Estimation of the Soil Toxicity in the Coastal Zone of the Kizan River in the Astrakhan Region in the Area of the Oil Sludge

A V Kotelnikov, Z Y Pyurbeeva *, S V Kotelnikova

Astrakhan State Technical University, 414056, Astrakhan, Tatishcheva street, 16, Russia

E-mail: * zayana1993pzu@mail.ru

Abstract. In the Astrakhan Region (Russia) on the bank of the Kizan River, which is a tributary of the Volga River, there are two oil sludge collectors, called “Sokolov pits”. They were created in the early twentieth century and now they are a major threat to the ecosystem of the delta river Volga. In this regard, it is topical to conduct studies to assess their environmental safety. The content of petroleum products and the biotoxicity of the soil in the territory of oil sludge accumulators are investigated. The seeds’ germination of watercress (Lepidium sativum) of plants was analyzed. During the study period (2017-2019) the dynamics of phytotoxicity of soils taken from the surface of oil sludge accumulators "Sokolov pits" was of an oscillatory nature. At the same time, the large phytotoxicity of the soil was abolished in 2017. On the territory of oil sludge accumulators "Sokolov pits" the greatest toxicity is the soil from the edge of the oil fields facing the river bank, the smallest is the soil from the edge, far from the shore. Thus, it can be noted a slight positive effect of the reclamation activities, the negative impact on the soil is not eliminated.

Introduction

Particularly acute today are the problems of developing mechanisms for eliminating environmental damage associated with past economic activities. On the territory of the Astrakhan region, objects of past economic activity have been identified that need rehabilitation, which include the Sokolov oil pits in the Volga region of the Astrakhan region, the operation of which began at the beginning of the last century.

At the beginning of the 20th century, earthen pits for storing petroleum products, organized by the merchant Sokolov and Assadulaev, were called Sokolovskie oil pits, which were earthen pits with inclined walls, of significant size, for the temporary reception of scooped up oil, kerosene, fuel oil and other petroleum products. In addition to the adverse effect on the soil, oil pits cause damage to water bodies. Oil sludge is washed out of the pits by the waters of the Kizan River and carried to the Volga and then to the Caspian Sea. This process is especially intense in the summer under the influence of high temperatures. As a result, damage is caused to aquatic organisms, both directly and through changed environmental conditions. When oil masses enter the soil, profound changes in morphological, physical, physicochemical properties occur [1].

In this regard, it is necessary to conduct regular monitoring studies, development and implementation of environmental measures at these sites.

In evaluating the state of the environment, biological tests are of particular importance. This is due to the fact that the results of the chemical analysis do not always allow us to assess the true danger of certain pollutants to the habitat, to predict the consequences of their impact on living organisms [2]. Polluting substances, getting into the environment, can undergo various transformations in it, changing their toxic effect. For this reason, it is expediently to use methods of biotesting [3].

The purpose of the research was to study the content of petroleum products in the sludge storage pits, as well as toxicity assessment of the upper soil layer by the method of biotesting [4].
Object and methods of research

Oil sludge storage pits “Sokolovskie oil pits” are located in the Caspian lowland, on the territory of the Privolzhsky district of the Astrakhan region in the border of the coastal protective and water protection zone of the Kizan River, which are a source of household and drinking water supply and a watercourse of the highest fishery category. The northern boundaries of both sludge storage pits are directly adjacent to the river's coastal part, the boundary of the erosion of the walls of the former sludge storage pits is visually determined with the outlet to the day surface of oil sludge and oil soils that have direct contact with the water object [5]. The nearest existing residential development (private residential sector) is located at a distance of 10 meters from the site of pit № 2 and 160 meters from the site of pit № 1. The distance between the sludge storage pits is 360 meters.

Sludge storage pits are represented by two land plots: pit № 1, S = 9016 m² and pit № 2, S = 8520 m². There is no information about the depth of the objects.

Soil samples were taken from the surface of oil pit at three points:
1 - the edge of the oil pit, remote from the coast (the beginning of the pit);
2 - the central zone of the sludge collector (middle);
3 - the edge of the oil pit facing the river bank (the coastal zone of the pit).

In 2015, within the framework of the event "Environmental rehabilitation of the object" Sokolov pits ", provided for by the state program" Environmental Protection of the Astrakhan Region ", measures were taken to reclaim the upper soil layer in the alignment of the location of the oil pit № 1 and a protective barrier was erected on the border with the river.

The content of petroleum products in soil samples taken in the study area was determined by IR spectrometry. The analysis was carried out on the basis of the accredited laboratory of the North Caspian Sea Technical Directorate. The IR spectrometry method is based on the absorption, reflection and scattering of infrared radiation as it passes through a substance [6].

