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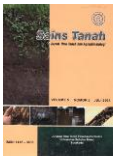

Approaches to the development of environmental standards for the content of petroleum hydrocarbons and Pb, Cr, Cu, Ni in soils of Greatest Caucasus

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ABSTRACT

The development of tourism and leisure infrastructure results in a continuous increase of anthropogenic impact on soils of wet and dry subtropics of the Greatest Caucasus. It is very important for the region to preserve the sustainable functions of soils and ecosystems, maintain a comfortable life and recreation environment create environmentally friendly agricultural products. It is conducted studies to determine the limits of resistance of soils in wet and dry sub-tropics to priority pollutants, especially petroleum hydrocarbons and heavy metals (Pb, Cr, Cu, Ni). It was found that the soils of wet and dry subtropics for resistance by Pb, Cr, Cu, and Ni are located as follows: southern chernozem > typical sod-carbonate soil ≥ brown typical soil ≥ brown carbonate soil = brown leached soil ≥ leached sod-carbonate soil = yellow soil >acid brown forest soil ≥ acid brown forest podzolized soil. In terms of the degree of resistance to oil pollution, studied soils create certain series: brown carbonate ≥ brown typical = sod-carbonate leached ≥ sod-carbonate typical > southern chernozem ≥ yellow soil ≥ brown leached soil > acid brown forest soil = acid brown forest podzolized soil. Heavy metals by ecotoxicity to the soils of wet and dry subtropics from the following series: Cr> Cu ≥ Ni = Pb. Based on the degradation of ecological functions of soils, we offer regional standards of the maximum permissible content of Pb, Cr, Cu, and Ni for the main soils of wet and dry subtropics.

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1. INTRODUCTION

A negative impact on all components of ecosystems is noted when exposed to toxic inorganic and organic substances. Heavy metals (HM) are the most dangerous pollutants in the environment due to their toxicity and ability to accumulate in the environment (Cai et al., 2019; Guan et al., 2018; Kabata-Pendias, 2010). Contamination with these elements is most often found because of recreational load (Memoli et al., 2019). Once entering the soil, heavy metals can be absorbed and accumulated in different parts of plants through the root system. Soil contamination by metal oxides occurs more often than in other chemical forms (Kabata-Pendias, 2010). An increase in the concentration of HM in the soil adversely affects not only the growth of the plants themselves, but also a negative effect on the size, activity, and composition of the microbial community was noted (Adesina & Adelasoye, 2014; Kolesnikov et al., 2019; Kolesnikov et al., 2021; Timoshenko et al., 2021).

Petroleum hydrocarbons are apriority pollutants of the environment due to their toxicity, spread, scale of pollution, and high migration ability (Bandura et al., 2015; Bieganowski et al., 2018). The development and operation of petroleum hydrocarbon fields, and violation of the rules of transportation lead to the pollution of natural ecosystems, in particular soil cover (Chen et al., 2019; Hewelke et al., 2018; Vodyanitskii et al., 2016). It is considered that soil pollution with petroleum hydrocarbons in this range (up to 10%) is most often observed in places of petroleum hydrocarbon production transportation and processing (Vodyanitskii et al., 2016). For decades, this region has been a transport route for the export of crude oil. All this leads to an increase in anthropogenic load on the soil cover, including an increased risk of oil and petroleum products entering the soil, which can lead to a decrease in its fertility and disruption of their functions.

The Black Sea coast of the Caucasus is an actively developing region with a progressively growing tourism and recreation infrastructure. But the construction of Olympic facilities, new buildings, oil pipelines, airports, roads, etc. constantly increases the risk of negative impact on the environment. To ensure sustainable functioning of soils of wet and dry subtropics, maintain a comfortable life and recreation environment, determine the maximum permissible anthropogenic load on the territory, obtain environmentally friendly agricultural products, it is necessary to establish the limits of soil resistance to priority pollutants, petroleum hydrocarbons and heavy metals. From 2020 to 2022, due to anti-COVID measures, there has been an increase in the tourist flow to the Black Sea coast of the Caucasus, which leads to the construction of new facilities, roads, oil pipelines, etc., which, in turn, increases the anthropogenic pressure on the environment.

At the same time, on the territory of soils of wet and dry subtropics of the Greatest Caucasus, there are protected and protected areas with a very diverse nature, unique for the world (Kazeev & Kolesnikov, 2015; Valkov et al., 2008). In the works of Chen et al. (2014) and Myrlyan and Bogdevich (2008) devoted to the study of soil pollution in dry and humid subtropics, the special sensitivity of these soils to chemical pollution is shown.

HMs have a significant effect on the state and composition of nutrients in soils, especially on compounds of mobile phosphorus and easily hydrolyzable nitrogen, converting them into insoluble states. HMs also affect the content of humus in soils. This is due to the influence of HMs on the binding of humic acids and their transformation into humates (Zybalov & Popkova, 2018). Many studies report a decrease in soil microbial activity and microbial biomass, inhibition of organic matter mineralization, and changes in the structure of the microbial community after HMs are introduced into the soil (Bai et al., 2021; Chu, 2018; Guo et al., 2017; He et al., 2016; Yao et al., 2017) TM ions have been shown to bind to cellular components such as DNA and proteins, causing DNA damage and conformational changes and may exhibit carcinogenic and genotoxic properties (Malar et al., 2014).

For soil microorganisms, petroleum hydrocarbons, on the one hand, are toxicants, and on the other hand, they are a source of nutrition. That is why their entry into the soil can lead both to an increase in activity and to the inhibition and degradation of the microbial pool. The response of the microbial pool to the presence of a pollutant is determined by the soil type, oil content, and characteristics of various groups of soil microorganisms (Kuznetsova et al., 2016).

