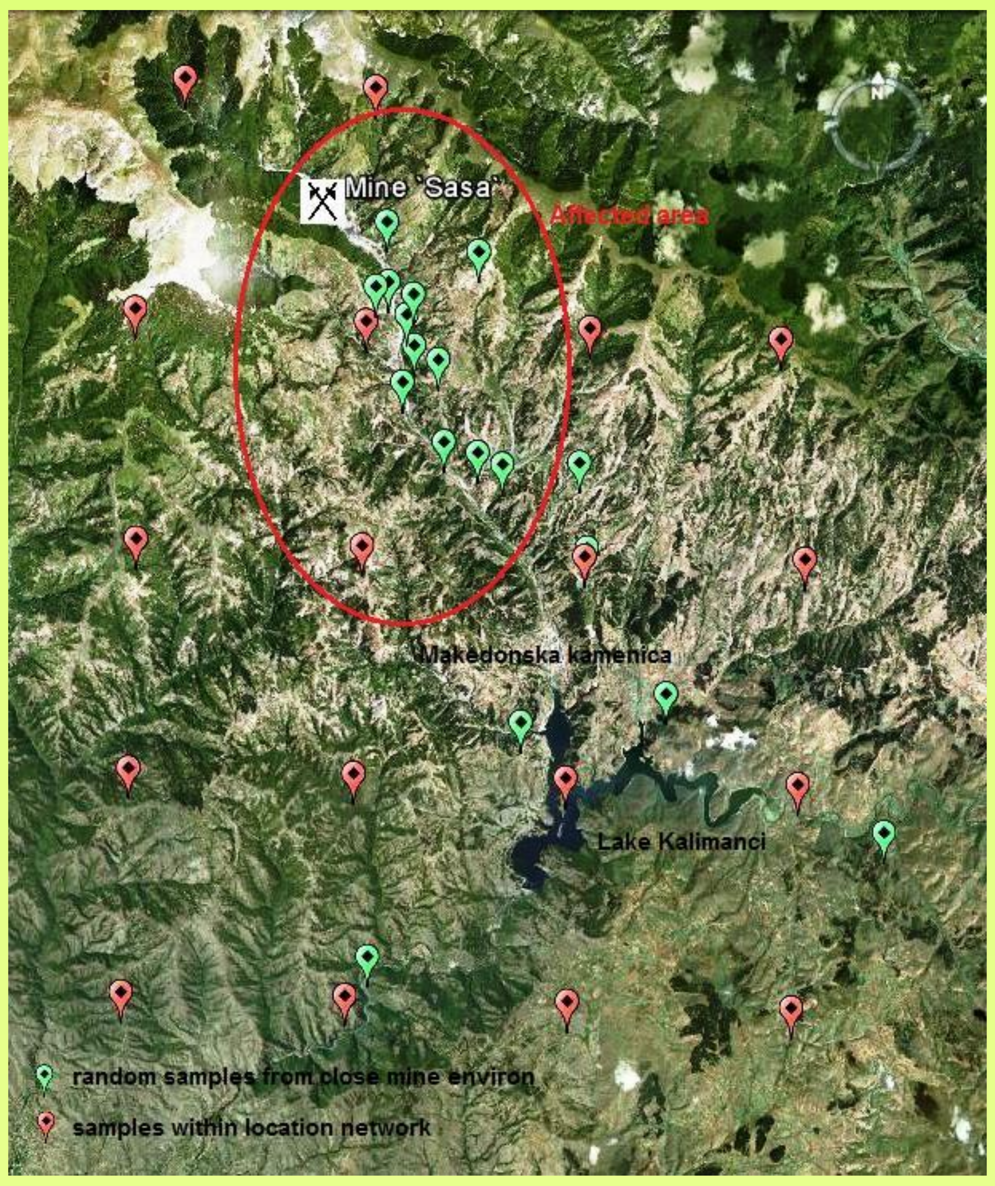

Fig. 1. Moss sampling locations

Sampling and sample preparation

Total of 36 moss samples of moss species (***Hypnum cupressiforme*** and ***Campothecium lutescens)*** were collected from the whole study area (Fig. 1). Random samples (green spots) and samples according to sampling network (5 x 5 km) were collected. The collection was performed according to the protocol adopted within the European Heavy Metal Survey. For digestion of moss samples, the **microwave digestion system** (CEM, model Mars) was applied.

