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Geochemical features of heavy metals distribution in soils of the karst region of oil production (Perm region)

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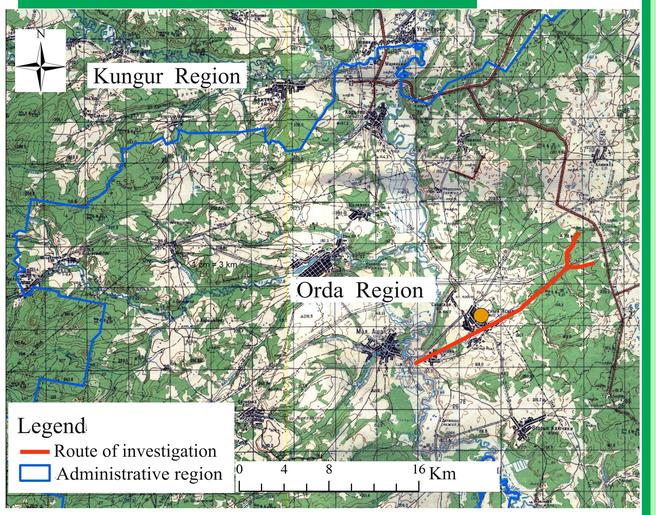
INTRODACTION

Different environments have chemical elements dissipated in uneven way. The knowledge of chemical content in investigated system or object helps to solve various environmental problems. Hydrocarbons deposits, oilfields, waste waters, industrial air emissions and car exhaust gas are considered as the general sources of petroleum and petroleum products entering karstlands. Soils are at the greatest risk of contamination among other karstlands' environments. They receive both upward and downward flows in the form of an industrial waste and emanations from oil plumes forming on the surface of karst waters in underground cavities respectively. Heavy metals pollution occurs when petroleum and oilfield brine enter soil at oil production sites. Heavy metals accompanying hydrocarbons and mineral salts enhance their negative influence and inhibit natural remediation process. It had been revealed that petroleum always contains two elements - Cr and Zn, and Cr with Zn are also detected.

MATERIALS & METODS

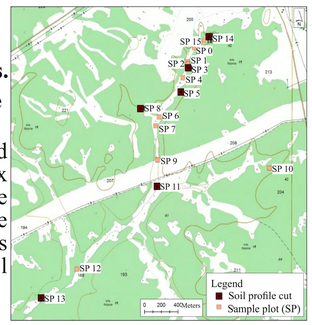


It is situated in oilfield affected zone, karst region of oil production.

The object of the research is soils.

The subject of the research is the content of heavy metals in soils.

In 2016 17 sample plots were laid out. Soil pits were located in six sample plots while 11 ones were provided with open test pits. The set of soil monitoring activities was performed, which includes soil sampling with further analysis.



Measurment of heavy metals content	By X-ray fluorescence spectrophotometry using wavelength-dispersive spectrometer «SPEKTROSKAN MAKS-G». Total content of the following elements was determined: Sr, Pb, As, Zn, Cu, Ni, Co, MnO, Cr, V, TiO_2.
The content of oil products	By infrared spectrometry.
Agrochemical analysis	pH of water and salt suspensions – by potentiometry; hydrolytic acidity – by Kappen's method; total exchangeable bases – by Kappen-Gilkowits method, cation exchange capacity (CEP) and degree of base saturation – by calculations; nitrate-nitrogen concentration by ion-selective method; labile phosphorous, potassium, sodium: in acid extract by Kirsanov's method; organic carbon content by Tyurin's method; calcareousness in acid extract by titration method.

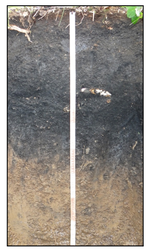
RESULTS

Investigated index	The results of the research
Active acidity	from acidic (pH=5.52) to neutral (pH=7.45)
Hydrolytic acidity	8,3–19,5 mg–eq/100 g
Total exchangeable bases	from medium (26 mg –eq/100 g) to high (47,5 mg –eq/100 g)
CEP index	from the values above the average to very high
Organic carbon content	from low (1.4%) to high (10.4%)

The soils have a low content of phosphorous and potassium, while the content of sodium varies from low to high. This could come from salinization connected with the influence oil products.

These soils are characterized as slightly calcareous. Calcareousness grows insignificantly with depth of soil profile.Cation exchange capacity (CEP) index varied from the values above the average to very high, what indicates unharmed state of the soils. High CEP values indicates buffering providing resistance of soils to degradation. Organic carbon content in topsoil of the area varies from low (1.4%) to high (10.4%). Several soils showed increased organic content in a subsurface layer exceeding this value of humus horizon.