In the Krasnodar Territory and the Republic of Adygea, the main sources of pollutants are vehicles and JSC EuroChem - Belorechenskiye Minudobreniya. It should be noted that the emissions of JSC EuroChem - Belorechenskiye Minudobreniya actively affect the concentration of heavy metals in the soil (Pb, Zn, Cd), as well as the soil pH (Peredelsky, 2009). On the territory of soil sampling, the combined effect of the Novorossiysk cement industry and geomorphological features leads to a significant scatter (up to 4.5 times) of the average content of pollutants in soils: Pb (4.5 times), Sr (1.7), Ag (2.2), Cu (1.7), Zn (2.5), Ga (1.5), Sn (1.6), Yb (1.5) (Pashkevich & Alekseenko, 2015). The environmental impact of the increase in the number of tourists on the territory of the Black Sea coast is due to the fact that, to one degree or another, the development of tourism leads to an increase in the number of new settlements, roads, structures, which in turn leads to the further development of urbanization and the development of large territories. All this affects the use of resources and causes negative consequences for many natural components, as well as for the ecosystems of cities (Polyakova & Zabelina, 2014). In order to avoid negative consequences for humans, as well as to preserve fertility and environmental role, many countries have developed a system for standardizing the content of chemical elements in soils using maximum allowable concentrations (MAC) or screening levels (Soil Screening Values, SSV) (Semenkov & Koroleva, 2019). There are two approaches to the development of SSV in the world. The first is focused on ecosystems and/or their individual components and is implemented, for example, in the USA, where there are two separate groups of standards that reflect the level of substances in soils that is safe for biota and humans (EPA, 2018). The second one prevents dangerous doses of substances from entering the human body with food and water and is practically implemented in "pure form" in Germany (für Altlasten et al.) and New Zealand (ANZECC, 1992). In Russia (GN 2.1.7.2041-06, GN 2.1.7.2511-0), the Netherlands (Brand et al., 2013; Crommentuijn et al., 2000; Lijzen et al., 2001) and Canada (CCME, 2018) both approaches harmoniously complement each other.

The purpose of the work is to develop ecological standards for the maximum content of petroleum hydrocarbons and Pb, Cr, Cu, Ni on soils of wet and dry subtropics of Greatest Caucasus for change of biological parameters.

2. MATERIALS AND METHODS

2.1 Study Site

Selection sites, names, and characteristics of the soils of Greatest Caucasus used in the study are shown in Figure 1 and Table 1. Soil samples for the model experiments were selected from the top layer of 0-10 cm, since most of the pollutants are retained in nonarable soils. The main soils of wet and dry subtropics were selected as objects of research. On this territory, there is a wide variety of soil types, which are probably distinguished by their resistance to anthropogenic influences. These are southern chernozems (chestnut), confined to dry steppes and characterized by a relatively small amount of soil organic matter, increased mineralization, and the presence of signs of salinity. Yellow soils, which have survived only in the Sochi region and make up 0.05% of the country's area (Gerasimova et al., 2010).

2.2 Heavy metals and petroleum hydrocarbons

Heavy metal (HM) and petroleum hydrocarbons contamination were simulated under laboratory conditions. It is investigated of contamination of soil with petroleum hydrocarbons and heavy metals: Pb, Cr, Cu, Ni. In the present study, heavy metals were introduced into the soil at concentrations of 100, 1,000 and 10,000 mg kg^{-1} (1, 10 and 100 MPC).

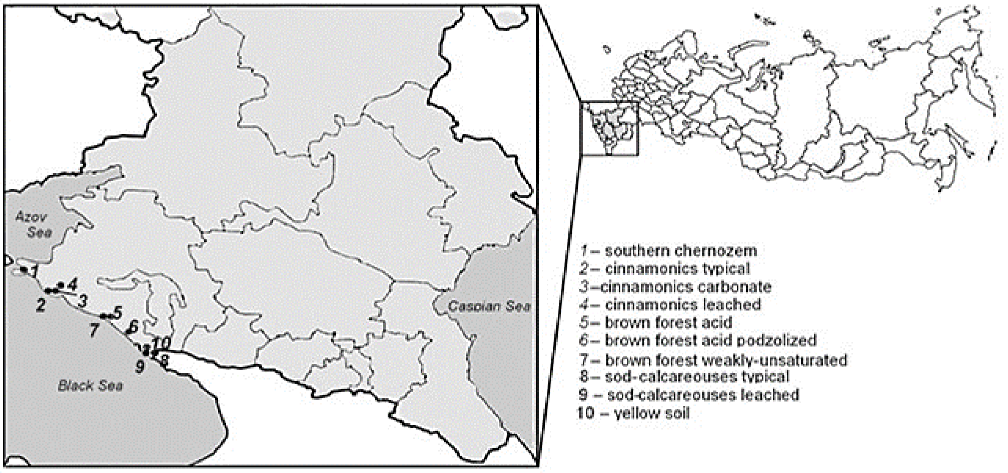


Figure 1. Schematic map of soil sampling sites on the Black Sea coast of the Greatest Caucasus

Table 1. Characteristics of the soils of wet and dry subtropics of soils of the Greatest Caucasus

No.	Type of soil	World Reference Base (2015)	Sampling place	Organic content (%)	pH	Soil texture
1.	Southern chernozem	Haplic Chernozems Pachic	Temryuksky District, city Taman	3.2	7.7	HL
2.	Brown typical soil	Haplic Cambisols Eutric	Anapsky District, State nature reserve “Utrish”	9.3	7.2	HL
3.	Brown carbonate soil	Haplic Cambisols Eutric	Anapsky District, State nature reserve “Utrish”	15.0	7.0	ML
4.	Brown leached soil	Haplic Cambisols Eutric	Anapsky District, State nature reserve “Utrish”	6.8	7.1	HL
5.	Acid brown forest soil	Haplic Cambisols Eutric	Tuapsinsky District, Gorskoe village	1.3	4.4	HL
6.	Acid brown forest podzolized soil	Haplic Cambisols Dystric	city Sochi, Lazarevsky City District, Sochi National Park	1.7	4.1	LL
7.	Sod-carbonate typical soil	Rendzic Leptosols Eutric	Tuapsinsky District, Dzhubga village	5.4	7.5	HL
8.	Leached sod-carbonate soil	Rendzic Leptosols Eutric	city Sochi, Khostinsky City District, Caucasus reserve, Thysosamshitovaia grove	4.8	6.9	HL
9.	Yellow soil	Albic Luvisols Abruptic	city Sochi, Adlersky City District	3.2	5.2	HL

Remarks: HL - Heavy loamy; ML - Middle loamy; LL - Light loamy.