Working program

Step	Temperature/°C	Time/min	Power/W	Pressure/bar
1	180	5	500	20
2	180	10	500	20

microwave digestion system

Teflon digestion vessels

Closed digestion vessels

0.5 g of moss samples, 5ml concentrated nitric acid, HNO_3 and 2ml hydrogen peroxide, H_2O_2 (30%, m/V) were added

Determination of elements content

Atomic emission spectrometer with inductively coupled plasma, **ICP-AES (Varian, 715ES),** for Al, Ba Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, Zn.

Electrothermal atomic absorption spectrometer, **ETAAS (Varian, SpectrAA 640Z)** was applied for analysis of As, Co, and Cd.

Cold vapor atomic absorption spectrometer, **CVAAS (Varian, SpectrAA)** was applied for analysis of Hg.

QC/QA

Standard additional method	Recovery	
	ICP-AES	ETAAS and CVAAS
	98.5–101.2 %	96.9 % – 103.2 %
Reference materials	Moss samples: M2, M3	

Table 1. Descriptive statistics for elements content values in moss samples (given in mg kg^{-1})

Element	N	Dis	X_a	X_g	Md	min	max	P_{10}	P_{90}	s	CV	A	S
Al	36	log	3218	2510	2459	683	12841	971	5825	2508	77.9	1.97	5.23
As	36	log	2.91	2.07	2.01	0.56	12.8	0.88	7.11	2.87	98.5	2.12	4.26
Ba	36	log	49.1	39.7	44.5	11.0	142	16.5	94.0	32.3	65.8	1.12	1.06
Ca	36	log	6570	6222	6513	2878	14070	4047	9579	2251	34.3	1.05	2.12
Cd	36	log	0.63	0.37	0.31	0.06	3.66	0.141	1.74	0.82	130	2.55	6.55
Co	36	N	0.72	0.56	0.53	0.16	2.60	0.24	1.23	0.58	80.7	1.86	3.64
Cr	36	N	2.28	2.03	2.13	0.84	5.10	0.99	3.81	1.08	47.4	0.63	-0.11
Cu	36	log	11.0	8.30	7.18	3.60	56.6	4.25	21.1	11.5	104	2.96	9.13
Fe	36	log	3592	2769	2485	822	17875	1259	6622	3172	88.3	2.85	11.10
Hg	36	N	0.037	0.035	0.033	0.021	0.08	0.024	0.05	0.013	34.9	1.19	1.55
K	36	N	5154	4853	4598	1977	9745	3264	7978	1830	35.5	0.73	-0.09
Li	36	N	1.16	0.98	1.13	0.31	3.90	0.40	1.95	0.70	60.7	1.76	5.46
Mg	36	log	3180	3100	3159	1706	4750	2391	4344	722	22.7	0.41	0.12
Mn	36	log	189	154	157	42.8	550	70.3	394	126	66.6	1.28	1.21
Na	36	log	73.7	45.9	40.9	20.1	885	25.5	102	147	199	5.20	28.56
Ni	36	log	2.92	2.71	2.74	1.05	6.41	1.58	4.17	1.17	40.1	1.31	2.51
P	36	log	875	827	770	414	1477	555	1343	302	34.5	0.63	-0.88
Pb	**36**	**log**	**59.8**	**20.0**	**23.8**	**0.14**	**450**	**2.46**	**157**	**102**	**170**	**2.88**	**8.45**
Sr	36	log	18.5	16.8	17.4	7.17	36.3	8.65	30.5	8.09	43.6	0.46	-0.80
V	36	log	3.49	2.84	3.14	0.76	9.69	1.12	6.03	2.21	63.4	0.98	0.74
Zn	**36**	**log**	**75.6**	**43.8**	**35.6**	**11.4**	**457**	**16.9**	**233**	**105**	**139**	**2.59**	**6.27**

