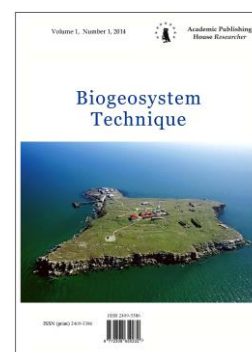


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## Assessment of South Russia Arid Soils Resistance to Gasoline Contamination Using Biological Indicators

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### Abstract

Arid ecosystems occupy a significant part of the world's ecosystems and play important role in the biodiversity and stability of natural ecosystems. At the same time, Soils of arid ecosystems significantly differ in their ecological and genetic properties, and, accordingly, in their resistance to chemical pollution. It has been established that the soil pollution of arid ecosystems by gasoline in Russia leads to decrease the biological activity: Inhibition of enzyme activity (activity of catalase and dehydrogenases), decrease the general number of bacteria in the soil, decrease the galore of bacteria of genus *Azotobacter* in the soil, phytotoxic properties, cellulolytic ability. In most cases, there is a significant decrease in all the studied parameters. The degree of decrease depends on the concentration of gasoline in the soil. The obtained sequence of arid soils resistance of the south of Russia to gasoline pollution: ordinary chernozem (haplic chernozem loamic) > chestnuts soils (haplic kastanozems chromic) > dark chestnuts soils (haplic kastanozems chromic) ≥ light chestnuts soils (haplic kastanozems chromic) ≥ sandy soils (calcaric arenosols) ≥ brown semi – desert soils (haplic calcisols) > solonetz medow (gleyic solonetz albic) > shor solonchaks (puffic solonchaks aridic).

Used in the study indicators of the soil biological state can be recommended for forecasting, assessment and control of chemical contamination of arid soils. Based on the assessment of soil ecological functions violation in oil industry, the quantitative regional standards landmarks were developed of the maximum permissible gasoline concentrations (MPC) in arid soil.

**Keywords:** arid soils, bio-testing, chestnut soil, sandy soil, gasoline, maximum permissible concentrations, pollution.

### 1. Introduction

High rate industrial activity increase demand for energy sources. This increases the oil extraction and production to meet the world energy needs. The number of cases The soil contamination with oil hydrocarbons is also growing (Engelking, 2000; Marinescu et al., 2010).

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During the oil extraction, transportation, distillation, and in result of accidents on pipelines, up to ten million tons of oil hydrocarbons are lost. The oil and oil products spill creates a constant threat for agriculture and forestry (Ogri, 2001; Agbogidi, 2003). Soil contamination by oil and oil products destroys the physical (Marin-Garcia et al., 2016; Gordon et al., 2018), chemical (Benka-Coker & Ekundayo, 1995) and biological (Agbogidi et al., 2003, 2007; Onwurah et al., 2007; Samedov et al., 2011; Singh et al., 2012; Golan et al., 2016; Girsowicz et al., 2018) soil properties, reduces fertility, and deteriorates the state of terrestrial ecosystems as a whole (Grechishcheva, Meshcheryakov, 2001; Ogri, 2001; Khalilova, 2015).

Unfortunately, soil pollution with oil and oil products, including gasoline, is common on the territory of the South Russia. Arid ecosystems have vast natural resources. Large reserves of hydrocarbons are located in the Volgograd, Astrakhan regions, in the Krasnodar Territory, Ingushetia Republic, and Chechen Republic. Oil production and supply increase can lead to soil pollution (Otchet o nauchno-proizvodstvennoi..., 2016). To maintain the biological diversity and stability of natural ecosystems, it is important to preserve the soil in the arid ecosystems (Zasolennye pochvy Rossii, 2006; Khalilova, 2015; Girsowicz et al., 2018).

On the territory of arid ecosystems in the South of Russia, there are zonal chestnut and brown semi-desert soils, as well as intrazonal sandy brown semi-arid soils (Natsional'nyi atlas..., 2011). The soils significantly differ in their ecological and genetic properties, and, respectively, in their resistance to pollution by gasoline (Kolesnikov et al., 2011).

Thus, the bio-testing of arid ecosystem soil resistance to gasoline pollution is highly relevant in order to predict the change of soil, as well as assess the condition of soil evolution.

## 2. Materials and methods

Contamination of the soil by gasoline was modeled in the laboratory conditions. The soils of arid ecosystems of the South Russia (dark chestnuts, chestnuts, light chestnuts, brown semi-desert, sandy soils, solonetz medow and shor solonchaks), as well as an ordinary chernozem, were the objects of study. For model experiments, soil samples were selected from the top 0-10 cm layer. In the non-arable soils, major amount of pollutants is accumulated in this surface layer.

The sample sites, the soil names and properties are presented in the Tables 1, 2.