For contamination of heavy metals was used metal oxides (PbO, CrO_3, CuO, NiO). The use of heavy metal oxides eliminates the effect on the soil properties of the accompanying anion, which is observed when the metal salts are introduced into the soil. For this purpose, the oxides, as the compounds that are practically insoluble in water, were previously grind up in a small amount of soil and then mixed with the rest of the soil mass.

The influence of 100, 1000, 10000 mg of HM per 1 kg of soil was studied, which corresponds to 1, 10, and 100 MAC of this element in Germany (Kloke, 2008). These values were chosen due to the fact that the permissible concentrations in the soil of the total content of copper and nickel in Russia have not been established, and the content of lead in Russian soils is several times higher than the established MPC (32 mg kg^{-1}). Thus, adding 100 mg kg^{-1} of Pb to the studied soils in addition to its background content gives the final concentration of lead in the soil equal to 3-4 background values. As shown earlier (Kolesnikov et al., 2019), many HMs begin to show a negative toxic effect just when a concentration of 3-4 backgrounds is reached.

Petroleum hydrocarbons were introduced in concentrations of 1, 5, 10% by weight of soil. Petroleum hydrocarbons was introduced into moist soil. In this study, the soil was subject to uniform contamination: after adding contaminant, the soil was stirred.

2.3 Experimental details

Three samples of contaminated soil were incubated in plastic vessels at 20 - 22 °C and 60% of water field capacity. The 30-day period is the most informative for assessing the chemical effect on soil since maximum decrease in values is observed within this period for most biological indexes.

2.4 Measurement procedures

To determine the biological properties of the soil, methods common to soil biology were used (Kolesnikov et al., 2019). The most sensitive and informative biological indicators have been studied. The total number of bacteria in the soil was taken into account using direct luminescence microscopy, taking into account the number of soil bacteria after staining with acridine orange dye (Kazeev et al., 2016). The state of the reducents in the ecosystem reflects the indicator of the total number of bacteria (Kolesnikov et al., 2020).

The abundance of bacteria of the genus Azotobacter sp. Abundance was taken into account by the method of fouling lumps on the Ashby medium. The medium was poured into Petri dishes and lumps of moistened soil were placed (25 pieces per 1 cup, incubation temperature 22-25 °C). These operations were performed in an antibacterial box. The number of fouling lumps was calculated 14 days after the start of the experiment. Catalase activity was determined by the method of Galstyan, estimating the volume of oxygen released after the decomposition of H_2O_2 in contact with the studied soil. The activity of dehydrogenases was determined by the method of reducing triphenyltetrazolium chloride to triphenylformazane according to the Galstyan method modified by (Khaziev, 2005). The indicator of the cellulose activity of soils was the volume of the decomposed the cotton cloth for 30 days. The size of the canvas matched the size of the bottom of the model box. Under laboratory conditions, the cotton cloth was laid in the soil at the beginning of incubation and after 30 days it was removed (Kazeev et al., 2016). The final stage - the cotton clothes were weighed. The volume was calculated from the difference in the weights of the lot before and after incubation, expressed as a percentage. Cellulolytic activity was estimated as % of the initial weight of the cotton cloth. The phytotoxic properties of the soil were assessed by the intensity of the initial growth of radish seedlings (Raphanus sativus L.). Previously, it was found that the speed of seed germination and root formation is most informative for radish plants (Kolesnikov et al., 2013); (Plekhanova et al., 2019); (Nikolaeva & Terekhova, 2017). Radish seeds were planted in a Petri dish from the soil mass - 25 seeds in Petri dishes. After 7 days of the experiment, radishes were extracted from the soil and the length of the radish roots was determined.

To establish the general patterns of change of biological properties of soils using the above indicators, we determined the integral index of the biological state (IIBS) of soils (Kolesnikov et al., 2019). For this purpose, indexes of unpolluted soil (control) were taken as 100%. Values of biological characteristics in unpolluted soil (control) were taken as 100%. The values of indexes in contaminated soil (variants of the experiment) were expressed as a percentage relative to above values (Equation 1).

$$IIBS = \frac{(V_1 + V_2 + V_3 + \cdots + V_n)}{N} \qquad [1]$$

Where, V_1, V_2, V_3, V_n – percentage value for each biological parameter of control; N – is the number of biological indicators.

2.5 Data analysis

To assess the reliability of the differences between the study options, an analysis of variance was carried out with a further determination of the LSD (least significant difference). Correlation analysis of the data was used to assess the information content of various biological parameters of soils, and regression analysis was used to determine the MPC values for oil in soil. The computer programs Statistica 12.0 and Python 3.6.5 Matplotlib were used for statistical processing.

3. RESULT

3.1 Ecotoxicity of chromium

It was carried out comparative assessment of resistance of the bulk soils of wet and dry subtropics to heavy metal pollution by the degree of decrease in soil IIBS. Soils of wet and dry subtropics do not have same resistance of biological indicators to pollution by different heavy metals. Series of soils ranked by the degree of negative change in biological indicators (the rows are averaged overdoses of a HM and petroleum hydrocarbons) are shown below (Table 2).