Dis-distribution (log-lognormal; N-normal); X_a-aritmetical mean; X_g-geometrical mean; **Md**-median; **min**-minimum; **max**-maximum; **s**-standard deviation; P_{10}-10 percentile; P_{90}-90 percentile; **CV**-coefficient of variance; **A**-skewness; **E**-kurtosis

Significant higher values for Pb and Zn

RESULTS

Table 2. Matrix of dominant rotated factor loadings (F> 0.70)

Element	F1	F2	F3	F4	Comm
Cd	**0.74**	0.17	0.55	0.21	0.99
Cu	**0.77**	-0.01	-0.17	-0.03	0.85
Pb	**0.75**	0.11	0.58	0.16	0.99
Zn	**0.77**	0.13	0.51	0.22	0.99
Hg	0.67	0.32	0.18	0.08	0.78
Al	-0.12	**0.91**	0.18	0.14	0.99
Cr	0.30	**0.89**	0.03	0.10	0.95
Li	-0.01	**0.93**	0.02	0.18	0.97
V	0.29	**0.88**	0.07	0.17	0.98
As	0.04	-0.04	**0.75**	0.18	0.75
Fe	0.16	0.63	**0.70**	0.11	0.98
K	-0.30	0.16	0.48	**0.75**	0.94
P	0.29	0.10	0.06	**0.87**	0.95
Totl. Var.	25.0	27.3	13.6	13.4	93.1

