Monitoring of technogenic pollution of soil in the region

L N Zhichkina¹, V V Nosov², K A Zhichkin³, P V Starikov², A T Vasyukova⁵ and Z A Smirnova⁶

¹ Department of Land Management, Soil Science and Agrochemistry, Samara State Agrarian University, 2 Uchebnaja Street, 446552, Kinel, Russia
² Department of Economics and Management, K.G. Razumovsky Moscow State University of technologies and management, 73 Zemlyanoy val, 109004, Moscow, Russia
³ Department of Economic Theory and Economics of AIC, Samara State Agrarian University, 2 Uchebnaja Street, 446552, Kinel, Russia
⁴ Department of Humanitarian and Socio-Economic Disciplines, Academy of the Investigative Committee of the Russian Federation, 12 Vrubel Street, 125080, Moscow, Russia
⁵ Department of Product Technology, Public Catering and Merchandise, K.G. Razumovsky Moscow State University of technologies and management, 73 Zemlyanoy val, 109004, Moscow, Russia
⁶ Volga Cossack Institute of Management and Food Technologies (branch), K.G. Razumovsky Moscow State University of technologies and management, 73 Zemlyanoy val, 109004, Moscow, Russia

E-mail: novla@list.ru

Abstract. The purpose of the study is to conduct monitoring of technogenic pollution of soil in the Samara region. The objectives of the study are to identify the sources of technogenic pollution of soil, to analyze the minimum and maximum concentrations of heavy metal on long-term observation plots and background plots, to assess the average and the maximum values of total petroleum hydrocarbons (TPH) in soil of observed land plots. The allowable concentration levels of heavy metals (manganese, lead, cadmium, copper, nickel and zinc) in the soil of the Samara region are not exceeded. Mean heavy metal concentrations in soil did not exceed the maximum permissible concentration (MPC) and the approximate permissible concentration (APC) and was 0.1-0.6 MPC (APC). The maximum concentration of metals in soil was 0.1-0.9 MPC (APC). However, the obtained results were higher than background concentrations of metals. The mean concentrations of aluminium exceeded the background levels by a factor of 3.4-6.7. The maximum concentrations of aluminium in soil was observed in the area of the Samara metallurgic plant (ZAO ‘Arconik’) and was 9.2 of background.

1. Introduction

Soil is the capital stock of Russia’s resources. It is closely linked to food, ecological and economic security of the country. Soil is a complex multiple-factor open bioinert system that has the capacity to supply nutrients, water, air and warmth to plants - fertility, which is the component of overall soil productivity. Soil properties can change during the production process [1-4]. Men use soil in various
ways: it serves as the foundation for settlement, industrial plants and transportation nets, satisfies recreational needs of people, and is used for storage of industrial waste [5-9]. The most fundamental soil properties to people are those which provide a decent living environment and biological productivity [10].

Soil is a component of biocoenosis that performs physical, physicochemical, chemical, informational and ecosystem functions. The role of soil in the biosphere is crucial: it is an indispensable energy accumulator that regulates the interaction between the geologic and biological cycles, life on Earth, the composition of the atmosphere, hydrosphere and biosphere processes [11-14]. Hydrospheric functions of soil are expressed in the formation of streamflow, transformation of surface water into groundwater, provision of organisms living in bodies of water with carried soil compounds, and act as an adsorption barrier that protects water area from contamination. Atmospheric functions of soil are expressed in absorption and reflection of solar radiation, regulation of moisture circulation and gaseous regime of air conditions, in particular, prevention of atmospheric escape of some gases. Soil plays a role in the biogeochemical transformation of the upper lithosphere being a source for the formation of minerals and rocks, and ensure the transfer of stored solar energy to the lower parts of the crust of Earth, protecting it from erosion [15-17].

The intensive economic activity of people is closely tied to the environmental impact. Its negative impact on people's health and ecosystems can be explained by the use of natural resources, accidents, emergencies and poisonous effect of contaminants [18-22]. Therefore, the sanitary functions of soils, that is, their ability to self-purify and self-restore, are of particular importance. This occurs due to the mineralization and destruction by soil microorganisms of organic and inorganic residues (garbage, various household and industrial wastes) entering the surface and into the soil. The specified function is associated with the absorption of gases, liquids, molecules, ions, chemical absorption of substances, with the formation of insoluble compounds, sorption of microorganisms.

2. Methods and materials
One of the main criteria for the assessment of the level of soil contamination by chemicals is the maximum permissible concentration (MPC) of the substance. Another important criterion is the approximate permissible concentration (APC) of heavy metals in the soil. If soil is contaminated with substances without data on their MPC (APC), then the levels of contamination are compared with natural background contents. We assume that background contents of chemical elements in the soil are their concentrations in soils that were not influenced by men and are 20-50 km distant from the emission source. Note that soils of background plots should be analogues of contaminated ones [23]. Soil sampling was carried out in the upper part of the soil profile (at a depth of 0-10 cm). The mass fraction of acid-soluble forms of manganese, lead, cadmium, copper, nickel, zinc and aluminum was determined in them. The soils of all the studied areas are chernozems of heavy granulometric composition, which are the most common in the conditions of the Samara region.