The sod-carbonate typical soil was found to be the most resistant soil to chromium pollution according to the change in IIBS - the indicator decreased by 37% below the control (Figure 2). Brown typical, brown carbonate, brown leached, acid brown forest podzolized soils are least resistant to chromium pollution - IIBS decreased by 48, 49, 51 and 52% relative to the control, respectively. Average indicators for resistance in the following types of soils: southern chernozem, yellow soil, leached sod-carbonate soil, acid brown forest soils - a decrease in the indicator by 43, 43, 44 and 46% relative to the control, respectively.

In case of chromium contamination: sod-carbonate typical soil (63) > southern chernozem (57) = yellow soil (57) ≥ sod-carbonate leached soil (56) ≥ acid brown forest soil (54) ≥ brown typical soil (52) ≥ brown carbonate soil (51) ≥ brown leached soil (49) ≥ acid brown forest podzolized soil (48).

3.2 Ecotoxicity of copper

The highest resistance to copper (Cu) contamination with respect to changes in IIBS was found in southern chernozem, brown leached and brown typical soils - IIBS is lower by 18, 20, and 21% relative to the control, respectively (Figure 3). Acid brown forest and acid brown forest podzolized soils were found to be least resistant to the effect of Cu. For these soils, a 38% and 42% decrease in IIBS was noted relative to the control, respectively. Average resistance indicators were found in brown carbonate soil, sod-carbonate typical soil, yellow soil leached sod- carbonate soil - a decrease of 25, 25, 26 and 30% relative to the control, respectively.

In case of copper contamination: southern chernozem (82) ≥ brown leached soil (80) ≥ brown typical soil (79) > brown carbonate soil (75) = sod-carbonate typical (75) ≥ yellow soil (74) > leached sod-carbonate soil (70) >acid brown forest soil (62) > acid brown forest podzolized soil (58).

3.3 Ecotoxicity of nickel

The southern chernozem was a more stable soil with the application of nickel (Ni) according to the change in IIBS - a decrease in the indicator by 15% (Figure 4). The least resistant to Ni contamination were acid brown forest soil and acid brown forest podzolized soil. In these soils, a 38% decrease in IIBS was recorded relative to the control. The average value for resistance was found in the following types of soils: brown carbonate soil, brown typical soil, sod-carbonate typical soil, brown leached soil, sod-carbonate leached soil, yellow soil - there was a decrease in IIBS by 22, 23, 23, 25, 25, and 28% of the control respectively. Nickel contamination: southern chernozem (85) > brown carbonate soil (78) ≥ brown typical soil (77) = sod-carbonate typical soil (77) ≥ brown leached soil (75) = sod-carbonate leached soil (75) ≥ yellow soil (72) > acid brown forest soil (62) = acid brown forest podzolized soil (62).

3.4 Ecotoxicity of lead

Under the influence of lead (Pb), the most stable soil according to IIBS is the southern chernozem – a decrease of 15% relative to the control (Figure 5). The least resistant soils to Pb pollution: acid brown forest and acid brown forest podzolized soils – decrease in IIBS by 35 and 41% relative to control, respectively. Average values of resistance in soils: typical brown soil, sod-carbonate typical soil, brown leached soil, brown carbonate soil, leached sod-carbonate soil, yellow soil – a decrease in the indicator by 21, 23, 24, 26, 26 and 26% relative to the control, respectively. Lead contamination: southern chernozem (85) > typical brown soil (79) ≥ sod-carbonate typical soil (77) ≥ brown leached soil (76) ≥ brown carbonate soil (74) = leached sod-carbonate soil (74) = yellow soil (74) > acid brown forest soil (65) > acid brown forest podzolized soil (59).

3.5 Ecotoxicity of petroleum hydrocarbons

When petroleum hydrocarbons (PHC) were applied by the most stable soils of wet and dry subtropics, according to the IIBS indicator, brown carbonate, brown typical and leached sod-carbonate soils showed themselves to be 26, 29 and 29% lower than in the control, respectively (Figure 6). Acid brown forest soils and acid brown forest podzolized soils were found to be least resistant to PHC impact – a decrease in IIBS by 43% relative to the control. Average soil stability is typical sod-carbonate soil, southern chernozem, yellow soils, brown leached soils – a decrease of 31, 35, 37, 38% relative to control is co-responsible.

In terms of resistance of soils of wet and dry subtropics after PHC (average) contamination, the following series are formed: brown carbonate soil (74) ≥ brown typical soil (71) = leached sod-carbonate soil (71) ≥ typical sod-carbonate soil (69) > southern chernozem (65) ≥ yellow soil (63) ≥ brown leached soil (62) > acid brown forest soil (57) = acid brown forest podzolized soil (57).

4. DISCUSSION

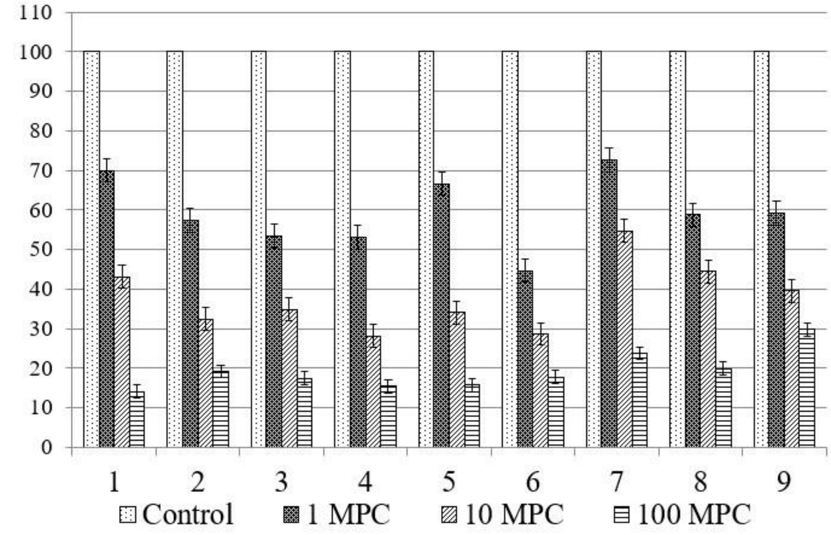
It is incorrect to compare the effects of heavy metals and PHC, as it is not possible to measure their concentration in the soil. The highest resistance to pollution with heavy metals (Cr, Pb Ni, Cu) was found in southern chernozem, and to PHC – in brown carbonate, brown typical and leached sod-carbonate soils. In term of degree of resistance to heavy metal pollution of soils of wet and dry subtropics, the following series (on average for Cr, Pb Ni, Cu) form: southern chernozem (77) > sod-carbonate typical (73) ≥ brown typical (72) ≥ brown carbonate (70) = brown leached (70) = sod-carbonate leached (69) = yellow soil (69) > acid brown forest (61) ≥ acid brown forest podzolized (57).