The IR spectrum allows for a fairly accurate determination of functional groups, especially when it is required to jointly carry out qualitative and quantitative analyzes. In its capabilities, the IR spectrometry method is almost universal. The test samples can be liquid, solid or gaseous [7].

The phytotoxicity of the soil of the Sokolov pits was determined by the method of biotesting. The method is based on the reaction of a test culture for the content of chemical substances in the soil and makes it possible to reveal both inhibitory and stimulating effects of pollutants.

For a comprehensive assessment of the impact of pollution on soil toxicity, a number of indicators adopted in seed production are taken into account: germination, germination energy, germination friendliness, germination rate, morphological parameters (length of roots and aerial parts of seedlings). In our article we will only consider germination. Germination - the number of germinated seeds, expressed as a percentage of the total number of seeds [8]. Seed germination of the test object is one of the main indicators of viability. The germination rate of watercress (Lepidium sativum) seedlings shows the effect of soil toxicity on seeds.

Each soil sample was planted with 100 watercress seeds (Lepidium sativum). Watering was periodically carried out with equal amounts of settled tap water. Observations were carried out for 10 days. The studies were performed in triplicate [9]. Seed germination is the number (expressed as a percentage) of normally germinated seeds over a certain period of time (10 days).

The data obtained were statistically processed using the Student's t-test.

The results and discussion

The content of petroleum products in the ground. The results of laboratory studies of soil samples are presented in Table 1.
Table 1. To determine the maintenance of petroleum products in the surface layer of oil sludge accumulators (mg / kg)

| Name of sample          | Winter          | Season | Summer       | Autumn        |
|-------------------------|-----------------|--------|--------------|---------------|
| Pit № 1 (beginning)    | 41.0±14.43      |        | 115.0±29.08  | 115.0±29.15   |
| Pit № 1 (middle)       | 166.2±41.62     |        | 102.2±26.09  | 168.3±42.43   |
| Pit № 1 (coastal zone) | 579.5±144.91    |        | 27728.4±6932.24* | 1290.3±322.20* |
| Pit № 2 (beginning)    | 722.0±180.53    |        | 378.2±95.32  | 777.2±194.14  |
| Pit № 2 (middle)       | 555.7±138.91    |        | 3760.1±940.27* | 221.0±55.34   |
| Pit № 2 (coastal zone) | 1235.0±308.82*  | 11140.0±2785.05* | 7340.4±1835.41* | 17044.3±4261.04* |

* - MAC = 1000 mg/kg

For pit № 1 for all seasons, the excess of the TEC was observed only in the coastal part of the pit. The highest content of oil products in the soil was noted in the summer, and amounted to 27728.4 ± 6932.24 mg/kg of soil, which exceeds the maximum admissible concentration (MAC), which is 1000 mg/kg by 27 times. This is due to the fact that the samples were taken behind the protective target; because there was ebb (we take the soil closest to the water). The excess of the MAC was also noted in the samples taken in spring and autumn. But they were not as critical as in the summer, because select them already behind the protective target. In the spring, the amount of oil products in the soil was 2370.0 ± 593.09 mg/kg (exceeding the MAC by 2 times), and in the autumn 1290.3 ± 322.20 mg/kg.

For pit № 2, in all seasons, the excess of the MAC was observed not only in the coastal part of the pit, but also in the central zone. The maximum amount of oil products was observed in the soil sampled in autumn and amounted to 17044.3±4261.04 mg/kg of soil, which exceeds the MAC by 17 times. In the spring, in the coastal part of the pit, the amount of oil products in the soil was 11140.0±2785.05 mg/kg (exceeding the MAC by 11 times). In summer, in the coastal part of the pit, the amount of oil products in the soil was 7340.4±1835.41 mg/kg (the excess of the MAC by 7 times). In winter, in the coastal part of the pit № 2, the amount of oil products in the soil was 1235.0±308.82 mg/kg. Also, for the second pit, an excess of the MAC was noted in the central part of the pit, namely, in spring and summer. In the spring, the amount of oil products in the soil was 1530.0±383.03 mg/kg, and in the summer - 3760.1±940.27 mg/kg (exceeded the MAC by 3 times).

When comparing all seasons, it can be seen that summer samples are the most toxic than all other seasons. It is also observed for pit № 1 and pit № 2. This can be explained by the movement of groundwater and the pushing out of oil products to the surface of the oil sludge reservoir. The data obtained indicate that the territory of the second pit is the most polluted with oil products [10]. The territory of the first pit is characterized by a lower content of oil products in comparison with the second object. The most polluted area is the coastal zone of the pits.

