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STANDARDIZATION OF HEAVY METALS AND OIL CONTENT BY BIOLOGICAL INDICATORS IN THE SOUTHERN CHERNOZEMS OF THE TAMAN

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ABSTRACT

This paper provides an assessment of the resistance of Taman chernozems to contamination with heavy metals (Cr, Cu, Ni, Pb) and oil by biological parameters. As a rule, upon contamination of the Taman chernozems, a significant reduction was observed in the total bacterial count, activity of catalase and dehydrogenase, cellulolytic activity, abundance of the *Azotobacter* genus bacteria and in the radish germination intensity. The extent of the deterioration in biological properties was determined by two factors: the chemical nature of the metal and its amount in the soil. As a rule, a direct relationship was observed between the concentration of the pollutant and the degree of deterioration of the soil properties in this study. The metals studied had shown different ecotoxicity with respect to the chernozems of Taman: Cr > Cu ≥ Ni = Pb Regional norms for the maximum allowable content of Cr, Cu, Ni, Pb, and oil in the Taman southern chernozems based on a disturbance of the ecological functions of soils were proposed.

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1 Introduction

In December 2018, the construction of an automobile and railway bridge between the Taman and the Crimean Peninsula through the Kerch Strait, connecting the Azov and Black Seas, will be ended. A sharp increase in traffic flow through Taman to the Crimea and the development of associated road and resort infrastructure can cause increased pollution of the soils of the Taman Peninsula with heavy metals (HMs), oil and petroleum products.

Taman has unique soils that have no analogues in the world (Val'kov et al., 2008). Before 1977, they were called chestnut chernozem, according to the ecological and genetic classification of Russian soils of 1977 - southern chernozems (Classification and diagnosis of soil of USSR, 1977). In the substantive-genetic classification of Russian soils of 2000, there was no place for Taman chernozems (Val'kov et al., 2006). According to the World Reference Base for Soil Resources (WRB) classification, these soils are called Chernozems Calcic (World Reference Base for Soil Resources, 2006), which does not reflect their genetic and ecological characteristics.

The chernozems of Taman noticeably differ in their properties from other types and subtypes of black and other soils in southern Russia (Kazee & Kolesnikov, 2015; Kuzina et al., 2015). These differences in soil genetic characteristics determine their different resistance. However, to date, the limits of their resistance to chemical pollution have not been established.

The purpose of this work is to assess the resistance of the southern Taman chernozems to the contamination with HMs (Cr, Cu, Ni, Pb) and oil by biological indicators; and to determine quantitative guidelines for the development of regional standards for the maximum permissible concentration (MPC) of Cr, Cu, Ni, Pb and oil in the southern Taman chernozems based on the violation of ecological and agricultural soil functions.

2 Materials and Methods

Contamination with HMs and oil has been modeled in laboratory conditions. The southern chernozem (chestnut) of southern European facies (Russia, Krasnodar Region, Temryuk District, 2 km from the city of Taman to the south, 45° 10'51.73 "N, 36 ° 41'30.47" E) has been used as the object of the study. The soil for model experiments has been selected from the top layer of 0-25 cm, since this is the layer where most of the soil pollutants accumulate.

The soil under study is characterized by an average humus content in the upper horizon of 3.2%, neutral reaction of the medium of pH 7.7, heavy loam granulometric composition, high absorption capacity, good structural stability, oxidative conditions, sufficiently high biological activity (the total bacterial count – 4.2 bln/g of soil, catalase activity - 7.3 ml O_2/g of soil per 1 min, dehydrogenase activity - 16.5 mg TFP/10g of soil for 24 hours, and an abundance of the *Azotobacter* genus bacteria - 100% fouling mass) These properties have been defined using traditional methods (Soil Microbiology and Biochemistry Methods, 1991; Kazeev et al., 2016).