As a complex indicator of soil contamination by heavy metals, we used the total contamination index (Zc). To calculate it, we used mean concentrations of metals in the soil of the researched object and background concentrations for this region [24].

The study was conducted in the Samara region in 2018 on long-term observation plots: AO 'Arconik Samara Metallurgical Plant' (park of the Dubki recreational base, 60-years October Park), on territories of background plots (Samarskaya Luka National Park, Povolzhskaya AGLOS Agroforestry Research Station).

3. Results and discussion
The Samara region is one of the leading industrial regions with main industrial branches being machinery, metalworking, fuel, energy, chemicals, petrochemicals and non-ferrous metallurgy. The agricultural sector is also developed and is based on crop production, mostly wheat, rye, sunflower, barley, millet, buckwheat. Agricultural production has a major impact on the process of soil formation; therefore, every level of development of the productive forces corresponds to biocoenosis productivity.
High yields of crops are possible with the introduction of new resource-saving technologies, that include the use of plant protection agents, pesticides for control of phytophaga, phytopathogens and weeds.

Geomorphic conditions and human activities can influence the concentrations of heavy metals in soil. Heavy metals are components of ecosystems, biocatalysts and bioregulators of physiological processes. Their inhibitory and toxic for living organisms actions are most obvious when their concentrations in the biosphere are high, regardless of the sources (natural or technogenic). Heavy metals can accumulate on the soil surface or disperse in soil depending on the nature of geochemical barriers of the territory.

Contamination of lands by heavy metals is a global problem in developed regions. Is such lands are used for agriculture, heavy metals can accumulate in agricultural products. Accumulating in soil, they influence the biological properties of soil, humus level, soil structure and soil reaction, which leads to a decline in soil fertility [25, 26].

Natural processes can cause soil contamination by oil and petroleum products. However, under natural conditions, oil lies deep beneath the surface and does not affect the soil. Hence, the main source of soil contamination is human activity. Contamination occurs in oil-field regions, near oil pipelines and during oil transportation. Negative impact of oil on soils is evident in changes in morphological, physicochemical and microbiological properties of soils. Frequent oil spills contribute to solid resinous-asphaltene covers, which results in soil exhaustion and plants drying out. The specificity of soils contaminated by petroleum products is that plants do not grow in them and very few species of microorganisms survive in such soils. It also takes a long period of time for petroleum products to decompose.

As a result of direct and indirect human activities, soil often loses its fertility, degrades or erodes. It usually occurs when human activities become irrational and ecologically unsound. To avoid adverse impact on soil, monitoring should be conducted, and attention should be paid to the issues of rational use of soils and soil protection.

In accordance with GOST 17.4.3.04-85, soils with concentrations of contaminants at MPC levels or higher are categorized as contaminated soils. We determined that in the Samara region the mean concentrations of heavy metals in the park of the Dubki recreational base and the 60-years October park were 0.2-0.6 MPC (APC), maximum concentrations - 0.2-0.9 MPC (APC). The results are presented in table 1.

Table 1. Mean/maximum concentrations of heavy metals in soil, MPC (APC)\(^4\).

| Observation points, classes of hazards | pH  | Mn (MPC 1500 mg/kg) | Pb (MPC 32 mg/kg) | Cd (APC 2 mg/kg) | Cu (APC 132 mg/kg) | Ni (APC 80 mg/kg) | Zn (APC 220 mg/kg) |
|---------------------------------------|-----|---------------------|-------------------|------------------|---------------------|-------------------|-------------------|
| Park of the Dubki recreational base, 0.5 km from the AO ‘Arconik Samara Metallurgic Plant’ | 5.5 | 0.2 | 0.3 | 0.4 | 0.6 | 0.9 | 0.4 |
| 60-years October Park, 0.5 from the AO ‘Arconik Samara Metallurgic Plant’ | 5.5 | 0.2 | 0.2 | 0.5 | 0.3 | 0.3 | 0.6 |
| Samarskaya Luka National Park | 5.5 | 0.2 | 0.2 | 0.4 | 0.1 | 0.2 | 0.3 |
| Povolzhskaya AGLOS | 5.5 | 0.1 | 0.1 | 0.5 | 0.1 | 0.3 | 0.4 |
Agroforestry Research Station

| Class of hazard | 3 | 1 | 1 | 2 | 2 | 1 |
|-----------------|---|---|---|---|---|---|

* Composed by the authors.

According to GN 1.1.7.2041-06, GN 2.1.7.2511-09 and GN 1.2.3111-13, MPC is maximum permissible concentration, and APC is approximate permissible concentration.