**Table 1.** Soil sampling points

Name of soils	Ecosystem	Soil sampling point
Ordinary chernozem/Haplic Chernozem (Loamic)	typical steppe	Rostov region, Oktyabrskii district, Persianovskii village
Dark chestnut/Haplic Kastanozems Chromics	dry steppe	Rostov region, Orlovskii district, Maiorskii farm
Chestnut/Haplic Kastanozems Chromics	dry steppe	Rostov region, Remontnoe village
Light chestnut/Haplic Kastanozems Chromics	dry steppe	Republic of Kalmykia, Elista
Brown semidesert/Haplic Calcisols	semidesert	Republic of Kalmykia, Yashkulskii District, Khulkhuta Village
Sandy brown semidesert/Calcaric Arenosols	semidesert	Astrakhan region, Narimanovskii district, Novokucherganovka village
Solonetz medow/Gleyic Solonetz Albic	dry steppe	Republic of Kalmykia, Yashkul district, Gashun village
Shor Solonchaks/Puffic Solonchaks Aridic	the bottom of the dried estuary. rare halophytic vegetation	Astrakhan region, Narimanov district, with. Turkmen woman

**Table 2.** Soil properties

Name of soils	pH	Organic matter, %	Granulometric composition	Activity of catalase, ml O <sub>2</sub> /g of the soil per 1 minute	Activity of dehydrogenases activity, mg triphenylformazan /g per 24 hours
Ordinary chernozem/Haplic Chernozem (Loamic)	7.6	4.6	heavy loam	15.8	28.9
Dark chestnut/Haplic Kastanozems Chromics	7.6	3.5	heavy loam	13.5	25.9
Chestnut/Haplic Kastanozems Chromics	7.8	2.8	heavy loam	11.4	23.0
Light chestnut/Haplic Kastanozems Chromics	8.1	1.4	medium loam	9.8	20.6
Brown semidesert/Haplic Calcisols	8.3	1.2	light loam	6.4	19.6
Sandy brown semidesert/Calcaric Arenosols	8.3	0.8	Sandy	3.3	17.4
Solonetzes meadow/Gleyic Solonetz Albic	8.4	1.3	medium loam	7.8	13.4
Shor Solonchaks / Puffic Solonchaks Aridic	7.8	0.7	heavy loam	5.8	15.5

On the territory of arid ecosystems in the Astrakhan region there is the largest gas condensate field in Europe. This deposit produces about 500 thousand tons of gasoline and the same amount of diesel fuel every year. Therefore the gasoline was chosen as a pollutant in our research. The production, transportation, and processing of these substances ensures severe soil pollution.

In model experiment, the soil was incubated at a room temperature (20-22 °C) and the optimal moisturizing (60% of the field moisture capacity) in the vegetation vessels in three-fold repetitions.

Environment status of the soil was determined 30 days after pollution. To assess the soil chemical contamination effect, this duration is of most significance, since the biological indicators degradation degree is maximal (Kolesnikov et al., 2002). Laboratory analytical studies were performed using the conventional methods (Metody pochvennoi mikrobiologii i biokhimii, 1991; Kazeev et al., 2016). In this work, we determined in the soil the enzymatic activity (catalase and dehydrogenases), general number of bacteria, galore of bacteria of genus *Azotobacter*, cellulolytic ability, phytotoxic properties, and some other soil biological properties.

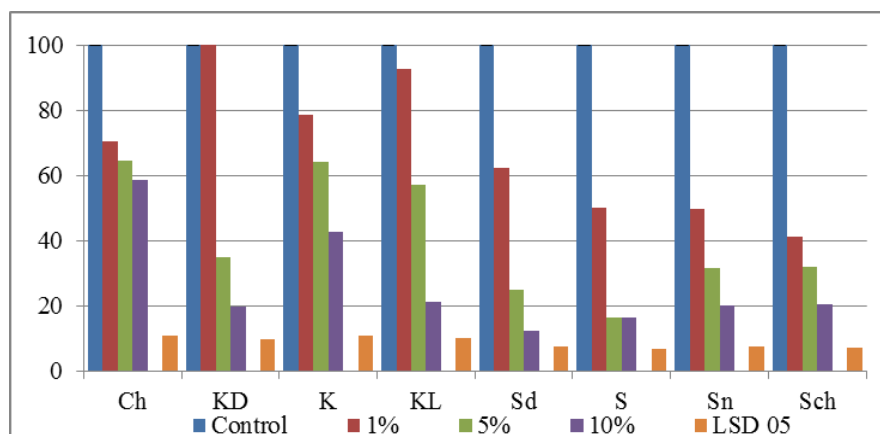
To combine a large number of indicators, a bio-testing method was developed of integral indicator of biological state of soil (IIBS) (Kazeev et al., 2016). The IIBS method allows to determine and evaluate the biological state of the soil as a whole.

