Study of soil enzymatic activity of oil fields in the Republic of Kalmykia

Study of soil enzymatic activity of oil fields in the Republic of Kalmykia

A A Buluktaev

Integrated Monitoring and Information Technology Department, Kalmyk Scientific Center of the Russian Academy of Sciences, Elista, Russia

E-mail: buluktaevaa@kigiran.com

Abstract. Pollution of soils with oil and oil products, for today, very actual problem. In the present study, the content of soil enzymes (catalases, phosphatases, ureases and invertases) in the soils of Kalmykia oilfields has been studied to diagnose oil pollution. The content of oil products in the soils of oilfields is studied. As a result of research, it is established that the most informative soil enzyme in relation to oil pollution is catalase. Activity of phosphatase, ureases and invertase even in the background soils is minimal, as the studied soils show weak biological activity. It is proved that the change of catalase activity, as a rule, is in direct dependence on oil content in soil, the higher the content of oil and oil products in soil, the lower the activity of catalase.

1. Introduction

Currently, the territory of the Republic of Kalmykia is under severe anthropogenic stress. One of the serious environmental problems of the region is the activity of oil producing enterprises. Emergencies in the production and transportation of oil products, obsolescence of equipment, personnel carelessness – all this can lead to the penetration of pollutants into the environment. Once in the soil, oil causes abrupt changes in its chemical and physical composition [1–4], in addition, oil pollution leads to disruption of plant growth and development [5–7].

It is worth noting that oil producing enterprises operating in the territory of the Republic of Kalmykia are located on the Black Earth. Besides, a part of oilfields is located in the specially protected natural territories – "Black Earth" Reserve and "Mekletinsky" Reserve of Federal importance. Black lands are a part of the Caspian lowland, the main soils composing this territory are brown semi-desert soils and their complexes with saline soils, salt marshes and sands of different degrees of consolidation, they are characterized by light granulometric composition and salinity of soil profile. The climate of the Black Earths is sharply continental, with very hot and dry summers and snowy, harsh winters. Vegetation cover is represented by desert and semi-desert species, which develop under conditions of very low moisture supply.

Many authors' researches proved that soil pollution with oil and oil products leads to disruption of soil enzymes activity, such as catalase, dehydrogenase, phosphatase, invertase, etc. [8–10]. At pollution of soils by oil and oil products in it all biological processes are broken that leads to change of activity of soil enzymes.

The purpose of this study is to study the activity of soil enzymes in the soils of Kalmykia oilfields. The following tasks have been set for the implementation of this goal: – to select soil samples; – to analyze the content of oil products in soils; – to study the activity of soil enzymes.

2. Methods and materials

Soils of Tengutinskoye, Severo-Kamyshanskoye, Nadezhdinskoye, Tsubukskoye and Ulan-Kholskoye oil, oil and gas and oil and gas condensate fields were used as objects of research. Soils were selected from wells, oil spills, reservoirs, as well as in the background areas. Soils were taken from the surface layer, control samples were taken at virgin areas far from power lines, roads and oil pipelines.

Sampling and laboratory tests were carried out according to generally accepted methods [11–13]. Petroleum products were determined gravimetrically. The enzymatic activity of soils was judged by the activity of catalase, urease, invertase and phosphatase. Determination of enzymatic activity was carried out under optimal conditions of temperature, at natural soil pH, according to recommendation A. S. Galstyan. Repetition is 3-fold.

Catalase activity was measured by Galstyan's methods, urease by Galstyan's method, phosphatase by Stefanik, Yarni, Tomescu's method, invertase activity was determined by Galstyan in Haziev's modification [14].

3. Results

The Nadezhdinskoye oil field is located in the Mekletinskoye reserve. The soil cover is composed of brown semi-desert soils in a complex with saline soils. Geobotanical survey of the area showed that the basis of the grass is made up of cereals and santonium santonite communities. Results of oil products content and enzymatic activity in soils of Nadezhda field are presented in the table 1.

As a result of chemical analysis of soils of Nadezhda field we have established that background soil samples do not contain oil products, catalase activity is 2.36 ml O2 1 g/1 min, urease activity, invertase and phosphatase are low. The highest content of oil products was recorded in the soils under the oil spill, the lowest in the soils of the non-functioning well ¹ 135. Negative correlation dependence (r=–0.94) is established between the content of oil products in soil and activity of catalase. So at the content of oil products in soil 12.5 % catalase activity is inhibited up to 0.23 ml O2 1 g / 1 min. At the average content of oil in soils the activity of catalase decreases in 2.36 times in comparison with background samples. A high degree of correlation (r=-0.87) is also observed between the content of oil products in soils and urease activity. So at the maximum concentration of oil 12.5 % in soils urease activity decreases to 0.82 mg NH3 10 g / 24 hours. Dependence of invertase activity change at oil pollution is as follows, at low concentrations of oil products in soils invertase activity increases, at high concentrations of this soil enzyme activity is inhibited. Correlation coefficient is –0.78. Phosphatase activity at oil pollution decreases (r=–0.87). It is necessary to note that at oil concentration in soil 12.5 % phosphatase activity decreases to zero values.

