STUDY OF HEAVY METAL CONTENTS IN SOIL, RIVER WATER, SNOW, NEEDLES AND MOSSES OF IVANOVO REGION

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Introduction

An increase of anthropogenic impact causes a degradation of environmental quality, heavy metals (HM) being one of the most dangerous pollutants. They exist in all natural environments and frequently have a tendency of bioaccumulation. Their expressed toxicity and high level of the influence define the urgency of investigation of heavy metals migration and transformation in natural ecosystems. This paper is concerned with the study of HM contamination level in Ivanovo region carried out in this scale for the first time.

Materials and methods

Ivanovo region situated at interfluve of the Volga and Klyaz'ma rivers with an area of 22 000 km^2 was the object of the investigation. There were 45 squares (Fig. 1) separated within the region with average area of 400 km^2. Samples of soil, needle of spruce (*Picea Abies*), mosses and snow were taken from each square. Water samples from the main rivers were also sampled.

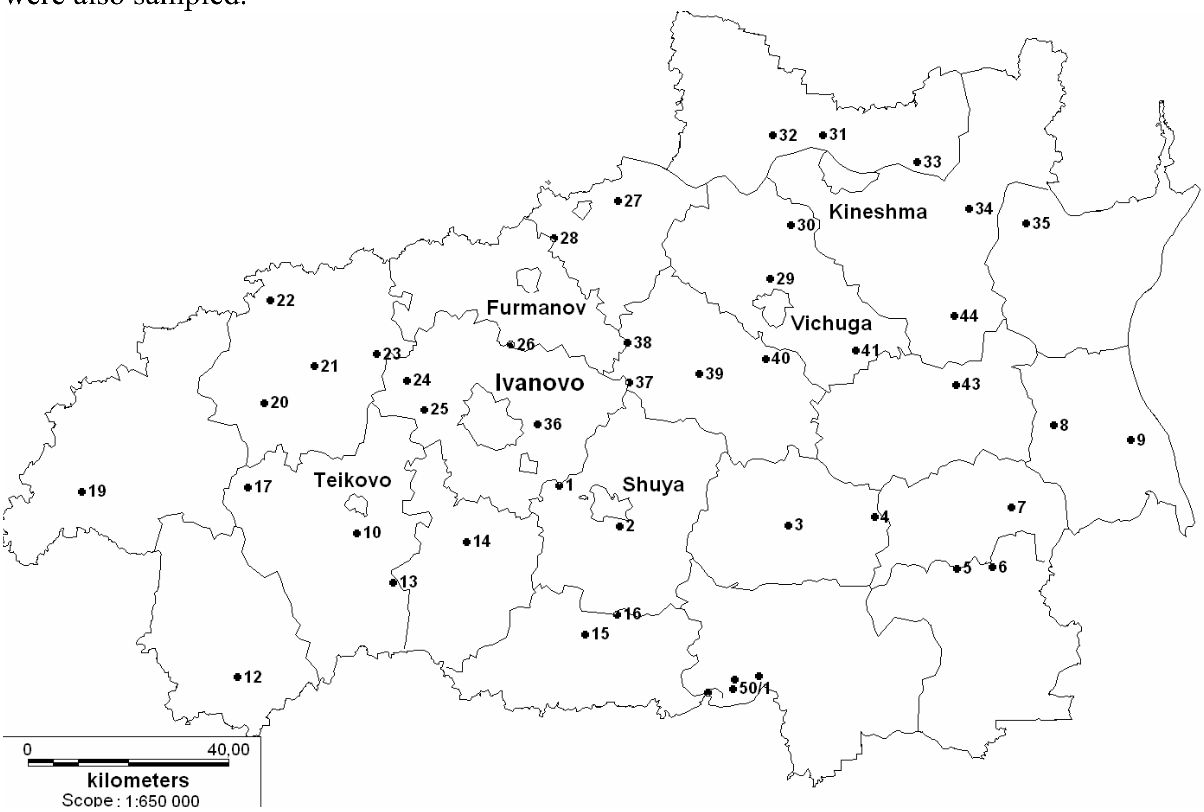

Fig. 1. Sampling map.

Sampling was made according to standard techniques for soil and needles [1], moss [2], snow [3] and water [4]. The analysis of HM content (Pb, Cd, Cr, Cu, Co, Ni, Mn, Fe and Zn) was carried out with the use of flame atomic absorption spectrometry. The concentration of gross and movable forms of the metals was measured in soil samples, while in others - only gross forms. Determination uncertainties were about 20-30%.

Results and discussion

The data visualization and statistical analysis were employed in results of investigation. Maps of spatial distribution of HM in the examined environments were created with the use of MapInfo software. We applied IDW (Inverse Distance Weighting) interpolation method for the subject maps.

The factor analysis of the given data was done to detect potential origins of the intake and establish the correlation of the HM content in different environments. Processing was carried out by principal component method with the Varimax rotation.