### 3. Results and discussion

In this model experiment, it was shown that the introduction of gasoline into the arid ecosystem soils causes the reliable changes in soil biological parameters. (Figures 1-7). Studied parameters decreased significantly, namely the enzymatic activity (catalase and dehydrogenases), general number of bacteria in soil, galore of bacteria of genus *Azotobacter* in the soil, cellulolytic ability, and phytotoxic properties. These changes influenced the IIBS values.

The introduction of 1 % gasoline into the soil caused a significant decrease in the number of bacteria in ordinary chernozem by 29 %, in chestnut soil by 21 %, in brown semidesert by 37 %, in sandy brown semidesert and solonetzes meadow by 50 %, and by 59 % in shor solonchaks. The gasoline dose of 5 % reduced the number of bacteria in ordinary chernozem by 45 %, and in chestnut soil by 37 %, in brown semidesert by 45 %, in sandy brown semidesert and solonetzes meadow by 50 %, and by 59 % in shor solonchaks.

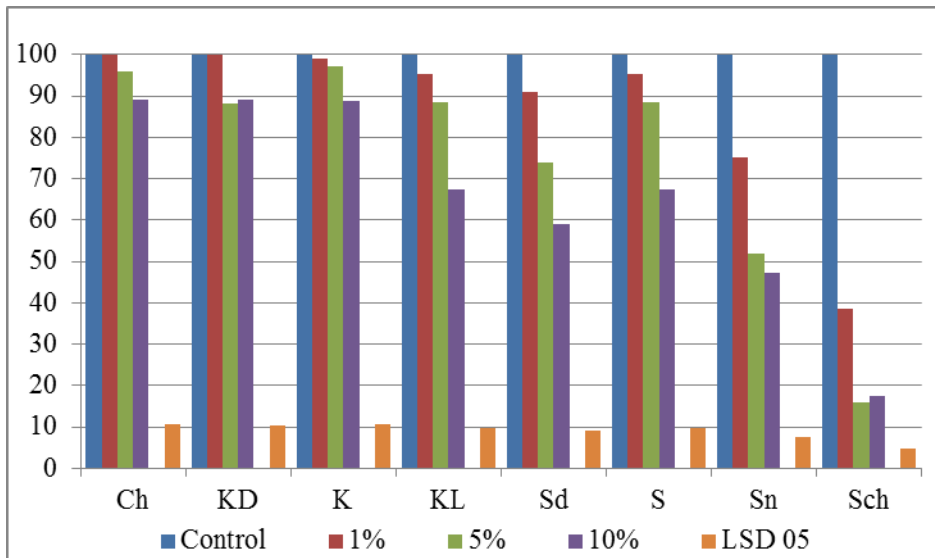
in chestnut soil by 46 %, in light chestnut soil by 53 %, in solonetztes meadow and shor solonchaks by 68 %, in brown semidesert by 75 %, and in sandy brown semidesert soil by 83 %. The gasoline dose of 10 % reduced the number of bacteria in ordinary chernozem by 41 %, in chestnut soil by 57 %, in brown semi-desert soil by 79 %, and in dark chestnut soil, in solonetztes meadow, and shor solonchaks by 20 % (Figure 1).



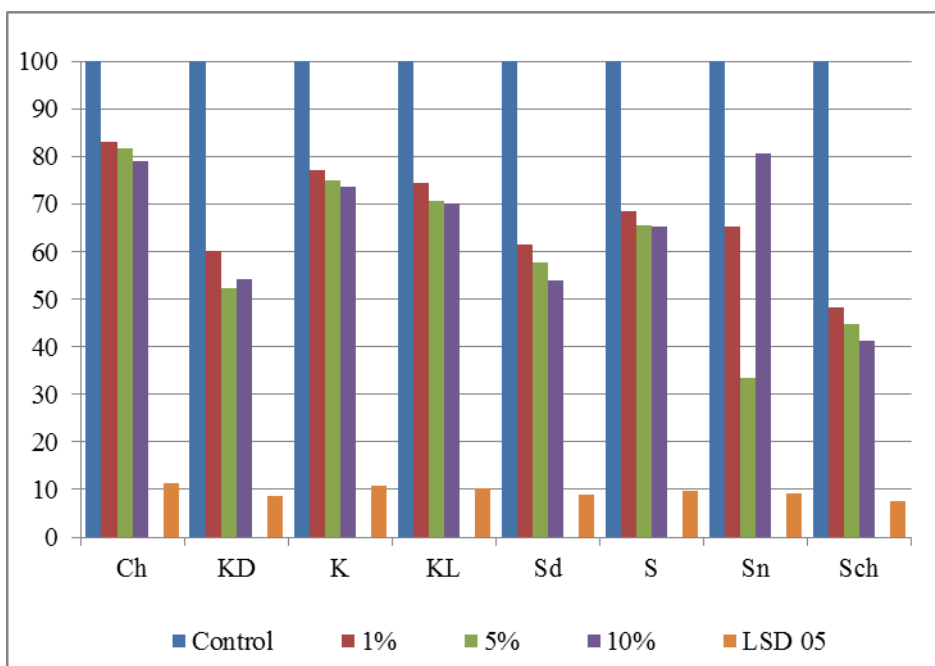
**Fig. 1.** Change in the total number of bacteria in the arid soil contaminated by gasoline. *Ch* – Ordinary chernozem/Haplic Chernozem (loamic), *KD* – Dark chestnut/Haplic Kastanozems Chromics, *K* – Chestnut/Haplic Kastanozems Chromics, *KL* – Light chestnut/Haplic Kastanozems Chromics, *Sd* – Brown semidesert/Haplic Calcisols, *S* – Sandy brown semidesert/Calcaric Arenosols, *Sn* – Solonetztes meadow/Gleyic Solonetz Albic, *Sch* – Shor solonchaks/Puffic Solonchaks Aridice