Regardless of the type of soil, chromium always shows greater ecotoxicity while lead, copper and nickel have less ecotoxicity. It was found that the pollution of the soils of wet and dry subtropics by PHC and heavy metals leads to a decrease in their biological parameters. It is noted that the change in the biological state of the soil directly depended on the properties of the soil itself, the concentration in the soil and the nature of the pollutant. However, in some cases stimulating effects of heavy metal on soil biological properties were observed, mainly in the 100 mg metal per kg soil. Such phenomena are widely known in ecotoxicology called as hormezis (a dose response phenomenon to xenobiotics or other stressors characterized by a low-dose stimulation). It is obtained series of heavy metal ecotoxicity with respect to the soils of wet and dry subtropics. Soil IIBS values averaged for three doses (1, 100, and 1000 MPC) are shown:

southern chernozem:
CrO_3 (57) > CuO (82) > NiO (85) = PbO (85)
brown typical soil:
CrO_3 (52) > NiO (77) ≥ CuO (79) = PbO (79)
brown leached:
CrO_3 (49) > NiO (75) ≥ PbO (76)> CuO (80)
brown carbonate soil:
CrO_3 (51) > PbO (74) ≥ CuO (75) > NiO (78)
acid brown forest soil:
CrO_3 (54) > CuO (62) = NiO (62) > PbO (65)
acid brown forest podzolized soil:
CrO_3 (48) > CuO (58) ≥ PbO (59) > NiO (62)
sod-carbonate typical soil:
CrO_3 (63) > CuO (75) ≥ NiO (77) = PbO (77)
sod-carbonate leached soil:
CrO_3 (56) > CuO (70) ≥ PbO (74) ≥ NiO (75)
yellow soil:
CrO_3 (57) > CuO (71) ≥ NiO (72) ≥ PbO (74)

Table 2. Change in the IIBS of soils of dry and humid subtropics of the Black Sea coast of the Greatest Caucasus with chemical pollution, % of control

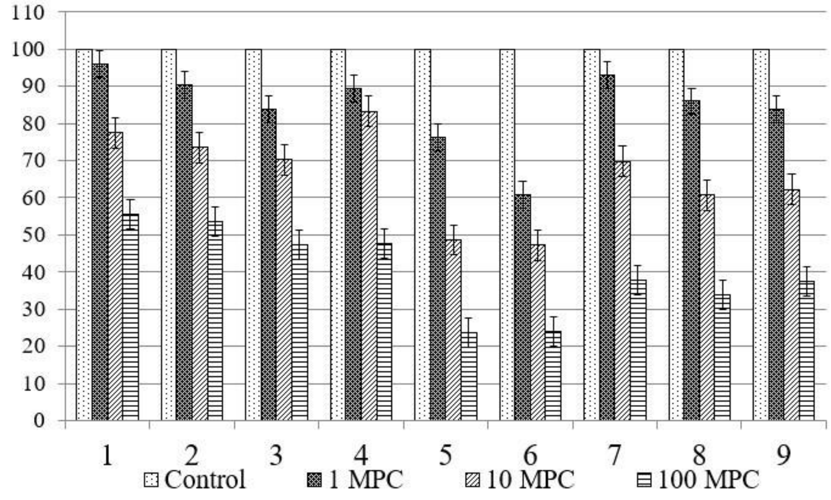
Chemical substances	The Concentration of the contaminant				Average value
	Control	1 MPC (1 %)	10 MPC (5%)	100 MPC (10 %)	
		Southern chernozem			
Cr	100	70	43	14	57
Cu	100	96	77	56	82
Ni	100	99	79	61	85
Pb	100	99	79	64	85
Petroleum hydrocarbons	100	71	52	35	65
		Brown typical soil			
Cr	100	57	32	19	52
Cu	100	90	74	54	79
Ni	100	87	73	48	77
Pb	100	90	76	51	79
Petroleum hydrocarbons	100	78	67	38	71
		Brown leached soil			
Cr	100	53	28	15	49
Cu	100	89	83	48	80
Ni	100	83	45	43	75
Pb	100	86	68	51	76
Petroleum hydrocarbons	100	66	55	28	62
		Brown carbonate soil			
Cr	100	53	35	17	51
Cu	100	84	70	47	75
Ni	100	89	70	53	78
Pb	100	80	71	45	74
Petroleum hydrocarbons	100	80	68	48	74
		Acid brown forest soil			
Cr	100	67	34	16	54
Cu	100	76	49	24	62
Ni	100	67	48	33	62
Pb	100	73	53	33	65
Petroleum hydrocarbons	100	66	40	21	57
		Acid brown forest podzolized soil			
Cr	100	45	29	18	48
Cu	100	61	47	24	58
Ni	100	70	48	32	62
Pb	100	61	47	29	59
Petroleum hydrocarbons	100	63	40	24	57
		Sod-carbonate typical soil			
Cr	100	73	55	24	63
Cu	100	93	70	38	75
Ni	100	98	63	47	77
Pb	100	93	71	46	77
Petroleum hydrocarbons	100	79	61	38	69
		Leached sod-carbonate soil			
Cr	100	59	44	20	56
Cu	100	86	61	34	70
Ni	100	89	65	44	75
Pb	100	88	63	46	74
Petroleum hydrocarbons	100	84	62	40	71
		Yellow soil			
Cr	100	59	40	30	57
Cu	100	84	62	37	71
Ni	100	84	64	39	72
Pb	100	86	65	44	74
Petroleum hydrocarbons	100	76	46	29	63