Assessment of soil toxicity. Analysis of the results of experimental data showed that in all seasons of the year the largest number of germinated seeds was in the sample taken at the beginning of pit № 1 (more than 80%). The lowest germination rate of the test object among all seasons of the year was 27% in a soil sample taken in the coastal zone of the pit (Fig. 1).

When comparing the 2017, 2018, 2019 years of the experiment, it can be noted that the maximum number of germinated seeds was recorded in the soil sampled in the winter of 2017. The minimum number of germinated seeds was recorded in the soil sampled in the summer and autumn of 2019.

Attention is drawn to the differences in the toxicity of the soil taken from different parts of the pit. At the beginning of pit № 1, the soil can be assessed as slightly toxic; more than 80% of the total number of seeds germinated in it. In the central part of the pit there is a decrease in the germination rate by almost 30% than at the beginning of the pit. On average from 50% to 56% of seeds germinated in the soil. The soil can be assessed as moderately toxic. At the bank of the pit № 1, there was the lowest germination rate (79-84%), therefore the soil is highly toxic.
No seasonal fluctuations were noted. Almost all seasons of the year were similar to each other. It can also be noted that from year to year the percentage of germination of watercress (*Lepidium sativum*) seedlings decreases, which means that the toxicity of the soil increases.

![Figure 1. Dynamics of germination of *Lepidium sativum* grown on the soil of pit № 1](image)

The indicators of germination of seedlings of watercress seeds (*Lepidium sativum*) grown on the soil of the oil sludge tank № 2 are shown in Figure 2.

The lowest germination rate was found in seeds grown on soil taken from the shore point of the pit. High toxicity in these samples manifested itself in all seasons of the year. Especially in winter and summer 2017, autumn 2019. For 10 days of observation, not a single seed sprouted here.

![Figure 2. Dynamics of germination of *Lepidium sativum* grown on the soil of pit № 2](image)
The highest germination capacity of the test object was noted in the soil taken at the beginning of the oil pit № 2. It was 49%. There is a large difference in germination rates between the two Sokolov pits. In the first hole in the coastal zone, the indicator ranges from 79-84%, in the second whole the seed germination rate does not exceed 49%.

In the central part of the oil sludge tank № 2, the maximum germination rate was 26% (in summer 2017 and winter 2019). In the second pit, no seasonal fluctuations were noted either. Almost all seasons of the year were similar to each other. In the second oil pit, seed germination is also inhibited from 2017 to 2019.

From the above, it can be concluded that the highest phytotoxicity was typical for the coastal zone of both pits (high toxicity for pit № 1 and very high toxicity for pit № 2). The soil from the central part of the first pit was characterized as moderately toxic, and the second - highly toxic. The soil from the beginning of the pit № 1 had a very weak toxicity, and from the pit № 2 - the average toxicity.

**Conclusion**

Thus, a slight positive effect from the reclamation measures carried out can be noted, the negative impact on the soil has not been eliminated [11].

The results of the studies have revealed a high degree of pollution of the soil with oil products in the territory of the location of the Sokolov pits oil sludge ponds. Exceeding the permissible level for the content of oil products in some areas is tens of times. The most contaminated with oil products was the soil of pit № 2 in the spring sampling.

Analysis of the results obtained allows us to draw the following conclusions:

1. The territory of the second pit is the most polluted with oil products. The more polluted area is the coastal zone of the pits. With the passage of time and the installation of a protective cross-section, on the territory of the first oil pit, the reduction of oil products in the soil is almost 70 times. In the pit № 2, the opposite dynamics is observed - an increased level of oil products in the soil is recorded (exceeding the MAC by 17 times).

2. During the period under study, the dynamics of phytotoxicity of soils sampled from the surface of oil sludge reservoirs was of an oscillatory nature. In both investigated oil pits, the most phytotoxic soil was taken from the coastal part, especially pit № 2, where 100% of seeds died, the least phytotoxic was the soil taken from the beginning of the Sokolov pits. Among all seasons of the year, the highest toxicity of tests was revealed in the spring and summer seasons of the year. The phytotoxicity of the soil of the second sludge pond was higher in all seasons compared to the first.

Previously, we found that the MAC was exceeded for the content of oil products in the soil layer in the territory of both oil storage ponds and the phytotoxicity of their soil extracts. As can be seen from the results of the study, the reclamation of the upper soil layer in the territory of the first oil sludge reservoir gave its own small positive effect. It should be noted that it was not possible to completely eliminate the negative impact on plants.

This is probably due to the fact that the source of oil sludge was not completely eliminated, and oil hydrocarbons continue to migrate to the upper soil horizons, maintaining an environmental hazard in the territory of the location of oil sludge storage.

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