Cr, Cu, Ni, and Pb have been chosen as pollutants, since the soils in southern Russia are largely polluted by these HMs (D'yachenko & Matasova 2016). Moreover, the HMs selected are interesting for comparison their maximum permissible concentration (MPC) (100 mg/kg of soil). In present study, MPC values developed in Germany (Kas'yanenko 1992) have been used, because there is no MPC has been reported from the soil of Russia (the gross content of copper, nickel and other components are less than the required for the estimation of MPC). The concentration of oil in the soil was expressed as a percentage. This is due to the fact that the oil MPC in the soil has not been developed so far.

HM was applied to the soil in the amount of 1, 10, 100 MPC (100, 1000 and 10,000 mg/kg, respectively), oil in the amount of 1, 5, 10% of the soil mass. The HM content up to 100 MPC or even greater is often found in areas soil near metallurgical, chemical and fuel industries. In addition to these sources, soil contamination up to 10 MPC is usually caused by road transport and/or as a result of agricultural activities: mineral fertilizers, pesticides, and seed disinfectants. Soil contamination with oil of up to 10% of the soil mass is more common in areas with oil production, transportation and refining (Kabata-Pendias 2010).

HM were introduced into the soil in the form of oxides: CrO3, CuO, NiO, PbO. There are two reasons for this. Most of the HM enters the soil in the form of oxides (Kabata & Pendias 2010). The use of oxides eliminates the influence of anions on the soil, as in the case of the use of salts.Contaminated soil was incubated in three replications for 30 days at a temperature of 20-22°C and a humidification of 60% of the field moisture capacity.

Biological properties of soil have been determined 30 days after contamination. This period is the most informative in assessing the chemical effect on the biological state of the soil (Kolesnikov et al., 2000).

The total bacterial count, the abundance of the bacterial genus Azotobacter, the activity of catalase and dehydrogenase, cellulolytic activity, phytotoxic properties of soils and other indices have been by using conventional methods (Soil Microbiology and Biochemistry Methods, 1991; Kazeev et al., 2010).

To combine a large number of indicators, special methodology has been developed for determining the integral index of the biological state of the soil (IIBS) (Kazeev et al., 2016). This technique allows assessing the biological state of the soil as a whole.

3 Results and Discussion

As a result of the study, it has been found that the pollution of the southern chernozems of the Taman with Cr, Cu, Ni, Pb, and oil leads to deterioration of its state (Table 1). In most cases, the values of all the biological indicators studied have been reliably reduced. The values of the dehydrogenase activity, the length of the radish roots, and the cellulosolytic activity have been declining. The abundance of Azotobacter bacteria, the total number of bacteria, and the catalase activity decreased to a lesser extent.

Table 1 The impact of chemical aggression on biological propertiesof the southern chernozems of the Taman

Element (substance)	Dose of pollutant				
	Control	1 MPC (1 %)	10 MPC (5 %)	100 MPC (10 %)	*LSD05**
Total bacterial count, billion per 1 g of soil (n = 720: 3 incubation vessels with soilx 3 soil samples x 4 square centimeters on specimen slides x 20 fields of view)					
Cr	4.2	2.9	1.6	1.3	0.3
Cu	4.2	4.1	2.7	1.7	0.2
Ni	4.2	4.3	2.8	1.9	0.2
Pb	4.2	4.1	3.3	3.1	0.3
Oil	4.2	2.9	2.4	2.2	0.4
LSD05		0.3	0.3	0.3	
Catalase activity, ml O_2 per 1 g soil for 1 min (n = 36: 3 incubation vessels with soil x 3 soil samples x 4 analytical replications)					
Cr	7.3	6.8	4.6	1.6	0.7
Cu	7.3	7.9	6.8	5.1	0.5
Ni	7.3	7.7	7.1	6.6	0.5
Pb	7.3	7.5	7.0	6.6	0.5
Oil	7.3	6.7	2.3	1.0	0.6
LSD05		0.6	0.6	0.6	
Activity of dehydrogenase, mg TTF per 10 g soil for 24 hours (n = 36: 3 incubation vessels with soil x 3 soil samples x 4 analytical replications)					
Cr	16.5	12.8	10.2	3.2	1.4
Cu	16.5	13.7	12.6	7.3	1.7
Ni	16.5	16.5	12.2	8.3	1.8
Pb	16.5	15.8	10.6	6.9	1.7
Oil	16.5	4.2	1.4	0.8	0.8
LSD05		1.4	1.1	0.9	
Cellulosolytic activity,% of control (n = 9: 3 incubation vessels with soil x 3 pulp webs)					
Cr	100	35	15	6	10
Cu	100	98	82	61	6
Ni	100	98	73	55	4
Pb	100	100	86	68	7
Oil	100	63	39	18	12
LSD05		8	9	11	