The abundance of bacteria of the genus *Azotobacter* did not significantly change in ordinary chernozem, dark chestnut soil and chestnut soil contaminated with gasoline at a concentration from 1-10 %. The introduction of gasoline at a dose of 1 %, a decrease in bacteria number was observed only in the solonetztes meadow by 25%, and in the shor solonchaks by 61 %. The addition to the soil of the gasoline 5 % caused a decrease in the number of *Azotobacter* bacteria in light chestnut soil and sandy brown semi-desert soil by 12 %, in brown semi-desert soil by 26 %, in solonetztes meadow by 53 %, and in shor solonchaks by 84 %. The 10 % concentration of gasoline in light chestnut soil reduced the abundance of *Azotobacter* by 33 %, in brown semi-desert soil by 41 %, in sandy brown semi-desert soil by 33 %, in Solonetztes meadow by 53 %, and in shor solonchaks by 83 % (Figure 2).

Catalase activity decreased with the introduction of 1 % gasoline in ordinary chernozem by 17 %, in dark chestnut soil by 40 %, in chestnut soil by 23 %, in light chestnut soil by 25 %, in brown semi-desert soil by 39 %, in sandy brown semi-desert soil by 32 %, in solonetztes meadow by 35 %, and in shor solonchaks by 52 %. When contaminated with 5 % gasoline, a decrease in catalase in ordinary chernozem was observed by 18 %, in dark chestnut soil by 48 %, in chestnut soil by 25 %, in light chestnut soil by 29 %, in brown semi-desert soil by 42 %, in sandy brown in semi-desert soil by 34 %, in solonetztes meadow by 67 %, and in shor solonchaks by 55 %. Contamination of 10 % of gasoline caused a decrease in catalase in ordinary chernozem by 21 %, in dark chestnut soil by 46 %, in chestnut soil by 26 %, in light chestnut soil by 30 %, in brown semi-desert soil by 46 %, in sandy brown semi-desert soil by 35 %, in solonetztes meadow by 19 %, and in shor solonchaks by 59 % (Figure 3).



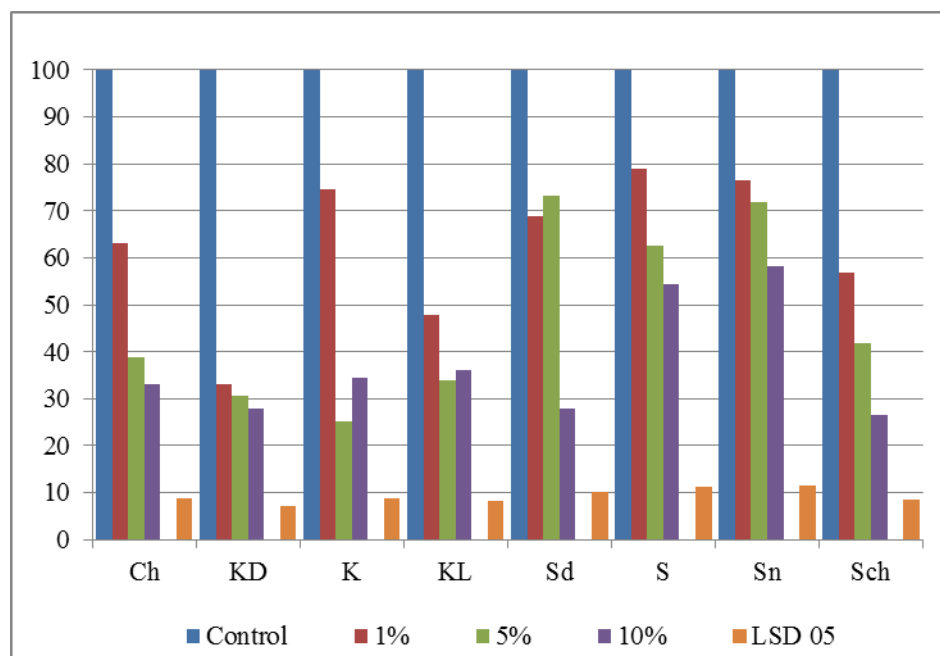
**Fig. 2.** Change in the abundance of bacteria of the genus *Azotobacter*, % of control when they contaminated by gasoline. Type codes: Ch – Ordinary chernozem/Haplic Chernozem (loamic), KD – Dark hestnut/Haplic Kastanozems Chromics, K – Chestnut/ Haplic Kastanozems Chromics, KL – Light chestnut/Haplic Kastanozems Chromics, Sd – Brown semidesert/Haplic Calcisols, S – Sandy brown semidesert/Calcaric Arenosols, Sn – Solonetztes medow/Gleyic Solonetz Albic, Sch – Shor solonchaks/Puffic Solonchaks Aridice