Ranking for resistance of soil types (% of IIBS):

7	1	9	8	5	2	3	4	6
Sod-carbonate typical soil	Southern chernozem	Yellow soil	Leached sod-carbonate soil	Acid brown forest soil	Brown typical soil	Brown carbonate soil	Brown leached soil	Acid brown forest podzolized soil
63	57	57	56	54	52	51	49	48

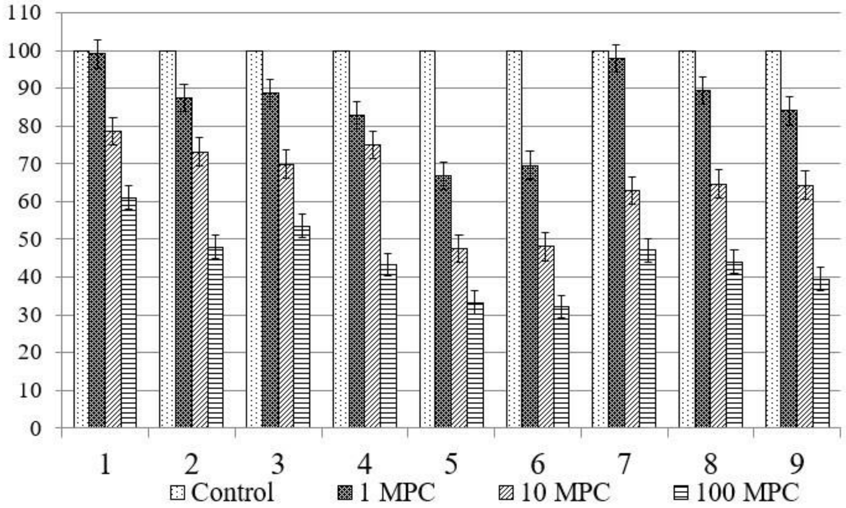
Figure 2. Ranking of resistance of type of soils of wet and dry subtropics of soils of the Greatest Caucasus by Cr contamination, % of control



Ranking for resistance of soil types (% of IIBS):

1	4	2	3	7	9	8	5	6
Southern chernozem	Brown leached soil	Brown typical soil	Brown carbonate soil	Sod-carbonate typical soil	Yellow soil	Leached sod-carbonate soil	Acid brown forest soil	Acid brown forest podzolized soil
82	80	79	75	75	71	70	62	58

Figure 3. Ranking of resistance of different type of soils of wet and dry subtropics of soils of the Greatest Caucasus by Cu contamination, % of control



Ranking for resistance of soil types (% of IIBS):

1	3	2	7	4	8	9	5	6
Southern chernozem	Brown carbonate soil	Brown typical soil	Sod-carbonate typical soil	Brown leached soil	Leached sod-carbonate soil	Yellow soil	Acid brown forest soil	Acid brown forest podzolized soil
85	78	77	77	75	75	72	62	62

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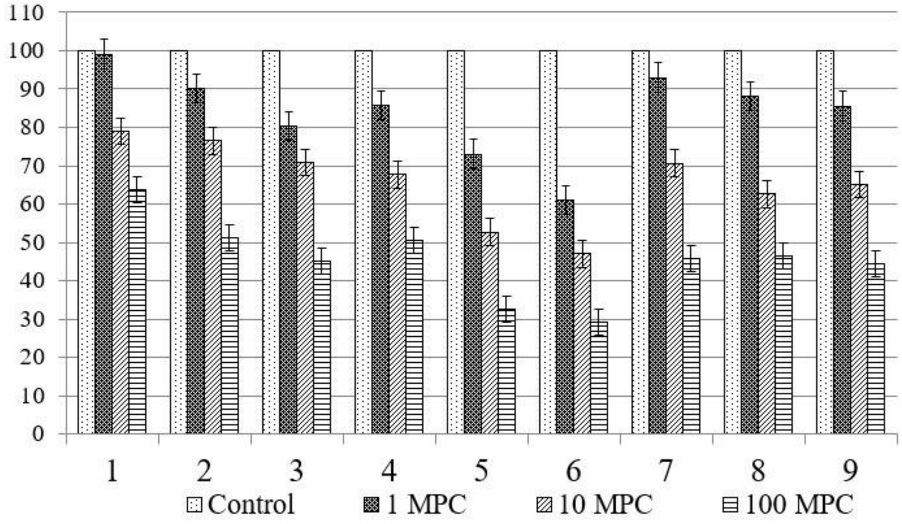
Figure 4. Ranking of resistance of different type of soils of wet and dry subtropics of soils of the Greatest Caucasus by Ni contamination, % of control

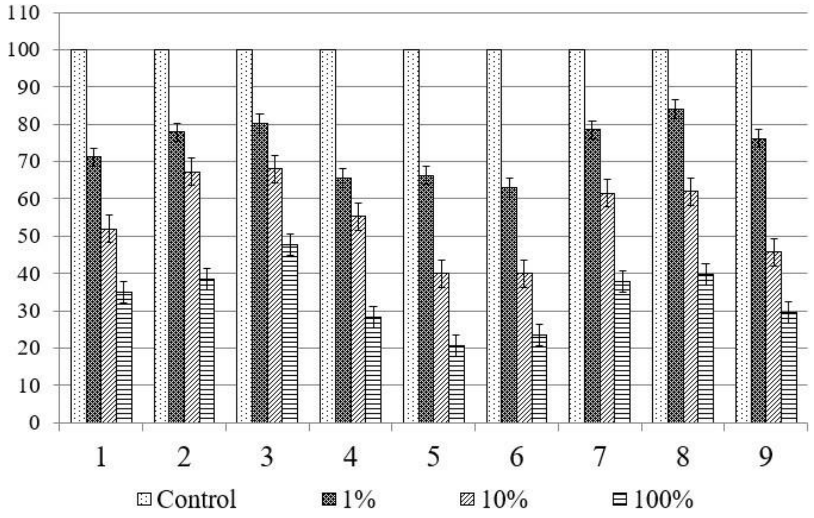


Ranking for resistance of soil types (% of IIBS):

