ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Biological Condition of the Brown Forest Soils of the Western Caucasus at Pollution by Cadmium, Zinc, Molybdenum and Selenium.

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ABSTRACT

In recent years, the anthropogenic load on the soil cover of Western Caucasus has grown considerably. It is associated with the strong economic, recreational and touristic development of the region, including the use of the infrastructure of the Winter Olympic games 2014 in Sochi. The limits of stability of soils of the region to the various anthropogenic impacts, including chemical pollution, are investigated insufficiently. Most of the territory of the Western Caucasus is a brown forest soil. Because of their ecological and genetic characteristics they have little buffer capacity to chemical pollution. As shown by the study, pollution with cadmium, zinc, molybdenum or selenium results in a deterioration of the biological properties of brown forest soils of the Western Caucasus. As a rule, the degree of reduction values of biological indicators is directly dependent on the concentration of soil contaminants. In terms of toxicity to the biological properties of brown forest soils of the studied elements form the following sequence: Cd > Se > Mo > Zn.

Keywords: Cadmium, zinc, molybdenum, selenium, pollution, brown forest soils, biological condition, Caucasus

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ISSN: 0975-8585

INTRODUCTION

In recent years, the anthropogenic load on the soil cover of Western Caucasus has grown considerably. It is associated with the strong economic, recreational and touristic development of the region, including the use of the infrastructure of the Winter Olympic games 2014 in Sochi. The limits of stability of soils of the region to the various anthropogenic impacts, including chemical pollution, are investigated insufficiently.

Most of the territory of the Western Caucasus is a brown forest soil [1, 2]. Because of their ecological and genetic characteristics (low humus content, acidic environment, low biological activity, etc.) they have little buffer capacity to the chemical pollution [3].

In previous works we have investigated the influence of the pollution of Cr, Cu, Ni, Pb [4, 5], oil, gasoline, fuel oil and diesel fuel on the biological properties of brown forest soils of the Western Caucasus to [5, 6].

The aim of this work is to investigate the status of the brown forest soils of Western Caucasus, according to their biological indicators in the conditions of a model experiment with the pollution of Cd, Zn, Mo, Se.

METHODS

As the object of the study was investigated brown forest soil (Russia, Adygeya Republic, Maikop district, a neighborhood of p. Nickel). According to the classification of a World Reference Base for Soil Resources (WRB) these soils are called Leptosols Yermic [7].

The investigated soil is characterized by a low content of organic matter in the upper horizon - 2.7 %, by an acidic environment - pH of 5.6, by a medium loamy granulometric composition and a low biological activity.

The soil for the experiments was selected from the top layer (0-20 cm). In this layer accumulates the main quantity of polluting ground substances.

As the pollutants were selected Cd, Zn, Se, Mo, as the contamination of soils by these elements in the South of Russia is not uncommon [8].

Zinc, cadmium and molybdenum were added to the soil in the form of oxides (CdO, ZnO, Mo_2O_3), selenium — in the form of selenous acid (H_2SeO_3). In such forms the studied elements are often immitted into the soil [9].

Was studied the effect of different concentrations of pollutants in the soil: 1, 10, 100 MPC. Were used the MPC values developed in Germany [9], because the MPC in the soil for the total forms of zinc, molybdenum and selenium in Russia was not developed. The MPC for Cd in an air-dry soil is 3 mg/kg, for Zn — 300, for Mo — 10, for Se — 10.

To compare properly the strength of the impact of various elements on the properties of the soil as the reference system of the element content in soil was adopted the MPC, but not the amount in mg/kg in the soil. First, the different elements contained in the soil are not comparable, if they are studied in mg, in quantities that differ in 100 times. Second, they have different toxicity.

The study attempts to analyze the whole range of concentrations of the studied elements in the soil, occurring currently in nature. The contents of up to 100 MPC and more in soil are often found in areas of the enterprises of chemical, metallurgical and fuel industry. Soil contamination of up to 10 MPC, in addition to these sources, is a consequence of agricultural activities — application of mineral and organic fertilizers, sewage, pesticides, plant growth stimulants, etc [9].

