Soil Contamination Assessment in Ivanovo Region: Urban and Background Aspects

Dunaev A.M., Rumyantsev I.V., Grinevich V.I.

Ivanovo State University of Chemistry and Technology, Russia, Ivanovo, F. Engels prospect, 7

Abstract. The paper is concerned with the heavy metal monitoring in Ivanovo region. The aspects of urban and background pollution of soils are discussed. Insignificant degree of natural soil contamination is established. Otherwise soil quality in regional center is inadequate.
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Introduction

Nowadays an environmental contamination problem in Central Russia is very important. During last years an increase of industrial activity may be caused negative influence on environment. Soil is the most conservative as compared with air and water. Therefore monitoring of soil is the key to assessment of ecosystem integrally.

One of the most dangerous pollutants is heavy metals (HM). 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.

The aim of the given research is to study the level of HM content in soil at large industrial city by example of Ivanovo city and at natural, unperturbed places, which are distant from cities.

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 were taken from each square in 2010.

Ivanovo city (Fig. 1) ape placed at the center of Ivanovo region. The population of Ivanovo city is about 400 000. Main branches of industry in Ivanovo city are mechanical engineering, textile and food industries. There was sampling of soil in 2009 and 2011 in Ivanovo city. 10 samples were collected in 2009 and 54 in 2011. Also in 2011 some physicochemical characteristics of soil, such as pH, acidity and cation-exchange capacity (CEC) were determined.

Sampling was made according to standard techniques [1]. The analysis of HM content 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%.

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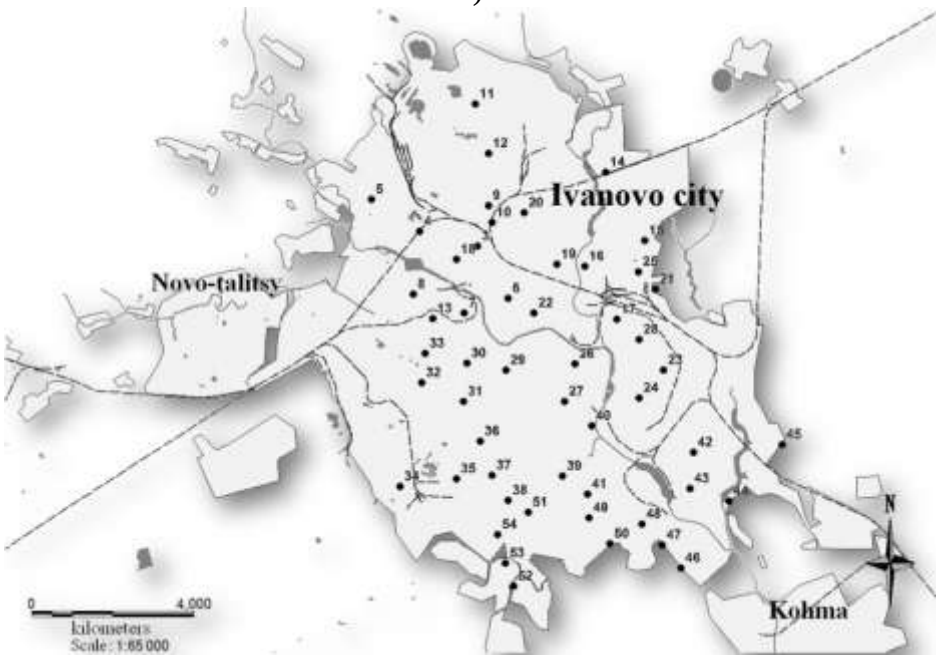

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Fig. 1. Sampling map. 1- Ivanovo region; 2 – Ivanovo city.

Results and discussion

The concentrations of HM in Ivanovo region soils indicated the low level for all elements under study. Only a few number of samples characterized by excess maximum permissible concentration for soil (MPC_S) or approximately permissible concentration (APC_S). It concerned gross forms of Cr, Mn and movable forms of Ni, Cu and Zn (Table 1). Last three elements have a medium and strong migration intensity, which might explain this phenomenon. MPC_S for chromium was established only for hexavalent form. Hence in practice this value was always exceeded.

Table 1. HM content (ppm) in soil of Ivanovo region.