Table 1. HM concentrations in soils and background concentrations (ug/g).

Metal	**min-max**	**mean**	**localbg[1)]**	**sod-podzolic soil [1]**	**podzolic soil [5]**	**sod-podzolic soil (Moscow region)[3)] [5]**	**podzolic soil [6]**
Cr	<0,01-1,67	0,12	0,29	140	180	46	47 (1,4-530)
Mn	<2,5-1880	420	144	650	715	590	270 (7-2000)
Fe[2)]	71,4-14400	5490	2930	-	-	-	-
Co	<0,02-4,58	1,3	0,88	-	8,4	7,2	5,5 (0,1-65)
Ni	<0,3-56,4	8,67	2,43	51	23,2	20	13 (1-110)
Cu	<0,2-20	6,24	<0,2	23	15,3	27	13 (1-70)
Zn	4,17-70	19,5	11,3	49	41,3	50	45 (3,5-220)
Cd	<0,002-0,25	0,03	0,03	-	0,7	0,3	0,37(0,01-2,7)
Pb	<0,02-3,32	0,23	0,33	19	11,5	25	22 (2,3-70)

[1]) – local background (average concentration for 10 samples with least concentrations);
[2]) – in [7] is value 38000 ug/g;
[3]) – value used for calculations in given work.

Average HM content in the soil samples was within the range of maximum permissible concentration (MPC). However, the increasing HM content in the soil near large industrial centers evidenced of their anthropogenic origin. The most of samples sites had a HM concentration, which was lower than background (Table 1).

Besides, the comparison of HM content in Ivanovo and neighboring regions was made (Table 2). The given data argued about lower level of HM content in Ivanovo region as compared with other regions. The soil of Nizniy Novgorod region was the closest in chemical composition.

Table 2. Data of HM content in soil in Ivanovo and neighboring regions (ug/g).

Metal	**Kostroma region, 2010 /8/**	**Vladimir region, 2000 /9/**	**Nizniy Novgorod region, 2007 /10/**		**Ivanovo region, 2010**	
Form	**Gross**	**Gross**	**Gross**	**Mov.**	**Gross**	**Mov.**
Cr	72,63	80	11,91	0,29	0,12	0,03
Mn	645,2	692	-	-	420	40,4
Fe	18398,8	27700	-	-	5490	84
Co	15,63	6	-	-	1,3	-
Ni	23,39	29	20,46	0,78	8,67	0,99
Cu	23,23	-	8,05	0,29	6,24	0,77
Zn	48,40	47	25,91	0,59	19,5	3,66
Cd	-	-	0,39	0,13	0,03	<0,003
Pb	-	16	6,17	0,64	0,23	-

The factor analysis of the given data also confirmed anthropogenic character of areas with higher HM content. Six factors, which explained 76% of the dispersion, were separated. The three most important of them might be interpreted as a result of anthropogenic impact due to activity of different industries and automobile transport.

The analysis of needles showed the absence of Cd, Pb, Cr, Co and particularly Ni. Other elements likely had natural origin.

Table 3. Data of HM content in mosses in Ivanovo and other regions (ug/g).

	Tver+Yaroslavl (2000-2002) /11/			**Tula (1998-2000) /12/**			**Udmurtia (2005-2006) /13/**		
	min	**max**	**mean**	**min**	**max**	**mean**	**min**	**max**	**mean**
Cr	0,2	27	1,5	0,6	28	5	3	48	6,2
Mn	45	2200	400	35	820	300	43	700	210
Fe	68	3690	550	350	19700	2200	380	3545	890
Co	0,05	3,5	0,41	0,14	2,66	0,63	0,07	2,13	0,4
Ni	0,25	22	2	0,7	11,7	3,7	1	16	4,7
Cu	3,2	9,2	5,1	4	36	9	3	22	8,5
Zn	13	85	34	16	105	54	18	115	42
Cd	0,03	0,82	0,27	0,04	1,22	0,32			
Pb	2,1	12,2	6	3,8	18,6	8,7			
min, max and mean- minimal, maximal and average concentrations respectively									

	Ivanovo (2010)		
	min	**max**	**mean**
Cr	<0,01	16,7	1,7
Mn	<2,5	1250	231
Fe	4,17	750	262
Co	<0,02	<0,02	<0,02
Ni	<0,3	16,6	4,3
Cu	<0,2	44	8,6
Zn	2,4	120	31
Cd	<0,05	1,25	0,14
Pb	<0,02	41,7	3,5

Heavy metals can migrate from soils into rivers. Thereby, it was also necessitate carrying out the analysis of river water. The content of Fe, Zn and Mn was below maximum permissible concentration for water for all rivers. The excess of this level was marked for Ni compound in two rivers – Matnya and Shacha. The increase of the content in these rivers was probably due to activities of industries of Shuya city and Furmanov city. The excess of copper content above MPC was fixed for seven rivers. The most probable reason of this metal arrival might be erosion from the bedrock and the influence of the river head often situated at swampy area enriched by metal compounds.