F1, F2, F3, F4-Factor loading; Comm - communality

Moss species interchangeable reproduce the values for metals content

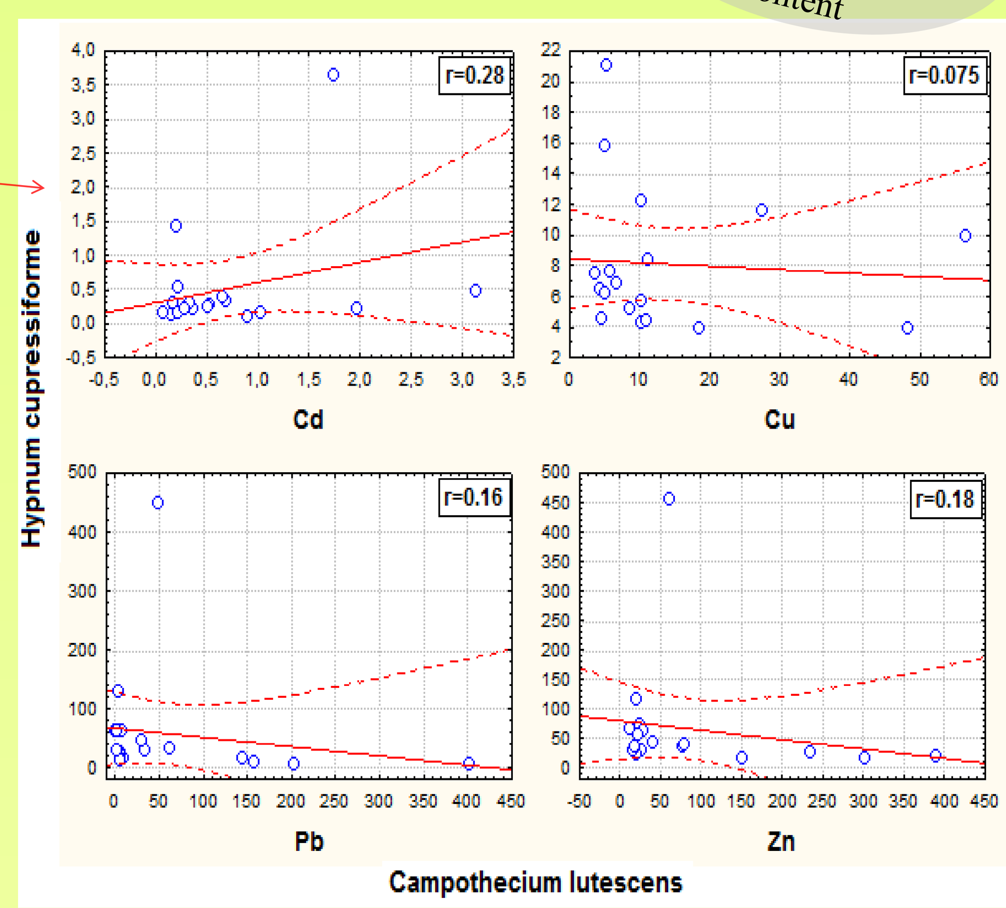

Fig. 2. Scatterplots for comparison of moss species for anthropogenic factor (Cd, Cu, Pb, Zn)