**Fig. 3.** Change in the catalase activity of arid soils when they contaminated by gasoline. Type codes: Ch – Ordinary chernozem/Haplic Chernozem (loamic), KD – Dark hestnut/Haplic Kastanozems Chromics, K – Chestnut/ Haplic Kastanozems Chromics, KL – Light chestnut/Haplic Kastanozems Chromics, Sd – Brown semidesert/Haplic Calcisols, S – Sandy brown semidesert/Calcaric Arenosols, Sn – Solonetztes medow/Gleyic Solonetz Albic, Sch – Shor solonchaks/Puffic Solonchaks Aridice

The activity of dehydrogenases decreased with the introduction of 1 % gasoline in ordinary chernozem by 37 %, in dark chestnut soil by 67 %, in chestnut soil by 26 %, in light chestnut soil by 52 %, in brown semi-desert soil by 31 %, in sandy brown semi-desert soil by 21 %, in a solonetztes medow by 24 %, and in shor solonchaks by 43 %. When contaminated with 5 % gasoline, a decrease

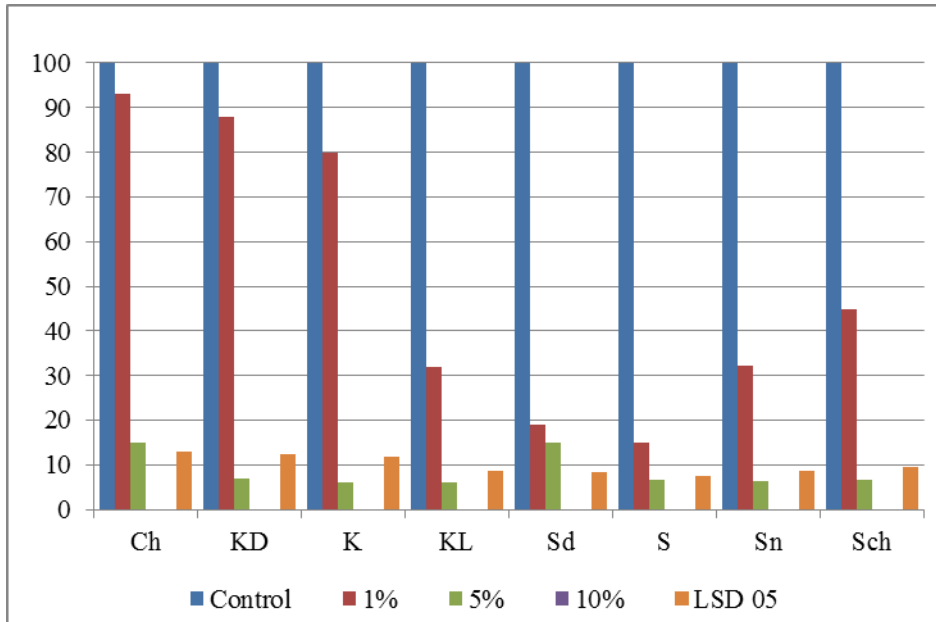
in dehydrogenases in ordinary chernozem was observed by 61 %, in dark chestnut soil by 69 %, in chestnut soil by 75%, in light chestnut soil by 66 %, in brown semi-desert soil by 27 %, in sandy brown semi-desert soil by 37 %, in solonetztes meadow by 28 %, and in shor solonchaks by 58 %. 10 % gasoline contamination caused a decrease in dehydrogenases in ordinary chernozem by 67 %, in dark chestnut soil by 72 %, in chestnut soil by 66 %, in light chestnut soil by 64 %, in brown semi-desert soil by 72 %, in sandy brown semi-desert soil by 46 %, in solonetztes meadow by 42 %, and in shor solonchaks by 74 % (Figure 4).