Element (substance)	Dose of pollutant				
	Control	1 MPC (1 %)	10 MPC (5 %)	100 MPC (10 %)	*LSD05**
Abundance of the Azotobacter genus bacteria, % of fouling mass (n = 241: 3 incubation vessels with soil x 3 soil samples in Petri cups x 25 fouling clusters)					
Cr	100	100	69	7	10
Cu	100	100	92	88	13
Ni	100	100	100	93	9
Pb	100	100	85	81	12
Oil	100	100	91	86	7
LSD05		12	12	14	
Length of radish roots (phytotoxicity),% of control (n = 241: 3 incubation vessels with soil x 3 soil samples in Petri dishes x 25 radish seeds)					
Cr	100	46	13	0	9
Cu	100	90	58	31	4
Ni	100	89	63	33	5
Pb	100	99	64	28	6
Oil	100	74	43	36	9
LSD05		11	8	6	
Integral indicator of the biological state of the soil (IIBS), % of control					
Cr	100	70	43	14	
Cu	100	96	77	56	
Ni	100	99	79	61	
Pb	100	99	79	64	
Oil	100	71	52	35	

* Note: If the difference between the test cases (for example, between Control and 1 MPC, or Control and 10 MPC, etc.) is greater than LSD05, then the impact of contamination is significant.

Since the MPC of all the four studied HMs is the same (100 mg/kg), it is possible to correctly compare their toxic effect with respect to the biological parameters studied. The results obtained from this study indicated that the chromium had most significant negative effect. Three other HMs (lead, copper and nickel) showed lesser impact as compared to this.

Accordingly, by the degree of negative impact on the chernozem of the southern Taman series of HMs looks as follows: Cr>Cu ≥ Ni = Pb. A similar pattern was obtained in the studies carried out using the same method with other soils in the south of Russia: ordinary chernozem, leached, typical, compacted, mountain (Kolesnikov et al., 2014), chestnut, brown semidesert, solonets, sandy (Kolesnikov et al., 2011), brown (Kolesnikov et al., 2016a), brown forest (Kolesnikov et al., 2016b), solonchaks (Kolesnikov et al., 2016c) etc.

However, such a sequence of HMs by their environmental hazard for soils does not always coincide with the previously obtained data on other types of soils (Van de Plassche & De Bruijn, 1992; Crommentuijn et al., 1997; Vodyanitsky 2012). It is possible that the higher toxicity of chromium in chernozems is due to the fact that chromium is more mobileze in higher alkaline and oxidizing conditions (Zachara et al., 1989), and low toxicity of lead is due to a higher content of humic acids in chernozems, which bind to the lead more strongly than copper (Morin et al., 1999; Manceau et al., 2002).

It is not advisable to compare the toxic effects of HMs and oil especially by using genetic methods (Trushin et al., 2013), since it is impossible to correctly compare their concentrations in the soil. As a rule, there is a direct relationship between the concentration of the pollutant in the soil and the degree of decrease biological parameters.