Metal	**min-max**	**Number of samples with excessive values**	**Mean**	**MPC_s (APC_s)**
Cr	<0.01-**1.67** <0.01-0.63	2	0.12 0.03	0.05 -
Mn	<2.5-**1880** <2.5-250	6	420 40.4	1500 500
Fe	71.4-14400 <0.02-286		5490 84	-
Co	<0.02-4.58 <0.5		1.3 <0.5	- 5
Ni	<0.3-56.4 <0.02-**8.76**	4	8.67 0.99	(80) 4
Cu	<0.2-20 <0.2-**5.8**	4	6.24 0.77	(132) 3
Zn	4.17-70 <0.25-**35**	1	19.5 3.66	(220) 23
Cd	<0.002-0.25 <0.002-0.08		0.03 0.003	(2) -
Pb	<0.02-3.32 -		0.23 -	32 6
Upper row contains data for gross form of metal, lower row – for movable forms				

However average HM content was sufficiently lower than permissible level for all metals. This fact pointed out an insignificant degree of soil contamination. 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 lower than the background one. Background concentrations were calculated for Ivanovo region (localbg) as the average of 10 concentrations from samples with the lowest content. Additionally the comparison with some literature values was performed (Table 2). There was not data for background concentration of iron in examined type of soil, the only value was 38000 ppm for all types of soils [2]. Background levels for Moscow sod-podzolic soils (as closest in structure) were chosen as reference levels and used in further calculations. The comparison of data from Table 2 showed a similar situation with permissible concentrations. The only manganese content was exceeded. It dealt with raised natural abundance of this element in Ivanovo region.

Table 2. Background concentration (ppm) of HM in soils.

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

Ivanovo region borders on Kostroma region on North, Vladimir region on South, Nizniy Novgorod on East and Yaroslavl' region on West. Therefore it was very interesting to compare results of soil analysis for Ivanovo and neighboring regions. This comparison (Table 3) confirmed good quality of soils in Ivanovo region. The Nizniy Novgorod soils were the closest in chemical composition.

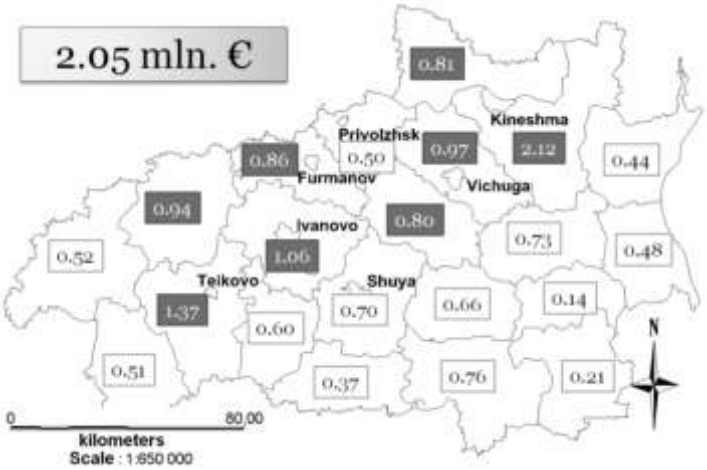
Table 3. HM content (ppm) in Ivanovo and neighboring regions.

Metal	Kostroma, 2010 [6]	Vladimir, 2000 [7]	Nizniy Novgorod, 2007 [8]		Ivanovo, 2010	
Form	Gross	Gross	Gross	Mov.	Gross	Mov.
Cr	73	80	11,9	0,29	0,12	0,03
Mn	645	692	-	-	420	40,4
Fe	18000	27700	-	-	5490	84
Co	15,6	6	-	-	1,3	-
Ni	23,4	29	20,5	0,78	8,67	0,99
Cu	23,2	-	8,05	0,29	6,24	0,77
Zn	48,4	47	25,9	0,59	19,5	3,66
Cd	-	-	0,39	0,13	0,03	<0,003
Pb	-	16	6,17	0,64	0,23	-

Risk assessment of soil contamination in Ivanovo region was also performed. Possible costs of maintenance of environmental quality were established. The probabilities of metal pollution were generally low. But they were equal to the unit for Kineshma, Teikovo and Furmanov districts with big industrial clusters. This fact means that contamination has already accomplished.

Spatial distribution of soil contamination risk in the Ivanovo region is depicted on Fig. 2. The largest values are fixed for Kineshma, Teikovo, Ivanovo, Vichuga, Komsomolsk, Furmanov, Zavolzhsk and Rodniki districts. The average risk cost for Ivanovo region was 2 million Euros. Calculated risks for each district were in very good agreement with values of

contaminants emission from stationary sources [9]. It was an evidence that anthropogenic impact was the major reason of HM intake by soil.



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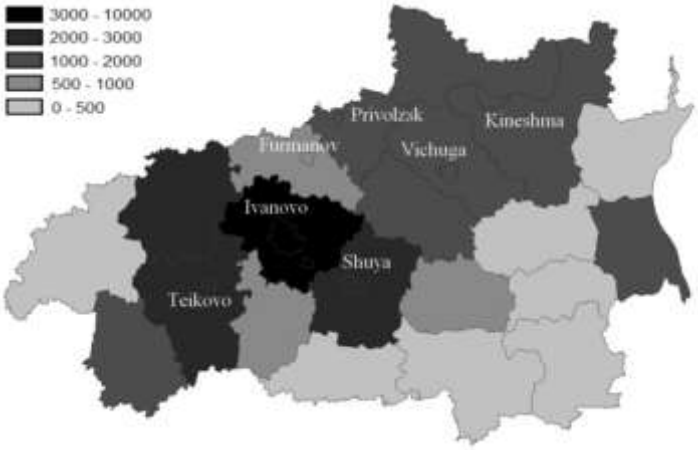

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Fig. 2. 1- Soil contamination risk distribution (mln. Euros); 2- Values of contaminants emission from stationary sources in 2008 (ton/year).