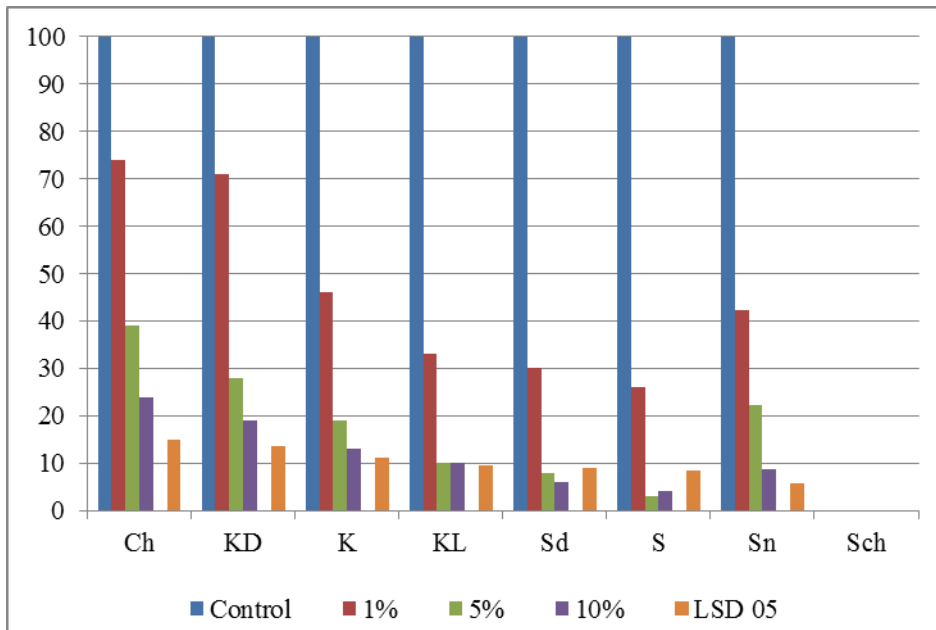
**Fig. 4.** Change in the dehydrogenases activity of arid soils when they contaminated by gasoline. Type codes: Ch – Ordinary chernozem/Haplic Chernozem (loamic), KD – Dark hestnut/Haplic Kastanozems Chromics, K – Chestnut/Haplic Kastanozems Chromics, KL – Light chestnut/Haplic Kastanozems Chromics, Sd – Brown semidesert/Haplic Calcisols, S – Sandy brown semidesert/Calcaric Arenosols, Sn – Solonetztes meadow/Gleyic Solonetz Albic, Sch – Shor solonchaks/Puffic Solonchaks Aridice

The soil cellulolytic activity when contaminated with gasoline at a dose of 10 % decreased to 0 in all variants of the experiment. With 1 % pollution, a significant decrease was recorded for chestnut soil (by 20 %), for light chestnut soil (by 68 %), for brown semi-desert soil (81 %), for sandy brown semi-desert soil (by 85 %), for solonetztes meadow (by 68 %), and for shor solonchaks (by 55 %). When contaminated with 5 % gasoline, a decrease in cellulolytic activity in ordinary chernozem was observed by 85 %, in dark chestnut and shor solonchaks by 93 %, in chestnut, light in chestnut and solonetztes meadow by 94 %, and in brown semidesert soil by 85 % (Figure 5).