The values of the index of water pollution were calculated. The results allowed ranking the water quality in examined rivers. Overwhelming majority (9 of 14) was characterized as first or second class of pollution and was pure. There were three only rivers with class of pollution above 3. It pointed out significant degree of contamination and required the development of measures for changing present situation.

Table 4. Factor analysis.

	Component						
	1	**2**	**3**	**4**	**5**	**6**	**7**
Cd_s_m	**0,957**		-0,124			-0,105	
Cr_s_m	**0,957**		-0,124			-0,105	
Cr_m	**0,853**		0,424				
Cu_m	**0,834**		0,487				
Cd_m	**0,661**	-0,100	-0,163	0,580			-0,168
Ni_s_m	**0,637**	0,394	-0,296			-0,102	
Mn_s_m		**0,932**	0,227				
Ni_s_g		**0,915**			0,154		
Pb_s_g		**0,768**	0,352		0,390	-0,164	
Fe_s_m	-0,184	**0,756**	0,150	-0,131	-0,250		
Fe_s_g	-0,115	**0,734**	-0,210		-0,122	0,298	
Cu_s_g	0,184	**0,638**		-0,126	0,400	0,135	
Pb_m			**0,902**		0,207		
Zn_m			**0,868**				0,191
Cd_s_g		0,370	**0,636**		0,589	-0,127	
Fe_n	-0,174	-0,292		**0,807**			0,167
Zn_n		0,251	-0,188	**0,785**		0,393	-0,187
Fe_m	0,218		0,269	**0,779**			0,197
Cr_s_g			0,170		**0,875**		
Co_s_g		0,228	**0,452**		0,484		
Cu_n				0,175		**0,887**	
Mn_s_g	-0,150	0,135			-0,108	**0,878**	-0,106
Ni_n							**0,928**

Zn_s_g		0,122	0,345				**0,795**
Mn_n	-0,246	0,223	0,129	0,148	-0,258	0,190	0,164
Ni_m	0,465		-0,265	0,347		-0,121	-0,267
Cu_s_m	-0,221	-0,132		-0,132	0,349	-0,182	-0,183
Zn_s_m	-0,103		-0,147			-0,142	
Mn_m	-0,258	-0,270			-0,297	-0,301	-0,149

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Indexes: s_g – soil gross; s_m – soil movable; m – moss; n – needles.

Data of 25 moss samples (*Hylocomium splendens, Pleurozium schreberi* and *Polytrichum commune*) were processed. All obtained metals were present in samples (Table 3). Values of HM content in moss were compared with the results of the research in Yaroslavl, Tver', Tula region and Udmurtia republic. All these data were measured by NAA method. In fact level of HM content in Ivanovo region was very close with neighbor regions.

Samples of snow were collected on March, 2011. HM content in bulk snow and solid fraction were measured. Composition of snow solid fraction (Zn, Mn, Fe) was an evidence of their soil origin. These metals were most common in soil and under wind transfer they could migrate in snow from roads. In bulk snow Cu, Zn, Mn and Fe were found. The concentrations of copper were the same as those of Nizniy Novgorod region, but zinc content in Ivanovo was less than in Nizniy Novgorod. Intensities of atmospheric deposition, which were calculated from the HM content in snow, were less than urban intensities of HM deposition [5].

Factor analysis of the total array of data of HM content in different environments was made (Table 4). As a result 9 factors, which explained 86% of whole dispersion, were singled out. The first four factors were most important and interesting.

The first factor concerned with movable forms of Cr, Cd and Ni in soil, and Cr, Cd and Cu in moss. Such coincidence might explain the origin of these elements in soil. Moss gets the nutrition elements only from air. Hence Cr and Cd had atmospheric origin.

The second factor combined gross forms of Pb, Ni, Fe and Cu in soil and movable forms of Fe and Mn, probably; being a group of elements migrated into soil from the bedrock. The 4^{th} factor was determined by the content of Fe in needles and moss, and Zn in needles.

The third factor included gross forms of Co and Cd in soil, and Pb and Zn in moss. Origin of this factor probably dealt with the influence of automobile transport.

The samples will be measured by the neutron activation analysis on the basis of the Laboratory of Neutron Physics of Joint Institute of Nuclear Research. It allows extend considerably the number of the observed elements. The results of the research will be included into European Atlas of HM deposition according to the Long Range Transboundary Air Pollution programme. The results of the research will be given in community ecological council for the development of measures of Ivanovo region aimed at the maintenance of favorable quality of environment.

It will be possible to define spatial and temporal trends of HM distribution in natural environments and determine the regularity of their behavior in the environment during next two years.

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