Some of the oil wells at the Severo-Kamyshanskoye oil field are located in the Mekletinsky Federal Wildlife Refuge. Soil cover is represented by sandy differences in the complex with saline soils. Swan-salt-santonium-santhonin communities form the basis of the grass stand. Oil product content and soil enzyme activity in soils of the Severo-Kamyshanskoye field are presented in the table below 2.

Table 1. Petroleum product content and soil enzyme activity in soils of the nadezhda field

Selection point	Oil products, %	Catalase activity, ml O_2 per 1 g of soil in 1 minute.	Urease activity, mg NH_3 per 10 g of soil in 24 hours.	Invertaza activity, glucose mg per 1 g of soil in 24 hours	Phosphatase activity. mg P_2O_5 per 1 g of soil in 1 hour.
Control	—	2.36	0.99	0.36	0.12
At the well No.37	2.3	1.46	0.90	0.38	0.08
At the well No.146	4.6	1.00	0.88	0.30	0.02
At the well No.135	1.8	1.70	0.99	0.41	0.08
Under the oil spill	12.5	0.23	0.82	0.28	0.00

Table 2. Petroleum product content and soil enzyme activity in soils of the north kamyshanskoye field

Selection point	Oil products, %	Catalase activity, ml O_2 per 1 g of soil in 1 minute.	Urease activity, mg NH_3 per 10 g of soil in 24 hours.	Invertaza activity, glucose mg per 1 g of soil in 24 hours	Phosphatase activity. mg P_2O_5 per 1 g of soil in 1 hour.
Control	—	2.12	0.74	0.25	0.08
At the well No.17	3.2	1.04	0.70	0.20	0.04
At the well No.20	2.1	1.56	0.66	0.22	0.04
A suspended well	1.0	1.82	0.80	0.25	0.05
At the pipeline	7.8	0.54	0.60	0.20	0.02

Soil analysis of the Severo-Kamyshanskoye oil field showed that the content of oil products in these soils is lower than in the soils of Nadezhda field. So the maximum content of oil products is fixed in soils at the pipeline – 7.8 %, the least in soils at the suspended, not functioning well without registration number – 1.0 %. The content of oil products in soils of operating wells No. 17 and 20 varies from 2.1 to 3.2 %. The background samples of oil products are not fixed, the activity of soil enzymes is low. Changes in the activity of catalase have the same nature as described above. So at concentration of oil products in soil 7.8 % activity of catalase decreases to 0.54 ml O_2 1 g/1 min. High catalase activity is noted in the soils of suspended well, which indicates the restoration of biological processes in soils. The catalase activity of soils under the wells No. 17 and 20 is lower than in the background samples and makes up 1.04 and 1.56 ml of O_2 1 g / 1 min. Change of catalase activity at oil contamination and in this case shows high degree of correlation (r=–0.95). Urease activity in soils under the action of oil and oil products is usually reduced, but the exception is the soil that is inactive, the borehole here is slightly more active than the activity of the enzyme in the background samples. This can also be explained by the restoration of the biological properties of soils. At the maximum petroleum product content in soils, urease activity drops to 0.60 mg NH_3 of 10 g / 24 h. The correlation coefficient is also high (r=–0.82). Not so unambiguous changes in activity have been revealed in the soil enzyme invertase, here and high and low concentrations of petroleum products cause a similar effect on the change in the activity of invertase. The activity of invertase decreases to 0.20 mg glucose 1 g / 24 h at concentration of oil products 7,8 and 3.2 %. Values similar to those of the background are revealed in the inactive well. The correlation coefficient of this indicator is –0.80. Activity of phosphatase at oil pollution decreases, at the maximum oil content in the soil the activity of this enzyme is inhibited up to 0.0_2 mg P_2O_5 1 g / 1 h. The correlation coefficient is high –0.86.