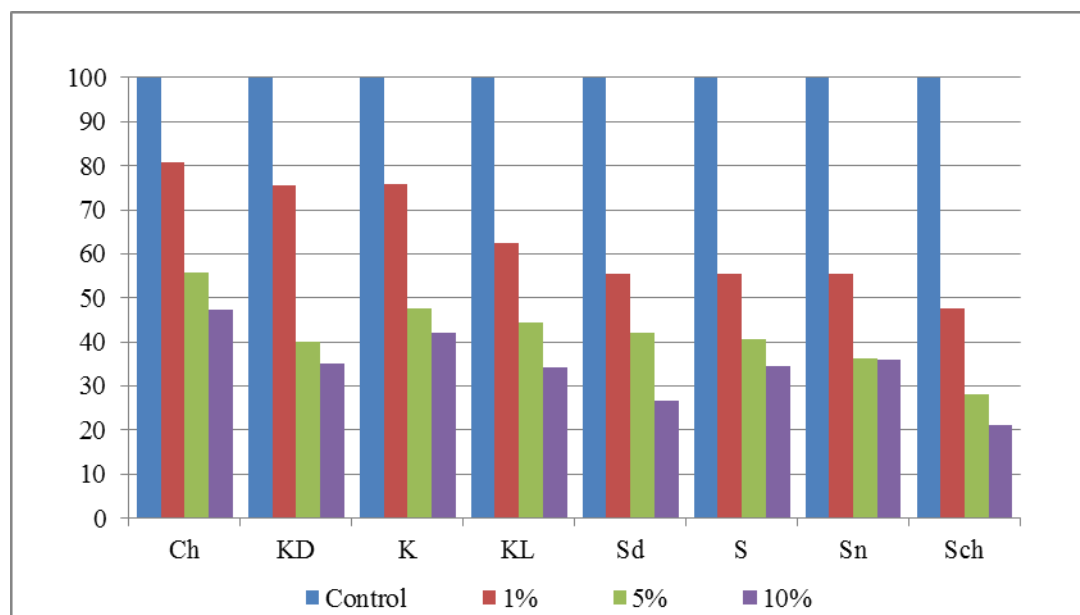
**Fig. 5.** Change in cellulolytic activity of arid soils when they contaminated by gasoline. Type codes: Ch – Ordinary chernozem/Haplic Chernozem (loamic), KD – Dark hestnut/Haplic Kastanozems Chromics, K – Chestnut/Haplic Kastanozems Chromics, KL – Light chestnut/Haplic Kastanozems Chromics, Sd – Brown semidesert/Haplic Calcisols, S – Sandy brown semidesert/Calcaric Arenosols, Sn – Solonetztes meadow/Gleyic Solonetz Albic, Sch – Shor solonchaks/Puffic Solonchaks Aridice



**Fig. 6.** Change in the length of the roots of radish of arid soils when they contaminated by gasoline. Type codes: Ch – Ordinary chernozem/Haplic Chernozem (loamic), KD – Dark hestnut/Haplic Kastanozems Chromics, K – Chestnut/Haplic Kastanozems Chromics, KL – Light chestnut/Haplic Kastanozems Chromics, Sd – Brown semidesert/Haplic Calcisols, S – Sandy brown semidesert/Calcaric Arenosols, Sn – Solonetztes meadow/Gleyic Solonetz Albic, Sch – Shor solonchaks/Puffic Solonchaks Aridice

Contamination with gasoline at a concentration of 1, 5 and 10 % turned out to be toxic for the growth of radish on a shor solonchaks. The length of radish roots decreased when 1 % gasoline was added in ordinary chernozem by 26 %, in dark chestnut soil by 29 %, in chestnut soil by 54 %,

in light chestnut soil by 67 %, in brown semi-desert soil by 70%, in sandy brown semi-desert soil by 74 %, and in solonetztes medow by 58 %. When contaminated with 5 % gasoline, a decrease in root length in ordinary chernozem was observed by 61 %, in dark chestnut soil by 72 %, in chestnut soil by 81 %, in light chestnut soil by 90 %, in brown semidesert soil by 92 %, in sandy soil. brown semi-desert soil by 97 %, and in solonetztes medow by 78 %. Contamination of 10% gasoline caused a decrease in the length of radish roots by 76 % in ordinary chernozem, in dark chestnut soil by 81 %, in chestnut soil by 87 %, in light chestnut soil by 90 %, in brown semi-desert soil by 94 %, in sandy brown semi-desert soil by 96 %, and in solonetztes medow by 91 % (Figure 6).



**Fig. 7.** Change in IBS of arid soils when they contaminated by gasoline. *Type codes: Ch – Ordinary chernozem/Haplic Chernozem (loamic), KD – Dark hestnut/Haplic Kastanozems Chromics, K – Chestnut/Haplic Kastanozems Chromics, KL – Light chestnut/Haplic Kastanozems Chromics, Sd – Brown semidesert/Haplic Calcisols, S – Sandy brown semidesert/Calcaric Arenosols, Sn – Solonetztes medow/Gleyic Solonetz Albic, Sch – Shor solonchaks/Puffic Solonchaks Aridice*

As a rule, extended soil biological indicators degradation in all studied is directly related to the concentration of pollutant in the soil. The obtained sequence of soil resistance of arid ecosystems in the South Russia to gasoline pollution is as follows: ordinary chernozem (haplic chernozem loamic) > chestnuts soils (haplic kastanozems chromic) > dark chestnuts soils (haplic kastanozems chromic) ≥ light chestnuts soils (haplic kastanozems chromic) ≥ sandy soils (calcaric arenosols) ≥ brown semi-desert soils (haplic calcisols) > solonetztes medow (gleyic solonetz albic) > shor solonchaks (puffic solonchaks aridic).