1	2	7	4	3	8	9	5	6
Southern chernozem	Brown typical soil	Sod-carbonate typical soil	Brown leached soil	Brown carbonate soil	Leached sod-carbonate soil	Yellow soil	Acid brown forest soil	Acid brown forest podzolized soil
85	79	77	76	74	74	74	65	59

→

Figure 5. Ranking of resistance of different type of soils of wet and dry subtropics of soils of the Greatest Caucasus by Pb contamination, % of control



Ranking for resistance of soil types (% of IIBS):

3	2	8	7	1	9	4	5	6
Brown carbonate soil	Brown typical soil	Leached sod-carbonate soil	Sod-carbonate typical soil	Southern chernozem	Yellow soil	Brown leached soil	Acid brown forest soil	Acid brown forest podzolized soil
74	71	71	69	65	63	62	57	57

Figure 6. Ranking of resistance of different type of soils of wet and dry subtropics of soils of the Greatest Caucasus by petroleum hydrocarbons contamination, % of control

Presented series of stability is determined by the ecological-genetic properties of the studied soils (Table 1), such as soil texture, pH and organic matter content. Southern chernozem showed the highest buffer capacity for heavy metal pollution. This soil is characterized by heavy granulometric composition, slightly alkaline reaction of the medium. Heavy loam granulometric compaction of soil evidence about high absorption capacity. The slightly alkaline medium promotes retaining of cation-forming metals. The brown and sod-carbonate soils are less resistant to pollution with heavy metals. Typically, these soils are characterized by a heavy-grained granulometric composition, high humus content, neutral or slightly alkaline reaction of the medium, and other properties that contribute to retaining of heavy metal. Excellent oxidation conditions in these soils and relatively high biological activity contribute to the decomposition of petroleum hydrocarbons.

Brown forest soils have demonstrated the least resistance to chemical pollution. This is due to the relatively low humus content, low enzymatic activity, acidic pH and, consequently, high mobility of heavy metals and low decomposition rate of petroleum hydrocarbons. Yellow soils were less resistant to heavy metal contamination than brown and sod-carbonate soils, but more resistant than brown forest soils. Yellow soils are characterized by intermediate values of humus content and medium response. The relatively high biological activity of yellow soils and their good structure make them relatively resistant to petroleum hydrocarbons pollution. Study results suggest that soil biological parameters used in this work can be recommended for use in the diagnosis of chemical contamination of soils of wet and dry subtropics.

Earlier, in the chernozems (Kolesnikov et al., 2013), it was found that high concentrations of organic matter to a greater extent provide soil buffering to chromium pollution, and high pH values more determine the soil resistance to copper, nickel, and lead. The study of the soils of wet and dry subtropics confirmed this pattern. Apparently, this is since the first three elements are more cation-forming, and their mobility, and, consequently, toxicity for biota, is more pronounced in acidic soils (Bezuglova et al., 2016; Kabir et al., 2012). Chromium has shown high toxicity not only in acidic, but also in slightly alkaline soils, where a highly mobile chromate is formed from chromium oxide (Li et al., 2017; Qafoku et al., 2010).

The results obtained confirm the previously established patterns about the negative impact of lead pollution on the biological parameters of soils (Moshchenko et al., 2020) as well as the relationship between soil resistance and their physicochemical and biochemical parameters (Yang et al., 2021). Previously, on the chernozems of southern Russia (Kolesnikov et al., 2013), it was found that high concentrations of organic matter to a greater extent provide soil buffering to chromium pollution, and high pH values determine the resistance of the soil to copper, nickel, and lead to a greater extent. The study of soils in wet and dry subtropics confirmed this pattern. Apparently, this is due to the fact that the first three elements are more cation-forming, and their mobility and, therefore, toxicity to biota are more pronounced in acidic soils. Chromium showed high toxicity not only in acidic, but also in slightly alkaline soils, where highly mobile chromate is formed from chromium oxide.

Table 3. Development of ecological standardization of the content of heavy metal in soils of wet and dry subtropics of the Greatest Caucasus, mg/kg (according to change in IIBS relative to control, in %)

Decrease in soil IIBS[1], %	< 5	5 – 10	10 – 25	> 25
Southern chernozem				
Pb	< 105	105-115	115-145	> 145
Cr	< 60	60-120	120-350	> 350
Cu	< 65	65-120	120-350	> 350
Ni	< 60	60-120	120-350	> 350
Brown typical soil				
Pb	<110	110-115	115-150	>150
Cr	<55	55-100	100-300	>300
Cu	<55	55-100	100-300	>300
Ni	<55	55-100	100-300	>300
Brown leached soil				
Pb	< 50	50-100	100-275	> 275
Cr	< 105	105-115	115-145	> 145
Cu	< 50	50-100	100-275	> 275
Ni	< 50	50-100	100-275	> 275
Brown carbonate soil				
Pb	<105	105-115	115-145	>145
Cr	<50	50-100	100-250	>250
Cu	<50	50-100	100-250	>250
Ni	<50	50-100	100-250	>250
Acid brown forest soil				
Pb	< 100	100-110	110-145	> 145
Cr	< 50	50-70	70-200	> 200
Cu	< 50	50-70	70-200	> 200
Ni	< 50	50-70	70-200	> 200
Acid brown forest podzolized soil				
Pb	< 90	90-110	110-140	> 140
Cr	< 40	40-65	65-170	> 170
Cu	< 50	50-70	70-200	> 200
Ni	< 40	40-65	65-170	> 170
Sod-carbonate typical soil				
Pb	< 110	110-120	120-155	> 155
Cr	< 60	60-100	100-250	> 250
Cu	< 60	60-100	100-250	> 250
Ni	< 60	60-100	100-250	> 250
Leached sod-carbonate soil				
Pb	< 100	100-110	110-145	> 145
Cr	< 50	50-100	100-200	> 200
Cu	< 50	50-100	100-250	> 250
Ni	< 50	50-100	100-250	> 250
Yellow soil				
Pb	< 105	105-115	115-150	> 150
Cr	< 50	50-100	100-220	> 220
Cu	< 50	50-100	100-220	> 220
Ni	< 50	50-100	100-220	> 220