Table 3. Petroleum product content and soil enzyme activity in the soils of the tengutinskoye field

Selection point	Oil products, %	Catalase activity, ml O_2 per 1 g of soil in 1 minute.	Urease activity, mg NH_3 per 10 g of soil in 24 hours.	Invertaza activity, glucose mg per 1 g of soil in 24 hours	Phosphatase activity. mg P_2O_5 per 1 g of soil in 1 hour.
Control	—	0.84	0.05	0.00	0.00
At the well No.260	5.1	0.42	0.00	0.00	0.00
At the well No.261	3.0	0.55	0.05	0.00	0.00
At the sludge dump	8.7	0.10	0.00	0.00	0.00
Under the oil spill	15.4	0.00	0.00	0.00	0.00
At the bullet	4.4	0.00	0.00	0.00	0.00

The Tengutinskoye oil and gas field is located on the territory of the Black Earth Biosphere Reserve, namely on its south-eastern border. Soil cover of this territory is composed of semi-desert saline soils and their complexes with brown semi-desert soils. Vegetation is represented by separate semi-desert communities. These are mainly motley grass-white and cereal communities. Table 3 presents oil product content and enzymatic activity of soils in the Tengutinskoye field.

Table 3 shows that the soil enzymatic activity of the Tengutinskoye field is very low, and the values of invertase and phosphatase activity even in the background samples are zero. In the control

samples of soils no oil products were registered, the values of catalase activity were 0.84 ml O_2 1 g/1 min, urease activity was 0.05 mg NH_3 10 10 g / 24 h. The highest content of oil products was recorded in the soils under the oil spill, the lowest in the soils of well No.261. The average concentration of oil products in the field in the soil is 7.32 %. Decrease of catalase activity, as a rule, depends on oil concentration in soil, but in soils of bullite the content of oil products is 4,4 %, and values of catalase activity are inhibited up to zero values. This can be explained by the fact that bullite is a reservoir where produced water is discharged. Formation waters of the Tengutinskoye field are highly mineralized Table 4.

Table 4. Salt composition of formation water of the tengutinskoye field, mg-eqv./l

pH	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^{++} K^+
5.4	4.5	1740.0	0.6	450.0	125.0	1170.1

High content of anions and cations in the formation water promotes secondary salinization of soils, respectively, the activity of catalase is inhibited not only by the content of petroleum products in soils, but also by soil salinization. Complete inhibition of catalase activity is also fixed in the soils under the oil spill, the correlation coefficient is –0.76. Activity of invertase and phosphatase both in the background soils and in the field soils have zero values. Urease activity in background samples and soils of well No. 261 is 0.05 mg NH_3 10 g / 24 h. In other soil samples urease activity decreases to zero.

Tsubukskoye gas field is also located in the territory of the reserve "Black Earth", but occupies the central territory of the biosphere reserve. It is worth noting that to date, this field is not functioning, all wells are sealed, structures and pipelines of the field are eliminated. From the results of the geobotanical study of this area, it can be concluded that the vegetation is practically the same as the background vegetation and is represented by annual herbs and sod grasses. There are areas devoid of vegetation – cortical solonetzes. Soil cover is represented by brown semi-desert soils in combination with sands of various degrees of consolidation. Conservation of the Tsubukskoye field was carried out in the 1960s, and during this period of time up to now the biogeocenosis of the area has almost completely recovered. However, the anthropogenic impact is still evident in this area.

The results of petroleum product content and activity of soil enzymes in the soils of the Tsubukskoye gas field are presented in Table 5.

Table 5. Petroleum product content and soil enzyme activity in soils of the zubuk field

Selection point	Oil products, %	Catalase activity, ml O_2 per 1 g of soil in 1 minute.	Urease activity, mg NH_3 per 10 g of soil in 24 hours.	Invertaza activity, glucose mg per 1 g of soil in 24 hours	Phosphatase activity. mg P_2O_5 per 1 g of soil in 1 hour.
Control	—	6,1	1,02	0,74	0,25
Central zone of the field	—	5,8	0,88	0,99	0,20
Sealed well	—	5,6	1,10	0,80	0,25
The outskirts of the field	—	6,0	0,70	0,70	0,18

As a result of chemical analysis of soils of the Tsubukskoye gas field it was found that the background soil samples and soils of the field do not contain any oil products, or the content of oil products is below the detection limits. Activity of soil enzymes in soils of the field practically corresponds to the indicators of enzymatic activity in soils of control samples. The high activity of the soil enzymes under study indicates the restoration of biological processes occurring in the soils of the field.

The Ulan-Kholskoye oil, gas and condensate field is located in the Lagansky district of the Republic of Kalmykia. The soil cover of the field is composed of sands with low humus content in combination with brown semi-desert soils. Geobotanical survey has shown that the background vegetation in this area is the white wormwood and fescue community. The results of oil products content and enzymatic activity of soils in the studied oil field are presented in Table 6.