When gasoline penetrates the soil, it is divided to the free liquid, vapor, adsorbed on soil particles or dissolved in water phases. The texture of the soil, the porosity of the soil, and the duration of pollution affect the gasoline phases distribution. Although petroleum hydrocarbons are usually considered insoluble in water, the lighter hydrocarbons, such as benzene, are more soluble in water than polycyclic aromatic hydrocarbons, which are often components of diesel fuel (for example, naphthalene, anthracene, or pyrene) (Cole, 1994; Bennett, 1999). Due to the relatively high solubility in water, these compounds will, as a rule, will be dissolved in the aqueous phase or evaporated throughout internal air spaces of the soil. Because of relative hydrophilic nature, the compounds will not be held up by soil particles and therefor under certain conditions can move for the long distances (Shayler et al., 2009).

Based on the results of the study, the regression equations were developed, which reflect the relationship between the IBS values and the gasoline content in the soil. Using these equations, the concentrations of gasoline, that cause a violation of one or another group of soil eco-



functions, were calculated, and a scheme of ecological regulation of pollution of arid soils by gasoline was proposed (Table 3).

**Table 3.** Rationing of gasoline content in arid soils of South Russia by degree of ecological function violation (biogeoholistic)

Soil contamination	Not polluted	Slightly polluted	Medium-polluted	Heavy-polluted
IIBS <sup>1</sup> change	< 5 %	5 – 10 %	10 – 25 %	> 25 %
impaired functions <sup>2</sup>	–	informational	chemical, physico-chemical, biochemical; holistic	physical
Gasoline content in the soil, mg / kg				
Ordinary chernozem/Haplic Chernozem (Loamic)	< 0.19	0.19 – 0.26	0.26 – 0.81	> 0.81
Dark chestnut/Haplic Kastanozems Chromics	< 0.17	0.17 – 0.22	0.22 – 0.47	> 0.47
Chestnut/Haplic Kastanozems Chromics	< 0.17	0.17 – 0.22	0.22 – 0.58	> 0.58
Light chestnut/Haplic Kastanozems Chromics	< 0.13	0.13 – 0.17	0.17 – 0.39	> 0.39
Brown semidesert /Haplic Calcisols	< 0.12	0.12 – 0.15	0.15 – 0.33	> 0.33
Sandy brown semidesert/Calcaric Arenosols	< 0.11	0.11 – 0.14	0.14 – 0.32	> 0.32
Solonetzes meadow/Gleyic Solonetz Albic	< 0.11	0.11 – 0.14	0.14 – 0.31	> 0.31
Shor Solonchaks/Puffic Solonchaks Aridic	< 0.12	0.12 – 0.14	0.14 – 0.24	> 0.24

<sup>1</sup> Determination of the integral index according to (Kolesnikov et al., 2002).

<sup>2</sup> Classification of ecological functions according to (Dobrovolsky and Nikitin, 1990).

According to Table 3, when the content of gasoline in the dark chestnut soil is less than 0.17 %, the soil performs its functions normally. If the concentration of gasoline is from 0.17 to 0.22 %, there will be a violation of informational ecological functions of the soil, from 0.22 to 0.47 % – in addition to information, chemical, physicochemical, biochemical and integral functions will be violated, more than 0.47 % – there will be the soil physical functions breakdown. To ensuring soil fertility, it is impossible to allow violations of the chemical, physicochemical, biochemical, and most important integral functions of the soil. Consequently, the concentration of 0.22 % gasoline in soil should be considered the maximum permissible concentration (MPC) of gasoline for the soils of arid ecosystems in the South Russia. Basing on bio-testing study, we propose to use the above mentioned concentration as the regional MPC (r MPC).

#### 4. Conclusion

The arid soil pollution by gasoline in the South Russia leads to decrease of the biological activity: enzymatic activity (catalase and dehydrogenases), the general number of bacteria in the soil, the galore of bacteria of genus *Azotobacter* in the soil, phytotoxic properties, cellulolyticability. In most cases, there is a significant decrease in all the studied parameters. The degree of decrease depends on the concentration of gasoline in the soil.

The sequence of the South of Russia arid ecosystem's soils resistance to gasoline pollution is as follows: ordinary chernozem (haplic chernozem loamic) > chestnuts soils (haplic kastanozems chromic) > dark chestnuts soils (haplic kastanozems chromic) ≥ light chestnuts soils (haplic kastanozems chromic) ≥ sandy soils (calcaric arenosols) ≥ brown semi – desert soils (haplic calcisols) > Solonetz medow (gleyic solonetz albic) > Shor Solonchaks (puffic solonchaks aridic).

We recommend the developed bio-testing indicators of the soil biological state for application in the forecasting, assessment, and control of chemical contamination of arid soils. Suggested quantitative landmarks will be useful to the development of regional standards for the maximum permissible concentrations of gasoline in arid soils based on the degree of violation of the soil ecological functions.

#### 5. Acknowledgements

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