ISSN: 0975-8585

The soil was incubated in pots at a room temperature and the optimum moisture content in triplicates.

The condition of the soil was determined in 30 days after contamination. This period proved itself as the most informative in the study of the effects of a chemical pollution on the biological properties of soil [10].

Laboratory and analytical studies were performed using standard methods in biology and soil ecology [11, 12]. We used biological indicators as the most sensitive and informative. We determined the abundance of bacteria of the genus *Azotobacter*, catalase and dehydrogenase activity, cellulolytic activity, phytotoxic properties of soils and other indicators.

For combining a large number of indicators were developed the methods of determining of the integral indicator of the biological status of the soil (IBSS) [12]. This technique allows assessing the biological condition of the soil in a whole.

RESULTS

In the result of the study it was found that the pollution of a brown forest soil of the Western Caucasus with Cd, Zn, Mo, Se led to the deterioration of its condition.

As a rule, it was observed a significant decrease of the values of all the studied biological indicators: catalase activity, dehydrogenase, cellulolytic activity, the abundance of bacteria of the genus *Azotobacter*, root length of radish, the IBSS of soil (table. 1).

Table 1: The effect of chemical pollution on biological properties of brown forest soils of the Western Caucasus

Element (substance)	Dose contaminants				
	Control	1 MPC	10 MPC	100 MPC	*HCP05*
The total number of bacteria, billion per 1 g of soil					
Cd	2,4	1,5	1,1	0,5	0,2
Zn	2,4	1,5	0,9	0,4	0,2
Mo	2,4	1,7	1,2	0,8	0,2
Se	2,4	1,9	1,2	0,8	0,2
HCP05		0,2	0,1	0,1	
The catalase activity, ml O2 for 1 gr of soil in 1 min					
Cd	2,9	2,7	2,3	1,7	0,2
Zn	2,9	2,3	2,2	0,9	0,2
Mo	2,9	2,6	2,5	1,9	0,2
Se	2,9	2,5	1,9	1,1	0,2
HCP05		0,1	0,2	0,1	
Activity of dehydrogenase, mg of TTF for 10 g of soil in 24 hours					
Cd	11,2	9,7	7,3	3,1	1,1
Zn	11,2	6,5	4,1	2,1	0,8
Mo	11,2	10,4	6,9	3,1	1,1
Se	11,2	8,9	6,0	2,6	1,0
HCP05		0,7	0,6	0,3	
Cellulolytic activity, % of control					
Cd	100	85	49	15	10
Zn	100	82	41	12	9
Mo	100	90	55	32	11
Se	100	87	39	19	10
HCP05		8	7	4	

ISSN: 0975-8585

The abundance of bacteria of the genus Azotobacter, % of lumps fouling					
Cd	23	20	17	10	3
Zn	23	17	11	8	2
Mo	23	21	17	14	3
Se	23	19	15	7	2
HCP05		2	1	1	
Root length of garden radish (phytotoxicity), % of control					
Cd	100	29	31	24	8
Zn	100	42	33	21	8
Mo	100	51	37	31	9
Se	100	72	57	51	12
HCP05		5	5	12	
The integral indicator of the biological status of the soil (IBSS), % of control					
Cd	100	74	57	32	
Zn	100	67	46	23	
Mo	100	81	61	42	
Se	100	81	55	33	

Similar patterns of deterioration of the biological conditions of brown forest soils were recorded earlier in their pollution of Cr, Cu, Ni, Pb [4, 5], oil, gasoline, fuel oil and diesel fuel [5, 6].

The degree of reduction of biological indicators in most cases was in a direct proportion between the concentration in soil contaminants.

The biological indicators used in a study (activity of catalase and dehydrogenase, cellulolytic ability, abundance of bacteria of the genus *Azotobacter*, root length of radish) can be used for monitoring, diagnostics and standardization of a chemical contamination of brown forest soil with Cd, Zn, Mo, Se.