The results of sampling in Ivanovo city carried out in 2009 and 2011 were relatively close. The sampling in 2009 was a pioneering research performed for approbation of methodic. Hence a few range of data was insufficient for statistical processing and needed additional research. Unfortunately, there wasn't a possibility to determine lead, cadmium and chromium in 2011. Therefore it was recommended to use data for these elements from research in 2009 along with data of 2011, which more preferable in the case of other metals.

Average content in soil for all metals was below maximum permissible concentrations. However, some samples exceeded this level. The most significant excess of HM concentration was fixed for Pb and Zn. It should be taken into account that this increased Zn and Pb content was only point contamination, which might be interpreted as the influence of solid waste. Values of soil pH were within the range of normal deviation. The situation with cation-exchange capacity was even worse. The only sample had CEC above 50. The soil underwent HM contamination if this condition is not fulfilled.

Table 4. Soil characteristics in Ivanovo city.

Metal	2009		2011		MPC_s (APC_s)
	Mean	**min - max**	**Mean**	**min - max**	
Cr (ppm)	**6.51** <0.01	<0.01-**50** -	-	-	0.05 -
Mn (ppm)	236 23.3	10-1300 2.50-121	208 66	43-545 <2.5-250	1500 500
Fe (ppm)	1850 209	286-7000 <2.5-2190	7120 257	100-17500 8.0-4170	-
Ni (ppm)	-	-	3.93 1.62	0.3-18.9 0.3-**8.66**	(80) 4
Cu (ppm)	25.1 **3.53**	5.27-129 <0.05-**13.7**	10.2 1.64	<0.2-23.3 <0.05-**10.0**	(132) 3
Zn (ppm)	76.7 21.8	4.29-**315** 3.57-**79.6**	135 **38.5**	23.4-**800** 10-**139**	(220) 23
Cd (ppm)	0.33 0.05	<0.002-1.99 <0.002-0.56	-	-	(2) -
Pb (ppm)	**88.3** **37.8**	<0.02-**478** <0.02-**239**	-	-	32 6
pH	-	-	7.0	**5.8**-7.6	6-8
Cation-exchange capacity (mg·eq/100g)	-	-	**30.6**	**7.0**-77.6	>50
Upper row contains data for gross form of metal, lower row – for movable forms					

Factor analysis of soil pollution data was also performed (Table 5). Six factors were extracted for data of Ivanovo region and five for Ivanovo city. First three factors, which were singled out for Ivanovo region, might be interpreted as the influence of industrial activities of different districts. It was electrochemical, mechanical and chemical engineering of Kineshma district (Factor 1); machine building industries of Vichuga district (Factor 2); various industries of Ivanovo city and motor transport (Factor 3). Other factors (4-6) probably had natural origin. Most of extracted factors for Ivanovo city were combined gross and movable forms of separate metals. It pointed out different sources of their elements in soil. First of all it might be motor transport, then solid wastes and finally power engineering.

The results were compared with the data of HM monitoring, which was carried out in 1998 for Ivanovo city [10]. The concentrations of Zn were insignificantly increased and for movable forms were still above permissible level (Fig. 3a,b). Otherwise, Cu content in soil was decreased last decade, especially for movable forms (Fig. 3c,d). The level of lead is still raised, in spite of the prohibition of usage Pb in fuel since 1998 (Fig. 3e). Probably, it might be dealt with the violation of this law.

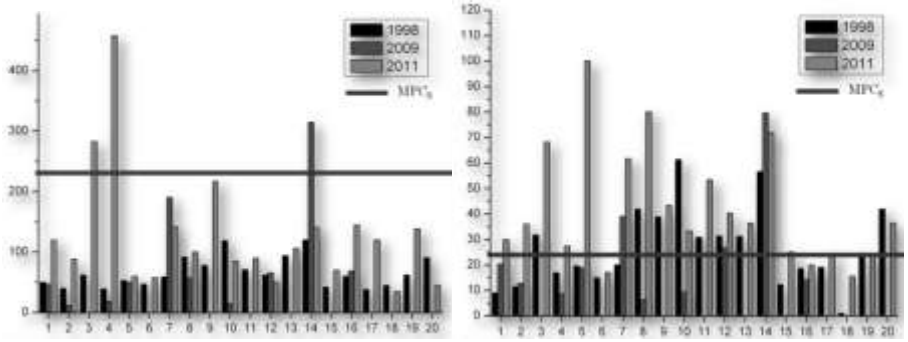
Table 5. Factor analysis of HM content in soils.