Table 6. Petroleum product content and soil enzyme activity in the soils of the ulaanbaatar field

Selection point	Oil products, %	Catalase activity, ml O_2 per 1 g of soil in 1 minute.	Urease activity, mg NH_3 per 10 g of soil in 24 hours.	Invertaza activity, glucose mg per 1 g of soil in 24 hours	Phosphatase activity. mg P_2O_5 per 1 g of soil in 1 hour.
Control	—	3.84	1.10	1.53	0.20
At the sludge dump	6.9	0.68	0.05	0.00	0.05
At the lagoon	12.2	0.26	0.00	0.00	0.00
At the torch	4.8	0.40	0.10	0.00	0.00

As chemical analysis of soil samples of the Ulan-Kholskoye field has shown – background or control samples do not contain oil products, soil enzymatic activity is low, but higher than in soils of the oil fields studied above. The maximum content of oil products is fixed in the soils of the lagoon 12.2 %. The sump is a pit with the depth of 2–3 m, where a large volume of waste solutions and oil products is merged, it should be noted that the bottom of this pit is not cemented, and oil products get into deeper soil horizons, polluting groundwater. The smallest amount of oil products is contained in the soils near the flare, where the accompanying gas is burnt. The content of oil products at the sludge storage facility is 6.9 %. Activity of all investigated soil enzymes is considerably inhibited that is apparently connected not only with presence of oil products, but also with different soil differences on background sites and oil field sites. If the background samples of soils are not saline, the samples of soils of oilfield are brown semi-desert strongly saline. Thus, phosphatase and invertase activity in oilfield soils are zero. Urease activity is minimal.

4. Conclusion

As a result of our research, we have established that

1) soils of oilfields are subjected to serious anthropogenic load, this is evidenced by the high content of oil products in the soils of the oil fields under study;

2) in oil-contaminated soils of oilfields biological processes are disturbed, there are cardinal changes in the enzymatic activity of soils;

3) the most informative indicator of oil pollution on the territory of the Republic of Kalmykia is the activity of soil enzyme – catalase, as the soils of the region are impoverished with elements responsible for biological activity, which is why the activity of urease, invertase and phosphatase even in control samples of soils have zero values;

4) the anthropogenic impact on soils decreases only over a long period of time, for example, the soils of the liquidated Tsubuk deposit.

Acknowledgment

The research was conducted as part of the government subsidy – the project "Development of rural areas in Southern Russia: a comprehensive analysis of socio-economic and environmental monitoring" (State Registration No.: AAAA-A19-1190111490037-8 (2019–2021).

References

[1] Gordon G, Stavi I, Shavit U and Rosenzweig R February 2018 Oil spill effects on soil hydrophobicity and related properties in a hyper-arid region *Geoderma* **312** 114–20

[2] Ammosova J M and Golev M J August 1998 Monitoring of soil degradation caused by oil contamination *Towards Sustainable Land Use* vol 2(31) (Proc. 9th Conf. of the Int.-Soil-Conservat.-Organisat. Germany) pp 791–6

[3] Gazaliev I M and Alibegova Z M 2009 Estimation of environment in conditions of oil and gas extraction in Dagestan *South of Russ.: ecol., development* **3** 95–101

[4] Pikovskij Yu I 1993 *Natural and technogenic streams of hydrocarbons in a surrounding medium* (Moscow: Moscow university Publ.)

[5] Buluktaev A A 2017 Phytotoxicity and enzymatic activity in soils of Kalmykia under the

influence of oil pollution *South of Russ.: ecol., development* **4** 147–56
[6] Adam G and Duncan H J 1999 Effect of diesel fuel on growth of selected plant species *Environmental Geochemistry and Health* **21** 353–7
[7] Ekundayo E O., Emede T O and Osayande D I 2001 Effects of crude oil spillage on growth and yield of maize (Zea mays L.) in soils of midwestern Nigeria *Plant Foods for Human Nutrit.* **56** 313–24
[8] Antonenko A M and Zanima O V 1992 Influence of oil on fermentative activity of alluvial soils of Western Siberia *Soil Sci.* **1** 38–43
[9] Kolesnikov S I, Zharkova M G, Kazeev K Sh et al 2014 Ecotoxicity assessment of heavy metals and crude oil based on biological characteristics of chernozem *Russ. J. of Ecol.* **3** 157–66
[10] Smirnova T S and Panina Ju Ju 2015 Monitoring of soil hydrocarbon contamination by analysis of its enzymatic activity *Environment protect. in an oil and gas complex* **12** 102–11
[11] Mineev V G 1989 *Workshop on agrochemistry* (Moscow: Publ. MGU)
[12] Kaurichev I S 1983 *Workshop on soil science* (Moscow: Publ. Mir)
[13] Kazeev K Sh, Kolesnikov S I and Val'kov V F 2003 *Biological diagnostics and indication of soils: methodology and methods of researches* (Rostov on Don)
[14] Khaziev F Kh 2005 *Methods of soil enzimology* (Moscow: Publ. Nauka)