The biological indicators used in the study (the bacterial count, the activity of catalase and dehydrogenase, cellulolytic ability, the abundance of the bacterial genus Azotobacter, the length of radish roots) had confirmed their compliance with the necessary requirements for indicators used to monitor, diagnose and normalize chemical contamination of soils. They are distinguished by high informativeness and sensitivity, sufficient reproducibility, allowable variation of the indicator, small error of the experiment, simplicity, low laboriousness and high speed of determination methods, abundance of methods, etc.

The study made it possible to establish quantitative benchmarks to develop regional standards for the MPC of Cr, Cu, Ni, Pb, and oil in chernozems of the southern Taman, based on a disturbance of the ecological and agricultural functions of soils.

Further, it was reported by Kolesnikov et al. (2002) that the disturbance of the ecological functions of the soil occurred in a certain order. Ecosystem functions are initially violated and followed by biochemical, physico-chemical and chemical ones. Physical functions are violated aftermost, already with very strong soil contamination (Classification of ecosystem functioning of soil is provided as per the Dobrovolsky & Nikitin, 1990). This pattern can be used for environmental regulation of soil pollution. It is useful to use IIBS to assess the violation of certain eco-functions. It has been established that when IIBS values have decreased by less than 5%, the soil normally fulfills its ecological functions while this reduction in IIBS values reached by 5-10% violation of informational eco-functions reached by 10-25% violation in biochemical, physicochemical, chemical and holistic functions and 25% violation was reported in physical functions (Kolesnikov et al., 2002). Using the results of the study, regression equations were constructed between the number of pollutant in the soil and the IIBS. The regression equations have determined the concentrations of pollutants that cause a violation of certain soils eco-functions (Table 2).

The suggested approach and the quantitative values of pollutant content in the soil that cause disturbance of different groups of ecological functions seem appropriate to be used in ecological standardization, where the main goal should be to preserve the ecological functions of the soil.

Conclusion

Pollution of southern chernozems of the Taman with oxides of Cr, Cu, Ni, Pb, oil leads to the deterioration of its biological properties, the total bacterial count, as well as the activity of catalase and dehydrogenase, cellulolytic ability, abundance of the Azotobacter genus bacteria decrease, and the germination and initial radish growth deteriorate. The extent of the deterioration of biological properties is determined by two factors: the chemical nature of the metal and its amount in the soil.

In most cases, a direct relationship between the pollutant content in soil and the degree of decrease in biological indices was recorded for all the HMs and oil studied. The investigated HMs form the following series in terms of the degree of negative effect on the biological properties of the southern chernozem (a series is averaged over the pollutant doses): Cr > Cu ≥ Ni = Pb.

Table 2 Scheme of ecological standardization of the content of HMs and oil in the southern chernozems of the Taman according to the degree of disruption of ecological functions

Soils	Non-contaminated	Weakly contaminated	Medium contaminated	Strongly contaminated
Degree of decrease in the integral indicator[1]	< 5 %	5 – 10 %	10 – 25 %	> 25 %
Disturbed environmental functions[2]	–	Informational	Chemical, physicochemical, biochemical; holistic	Physical
Element	HM content in soil, mg/kg			
Cr	<105	105-115	115-145	> 145
Cu	<60	60-120	120-350	>350
Ni	<65	65-120	120-350	>350
Pb	<60	60-120	120-350	>350
Substance	Oil content in soil,%			
oil	< 0.25	0.25-0.50	0.50-1.5	>1.50

Note: 1. Definition of the integral indicator by (Kazeev et al., 2016). 2. Classification of environmental functions by (Dobrovolsky & Nikitin 1990).

The conducted study confirmed the feasibility of the use of microbiological indicators, enzyme activity and phytotoxicity to assess soil conditions in the context of chemical contamination.Regional norms for the MPC of Cr, Cu, Ni, Pb, and oil in southern chernozems of the Taman based on the disturbance of the ecological functions of soils are proposed.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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