	Ivanovo region, 2010					
	1	2	3	4	5	6
Cu gross	**0,83**					
Fe gross	**0,76**					
Ni gross	**0,76**		0,25	0,29		
Cd mov.		**0,95**				
Cr mov.		**0,94**				
Ni mov.	0,20	**0,83**				
Cd gross			**0,88**			
Cr gross	-0,24		**0,82**			
Pb gross	0,21		**0,79**	0,29		
Co gross	0,41		**0,50**	-0,34	-0,28	
Fe mov.				**0,88**		
Mn mov.	0,29			**0,82**		
Zn mov.					**0,68**	0,22
Zn gross	0,36				**0,68**	-0,34
Mn gross	0,43		-0,34		**-0,45**	
Cu mov.						**0,91**

	Ivanovo city, 2011				
	1	2	3	4	5
Ni mov.	**0,88**				
Ni gross	**0,87**				
Mn mov.		**0,75**			-0,41
Mn gross		**0,71**	-0,25		0,31
Fe mov.		**0,70**	0,21		
Zn mov.			**0,79**		
Fe gross		0,21	**-0,66**		
Zn gross				**0,91**	
Cu gross	-0,29				**0,80**
Cu mov.	0,52			-0,42	**0,53**

Conclusion

The situation with soil contamination in Ivanovo region was not uniform. Soils of samples, which were far away for large cities, characterized high level of quality. However they underwent influence of anthropogenic impact. It became apparent in raised content of HM at Northern-West industrially developed part of region.



a) b)

Fig. 3. Comparison of HM content (ppm) in Ivanovo city soil in different sampling sites from 1998 to 2011: a) Zn gross forms; b) Zn movable forms;

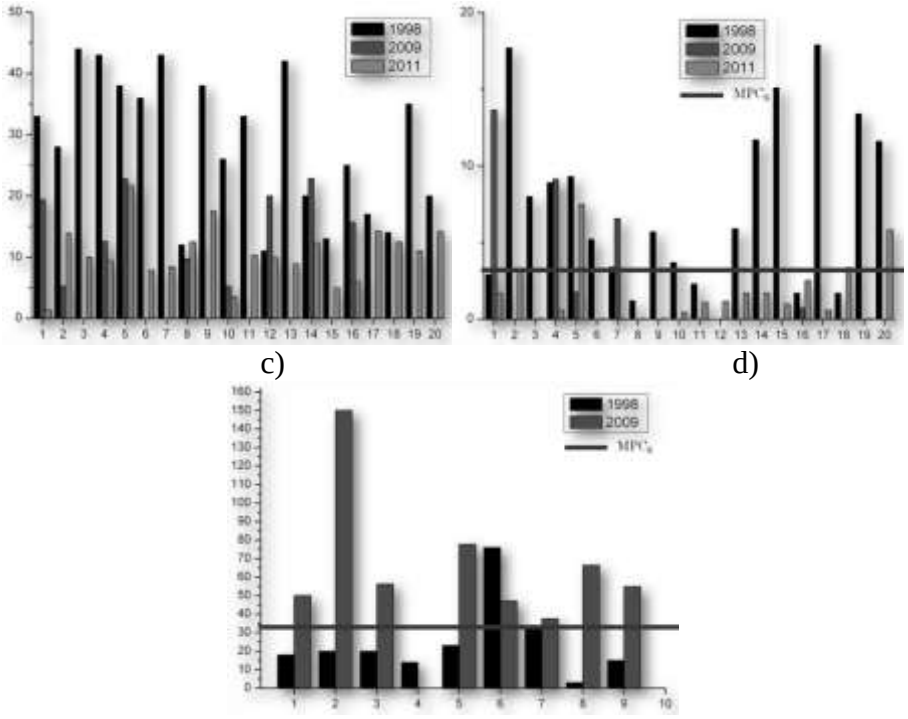


Fig. 3. Comparison of HM content (ppm) in Ivanovo city soil in different sampling sites from 1998 to 2011: c) Cu gross forms; d) Cu movable forms; e) Pb gross forms.

Otherwise soil contamination in Ivanovo city was very important. The concentrations of lead, copper, zinc and chromium were above permissible level. It pointed out a significant degree of anthropogenic stress caused activity of motor transport, power engineering and influence of solid waste.

It is necessary to do measures for detoxification of soils in regional center. HM can come to humans from soils and provoke diseases. Hence environmental monitoring must be carried out regularily.

Acknowledgements

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