The study has allowed establishing quantitative reference points for the development of regional standards for the maximum permissible concentration of Cd, Zn, Mo, Se in brown forest soils of the Western Caucasus on the basis of violation of the ecological functions of the soil.

In [13] it was shown that the violation of the ecological functions of the soil is in a predetermined rotation.

With increasing of chemical concentrations of soil a breakdown of ecosystem functions that it performs occurs in the following sequence: informational $\rightarrow$ biochemical, physicochemical, chemical and integral $\rightarrow$ physical. (Classification of ecosystem functions of soils is given according to [14]).

The fact that various ecological functions of soil are disturbed in the different concentration of the contaminant in the soil, can be the basis of ecological regulation of soil pollution. As a criterion of the degree of disturbance of ecological functions of soil are encouraged to use the IBSS. It is established that if the values of the IBSS decreased less than 5 %, then the soil will perform their ecological functions well, at lower values of the IBSS, if decreased less than 5-10% it would be observed a violation of informational ecological functions, on 10-25% - a violation of biochemical, physicochemical, chemical and integral functions, more than 25 % — physical functions [13].

According to the results of the present study was determined the regression equation, reflecting the dependence of the reduction of the values of the IBSS from a content of soil contaminants. According to these equations, we calculated the concentrations of pollutants at which there is a violation of certain groups of ecological functions of the soil (table. 2).

Table 2: The scheme of environmental regulation of the content of Cd, Zn, Mo, Se in brown forest soils of the Western Caucasus according to the degree of violation of the ecological functions

Soil	Not polluted	Slightly polluted	Medium polluted	Much polluted
A degree of an integral index reduction[1]	< 5 %	5 – 10 %	10 – 25 %	> 25 %
The violated ecological functions[2]	–	Informational	Chemical, physico-chemical, biochemical; holistic	Physical
Element	The content of heavy metals in soil, mg/kg			
Cd	< 0,5	0,5-1,0	1,0-4,0	> 4
Zn	< 80	80-100	100-250	> 250
Mo	< 2	2-4	4-20	> 20
Se	< 1	1-2	1-10	> 10

1.The definition of the integral index according to [12].
2.Classification of environmental functions according to [14].

The proposed approach and the obtained quantitative values of contaminants in the soil, causing the violation of different groups of environmental features, seems appropriate to use in an environmental regulation, where the main goal should be the preservation of the ecological functions of the soil.

As can be seen from table 2, the range of toxicity of the investigated elements according to the degree of negative impact on biological properties of brown forest soils as follows: Cd > Se > Mo > Zn. A similar pattern was obtained earlier for the black humus [15]. Such a sequence of elements according to their ecological hazard for soil partially coincides with the results of other researchers in which the selenium and cadmium were also more toxic than zinc and molybdenum [16-18]. A comparative assessment of ecotoxicity of different chemical elements and their compounds in different soils requires a further research.

CONCLUSION

Pollution with cadmium, zinc, molybdenum or selenium results in a deterioration of the biological properties of brown forest soils of the Western Caucasus: reducing the total number of bacteria, the activity of catalase and dehydrogenase, cellulolytic ability, the abundance of bacteria of the genus *Azotobacter,* are worsening the indicators of germination and initial growth of radish.

As a rule, the degree of reduction of values of biological indicators is directly dependent on the concentration of soil contaminants.

In terms of toxicity to the biological properties of brown forest soils the studied elements form the following sequence (the number-averaged doses of contaminants): Cd > Se > Mo > Zn.

Were proposed the quantitative targets for the development of regional standards for the maximum permissible concentration of Cd, Zn, Mo, Se in brown forest soils of the Western Caucasus on the basis of violation of the ecological functions of the soil.

ACKNOWLEDGEMENTS

Investigation was supported by the Ministry of Education and Science of the Russian Federation (6.345.2014/К) and by the Leading Scientific Schools program (NSh-9072.2016.11).

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