In soils of the Samarskaya Luka National Park and Povolzhskaya AGLOS Agroforestry Research Station, the mean and maximum concentrations were 0.1-0.5 MPC (APC) and 0.1-0.8 MPC (APC) respectively.

The results exceed background concentrations of researched objects. In the soil of the Dubki recreational base, the mean concentrations of aluminium exceeded the background levels by 4.1 times.

Table 2 shows that in soils of the 60-years October park, the mean concentration of copper, nickel, zinc and aluminium were 1.1-6.7 of the background levels.

| Observation points, classes of hazards | Mn | Pb | Cd | Cu | Ni | Zn | Al |
|---------------------------------------|----|----|----|----|----|----|----|
| Park of the Dubki, 0.5 km from the AO 'Arconik Samara Metallurgic Plant' | 0.9 | 0.7 | 0.3 | 0.9 | 0.7 | 0.8 | 4.1 |
| 60-years October Park, 0.5 from the AO 'Arconik Samara Metallurgic Plant' | 1.2 | 1.0 | 0.4 | 1.2 | 1.0 | 1.2 | 5.6 |
| Samarskaya Luka National Park | 0.7 | 0.5 | 0.4 | 0.8 | 0.5 | 0.8 | 3.4 |
| Povolzhskaya AGLOS Agroforestry Research Station | 0.6 | 1.3 | 0.9 | 2.4 | 1.0 | 1.6 | 7.3 |

* Composed by the authors.

In soils of the Samarskaya Luka National Park, the mean concentrations of aluminium exceeded the background levels by 3.4 times, the maximum concentrations of zinc and aluminium exceeded the background levels by a factor of 1.1-3.6. In soils of the Povolzhskaya AGLOS Agroforestry Research Station, the mean concentrations of zinc and aluminium exceeded the background levels by a factor of 1.1-6.0. The maximum concentrations of manganese and cadmium did not exceed the hygienic standards, but concentrations of other metals were 1.3-7.3 times higher than the background levels. Concentrations of nickel were equal to the background levels.

The study shows that soils on long-term observation plots fall under the category with tolerable levels of contamination, concentration of Zc less than 16 and low morbidity rates.

Oil spills result in contamination of surface waters, underground waters and soil cover, which has a negative impact on the ecosystem activity. Petroleum products can penetrate the soil, affecting its characteristics and properties, such as loss of ability to absorb and retain moisture, due to the formation of an oil film with hydrophobic properties, deterioration of the air regime, and changes in soil structure. In the region, the main sources of soil pollution by oil products are: existing and reserved exploratory and production wells, oil pipelines, transport and industrial enterprises. Territories that were studied for concentrations of heavy metals in soil were also studied for concentrations of petroleum products. Soils in Tolyatti, the Komsomolsk district and the Fedorovka residential area were also considered. Since the maximum permissible concentrations of petroleum products in soils are not available, the levels of soil contamination were assessed based on the background criteria of 50 million\(^3\) mg/kg. The study found
that the mean and maximum concentrations of petroleum products in soils of all observation plots exceeded the background values, as can be seen from table 3.

**Table 3.** Mean/maximum concentrations of TPH, background\(^a\).

| Observation points, classes of hazards                                      | Mean/maximum concentrations |
|---------------------------------------------------------------------------|----------------------------|
| Park of the Dubki recreational base, 0.5 km from the AO 'Arconik Samara Metallurgic Plant' | 1.9                        |
| 60-years October Park, 0.5 from the AO 'Arconik Samara Metallurgic Plant'     | 2.0                        |
| Samarskaya Luka National Park                                             | 2.7                        |
| Povolzhskaya AGLOS Agroforestry Research Station                           | 1.4                        |
| Tolyatti, the Komsomosk district, the Fedorovka residential area           | 2.7                        |
|                                                                            | 10.5                       |

\(^a\) Composed by the authors.

Mean concentrations of TPH in soils exceed background levels by a factor of 1.4-2.7, maximum concentrations - by a factor of 2.1-10.5.

4. Conclusion

Soils of the Samara region fall under the category with tolerable levels of contamination by heavy metals (manganese, lead, cadmium, copper, nickel, zinc). In 2018 the mean concentrations of heavy metals in soils did not exceed MPC (APC) levels and were 0.1-0.6 MPC (APC). The maximum concentrations of metals in soil were 0.1-0.9 MPC (APC). However, the obtained results were higher than background concentrations of several studied metals: the mean concentration of aluminium exceeded the background levels by 3.4-6.7 times. The maximum concentrations of aluminium in soil were found near the AO 'Arconik Samara Metallurgic Plant' being a major manufacturer of aluminum semi-finished products and were 9.2 of the background level.

The mean concentrations of petroleum products in the surface soil of long-term observation plots and background plots exceed the criterion value by a factor of 1.4-2.7. The mean concentrations of petroleum products in soils near the OOO "Samaraterminal" located in the Fedorovka residential area of the Komsomosk district, Tolyatti, exceeded the background levels by 2.7 times.

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