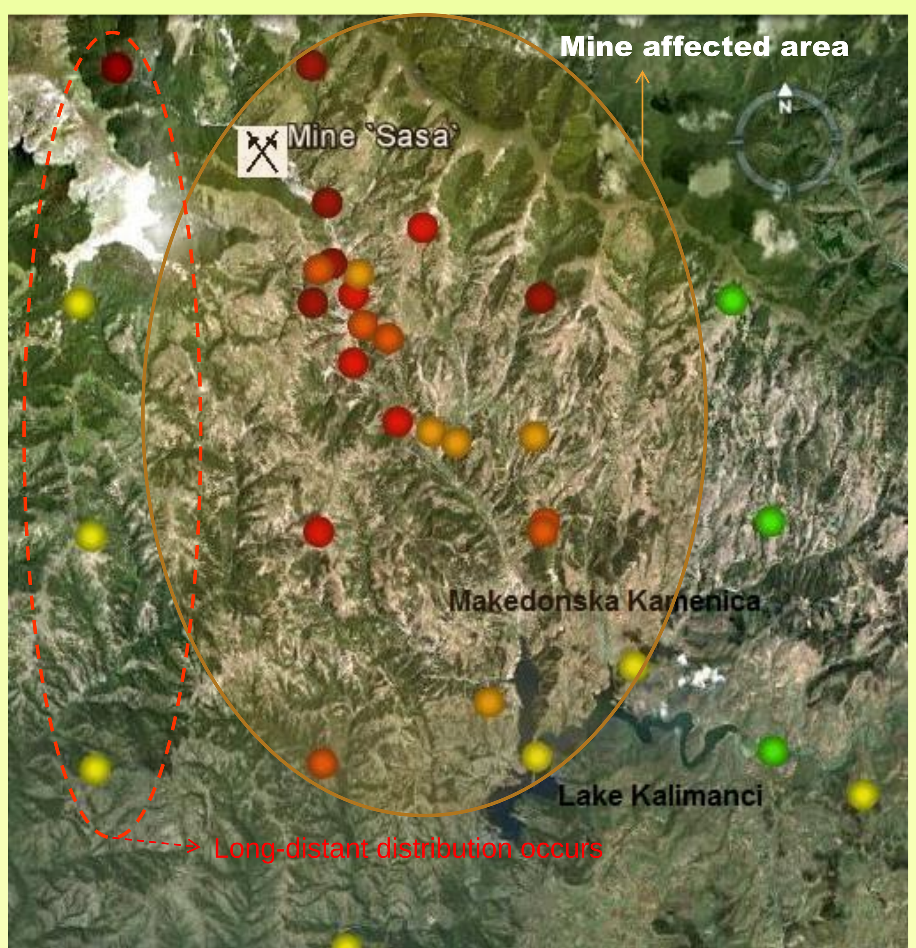

Fig. 3. Spatial distribution of Pb in moss species

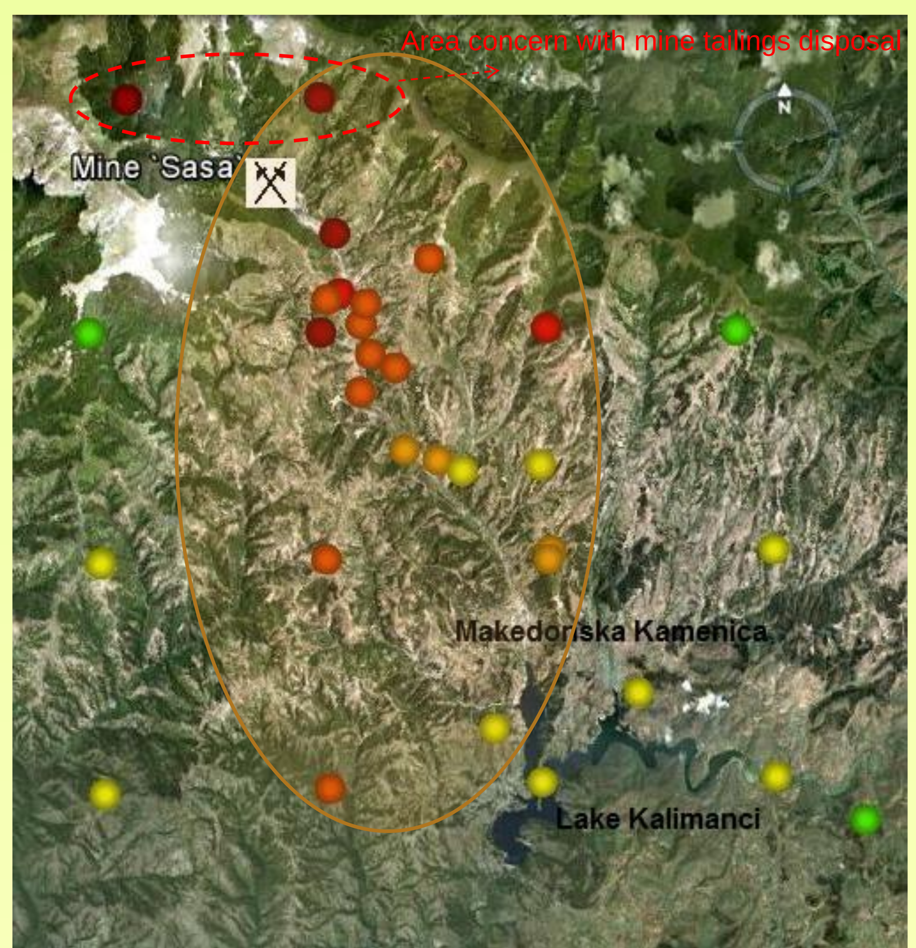

Fig. 4. Spatial distribution of Zn in moss species

CONCLUSION

Anthropogenic factor, F1 (Cd-Cu-Pb-Zn), with higher contents concern close mine environ – for lead long-distant distribution occurs.

F2, F3 and **F4** occurs as natural phenomena:

- distribution of F2 and F4 undergoes with geology of the region;
- distribution of F3 reveals on biological background media.

Extremely high contents for Pb and Zn in "Sasa" mine environ – max values **~ 450 mg/kg**

Moss species (*Hypnum cupressiforme* and *Campothecium lutescens*) can be used in selected areas, ranging from pollution-free background regions to highly polluted regions

Reference

[1] Stafilov, T., Balabanova, B., Šajn, R., Bačeva, K. and Boev, B. (2010). Geochemical at-las of Radoviš and the environs and the distribution of heavy metals in the air. Faculty of Natural Sciences and Mathematics, Skopje.

4th Congress of the Ecologists of Macedonia, Ohrid, 12-15 October 2012