The effect of petroleum hydrocarbons on changes in soil properties is associated with the presence of HM, aromatic hydrocarbons, and phenols in the petroleum hydrocarbons composition, which inhibit soil biota. Petroleum hydrocarbons clogs the channels and pores of the soil, like cement, binds soil particles, disrupting moisture exchange and changing their water-physical properties.

Based on results of the study, it was calculated regression equations to characterize the relationship between IIBS and the content of chemicals in the soil. Using these equations, we have calculated concentrations of pollutants, which lead to degradation of various ecological functions of soils (Table 3).

Disruption of soil ecological functions occurs in a certain order, and it is advisable to use soil IIBS as an indicator of degradation of soil ecological functions (Kolesnikov et al., 2019). If the IIBS is reduced by less than 5%, the soil function is not affected. Decrease of IIBS value by 5-10% show degradation of information functions and decrease of IIBS value by 10-25% evidence degradation of biochemical, physical, chemical and holistic functions and decrease of IIBS value by more than 25% evidence deterioration of physical functions.

According to Table 3, if, for example, Pb content in southern chernozem doesn't exceed 105 mg kg^{-1}, then the soil functions normally. Lead concentration from 105 to 115 mg kg^{-1} suggests the degradation of information ecological functions of the soil.

Lead concentration from 115 to 145 mg kg^{-1} suggests degradation of chemical, physico-chemical, biochemical, and holistic functions in addition to information function. Lead concentration above 145 mg kg^{-1} leads the degradation of physical functions of soils. It is obvious that degradation of chemical, physicochemical, biochemical, and most importantly holistic functions of the soil, ensuring soil fertility, is unacceptable. Consequently, the lead concentration of 115 mg kg^{-1} should be considered as MPC of lead in southern chernozem soils of wet and dry subtropics, or the regional MPC (rMPC).

The paper presents the most preferable methods of remediation of contaminated soils. So, with insignificant pollution with heavy metals, it is possible to carry out phytoremediation and soil leaching. The most preferred methods for remediation of petroleum hydrocarbons soils are presented below. So, with a small degree of petroleum hydrocarbons pollution, it is possible to activate the aboriginal hydrocarbon-oxidizing microflora by optimizing the agrophysical and agrochemical properties of contaminated soils. With an average - you will need the use of drugs with hydrocarbon-oxidizing microorganisms, the use of mineral or organo-mineral fertilizers, sowing of perennial legumes. With a high degree of petroleum hydrocarbons pollution, it is necessary to remove the contaminated soil layer and replace it with a new ecologically and agriculturally high-grade one and forecasting the state of soils and terrestrial ecosystems soils of wet and dry subtropics.

Research of soils of dry and humid subtropics should be continued using other chemicals that are often found in this area (non-metals, antibiotics, pesticides, petroleum hydrocarbons products (gasoline, fuel oil, diesel fuel)). It is important to study various concentrations of these substances to determine the limits of soil stability. In the future, it is promising to study soil contamination with different exposure periods (from 10 till 365 days) to look at the process of changing biological parameters in dynamics.

5. CONCLUSION

Contamination of soils with heavy metals and petroleum hydrocarbons in wet and dry subtropics worsens their biological condition: count of microorganisms, enzyme activity, growth and development indicators of plants are reduced. The degree of change of biological indicators of soils depends on the nature of pollutants and their concentration in the soil, as well as the genetic properties of the soils themselves, which determine its resistance to pollution. In terms of degree of ecotoxicity to studied soil of the Greatest Caucasus by heavy metal contamination the following series: Cr > Cu ≥ Ni = Pb. According to the degree of resistance to soils of the Greatest Caucasus by heavy metal contamination form the following series: southern chernozem> sod-carbonate typical ≥ brown typical ≥ brown-carbonate = brown leached = sod-carbonate leached = yellow soil > acid brown forest soil ≥ acid brown forest podzolized soil. We have obtained series of so soils of wet and dry subtropics of soils of the Greatest Caucasus by petroleum hydrocarbons contamination: brown carbonate ≥ brown typical = sod-carbonate leached ≥ sod-carbonate typical > southern chernozem ≥ yellow soil ≥ brown leached soil > acid brown forest soil = acid brown forest podzolized soil. Southern chernozem showed the greatest buffer capacity to heavy metal pollution. Heavy nature of this soil determines absorption capacity. The slightly alkaline medium promotes retaining of cation-forming metals. Brown forest soils showed the least resistance to chemical pollution. They are distinguished by the relatively low humus content, acidic reaction of the medium, low enzymatic activity and, therefore, high mobility of heavy metal and low rate of petroleum hydrocarbons decomposition. We pro-posed regional norms of maximum permissible content of Cr, Cu, Ni, Pb and petroleum hydrocarbons in soils of wet and dry subtropics, deter-mined based on degradation of ecological functions of soils.

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Declaration of Competing Interest

The authors declare that no competing financial or personal interests that may appear and influence the work reported in this paper.

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