Dark-grey forest
Haplic Phaeozem
(WRB 2014)
SP 5

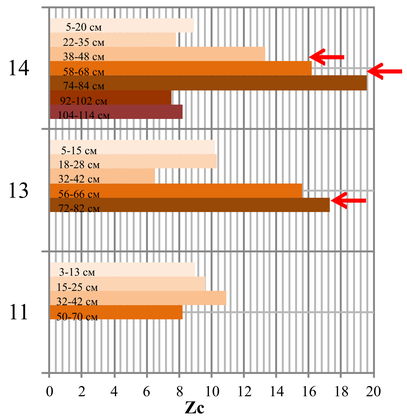


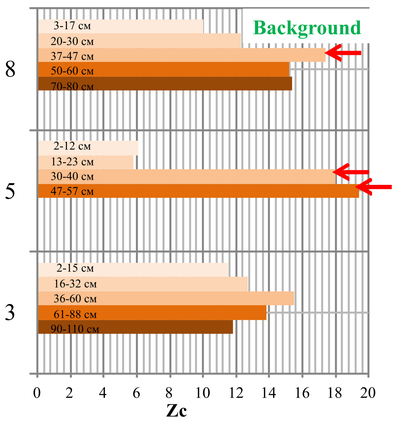
Alluvial humus
Umbic fluvisol
(WRB 2014)
SP 13

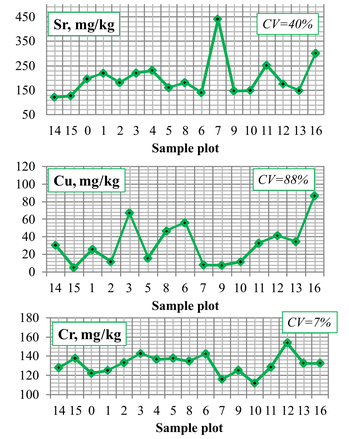
Grey forest
Grey luvic phaeozems
(WRB 2014)
SP 8

Toxilitestrate
Toxic technosol
(WRB 2014)
SP 3

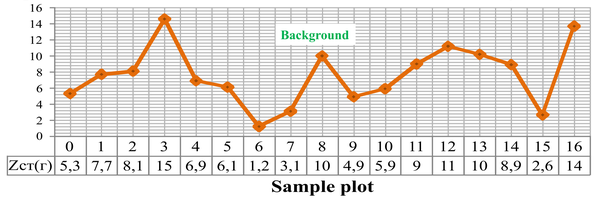
An extremely high level of contamination was revealed with the content of oil products exceeding 5000 mg/kg in two of analyzed samples (SP 3 in the depth of 90-110 cm and SP 16). Other samples show no exceedance of oil products level, however we can mark samples, besides from those, where high content was determined, that have more oil products than other: SP 2, SP 3 (2-15 cm, 2-32 cm), SP 15.







Considering the total of six sample plots (with background area) where soil pits were laid out we find the total level of pollution to be permissible (Zc is lower than 16), but some elements exceed allowable values and total level of soil pollution were revealed to exceed the level in the standard in some soil horizons. From this perspective we could define sample plots 5, 13 and 14 as the most contaminated with heavy metals.



	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Zcr(r)	5,3	7,7	8,1	15	6,9	6,1	1,2	3,1	10	4,9	5,9	9	11	10	8,9	2,6	14

All the values received lay within permissible limits of total chemical pollution of soils with heavy metals. The greatest index in upper horizons of soil was found in the sample plots 3, 12, 16 (the values exceed those in background area). Several sample plots (0, 1, 2, 4, 5, 6, 7, 9, 10, 11, 14, 15) have he same lower than in the background area.

Some series of elements has uneven distribution (according to the coefficient of variation – CV, %) within sample plots in the opposition to other evenly distributed. We found uneven distribution for Sr, Pb, Cu, Mn. Even distribution was found for As, Zn, Ni, Fe, Cr.

Correlation matrices

Sr	0,7							0,01 – 0,19	no correlation			
Pb	0,4	0,9						0,2 – 0,49	weak correlation			
As	-0,1	0,2	0,4					0,5 – 0,69	medium correlation			
Zn	0,3	0,8	0,8	0,7				0,7 – 0,99	high correlation			
Cu	0,4	0,9	0,8	0,1	0,8							
Ni	0,4	0,9	0,9	0,2	0,8	0,9						
Co	0,5	0,7	0,6	0,7	0,9	0,5	0,5					
Fe_2O_3	0,0	0,6	0,7	0,9	1,0	0,6	0,6	0,8				
MnO	0,5	0,4	0,2	-0,2	0,4	0,6	0,4	0,5	0,1			
Cr	0,4	0,0	-0,1	0,1	0,2	0,1	-0,2	0,5	0,0	0,8		
V	0,4	0,9	0,9	0,5	1,0	0,9	0,9	0,8	0,9	0,5	0,1	
TiO_2	0,1	0,2	0,1	-0,2	0,3	0,5	0,2	0,2	0,1	0,9	0,7	0,3
	Oil	**Sr**	**Pb**	**As**	**Zn**	**Cu**	**Ni**	**Co**	**Fe_2O_3**	**MnO**	**Cr**	**V**

We found high level of correlation between the concentration of oil products and Sr content. The medium degree of correlation is found between oil products content and the content of Co and MnO. A weak correlation is between Pb, Zn, Cu, Ni, Cr, V content and oil products content.

CONCLUSION

To sum up, comparison of the data on the content of heavy metals in the upper horizon of studied sample plots and background area provides us with the understanding that they are all quite comparable in their extent. However, we have few exceptions, which significantly differ from the background, as you can see in the graphs.

In addition, the content of heavy metals within the area doesn't exceed standards, and total chemical pollution stands within permissible limits.