The Samara region soil contamination with industrial toxicants

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Abstract. Currently, the problem of environmental pollution by toxicants of industrial origin has great ecological, social and economic importance. The research aim is to analyze the soils contamination in the Samara region with industrial toxicants. The objectives of the research included: to reveal the soil pollution dynamics with nitrates and sulfates over the years, to assess their content in the areas of soil contamination and in the background areas. The studies were carried out in 2014-2018 in the Samara city (near the territory of JSC "Arkonik SMZ") and in the background areas (FSBI "National Park Samarskaya Luka" and Povolzhskaya AGLOS-Branch of FSC Agroecology RAS). In 2014-2018 the content of nitrate ions in the soils of the background plots and in the areas adjacent to JSC "Arkonik SMZ" varied from 7 to 66 mg/kg (1-9.4 F), sulfate ions from 13 to 303 mg/kg (0.4-8.7 F). During the studied observation period, there is a tendency to a decrease in the content of nitrates in the soils, the MPCs were not exceeded, which makes it possible to classify these soils as a pollution acceptable category. Exceeding the MPC of sulfates in research certain years (2014 in soils 5 km from JSC Arkonik SMZ and soils of FSBI National Park Samarskaya Luka, 2017 in soils 5 km from JSC Arkonik SMZ, 2018 in soils of the Volga region AGLOS-Branch of the Federal Research Center of Agroecology RAS) had a local character.

1. Introduction
Currently, the problem of environmental pollution by toxicants of industrial origin has great ecological, social and economic importance. Industrial enterprises, polluting the environment, can harm the health of the population, destroy the soil cover. Soil resources are one of the most important national resources of Russia and determine its food, environmental and economic security. The soil cover, performing
various ecological functions, is the environment for the existence of plants and soil biota, a component of natural and anthropogenic landscapes and the biosphere as a whole. More and more lands are subject to anthropogenic impacts that can change the chemical composition of the soil, contaminating it with toxic substances. Soil fertility is the main condition for the phytocenoses and agriculture productivity [1-8].

The soil is formed on the earth's surface in that part of the biosphere where the lithosphere, atmosphere and hydrosphere close and penetrate into each other, where the density of the planet's living matter reaches its maximum values. The soil lives in diurnal, annual, perennial and secular hydrothermal rhythms. In accordance with them, the speed and often the direction of soil processes change, there is a constant exchange of substances between soil, vegetation and other living organisms. Chemical elements and their compounds brought from outside can accumulate in the soil [9-16].

Soil degradation - negative changes, expressed in a decrease or loss of the soil's ability to perform the resources reproduction functions, environment and socio-economic functions. Soil degradation occurs under the combined action of anthropogenic and natural factors and leads to a change in the landscapes ecological functions, its recreational, sanitary and hygienic characteristics, and the occurrence of possible costs for soil restoration [17-22]. One of the reasons for soil degradation is its pollution with industrial toxicants, which leads to deterioration of the soil structure, its chemical properties and loss of fertility. Contaminated soil cover is a danger from the viewpoint of the toxic substances intake in the human body with food, it can be a source of air and groundwater pollution [23-29].

2. Methods and materials

The research aim is to analyze the contamination of soils in the Samara region with industrial toxicants. The objectives of the research included: to reveal the dynamics of soil pollution with nitrates and sulfates over the years, to assess their content in the areas of soil contamination and in the background areas.

The studies were carried out in 2014-2018 in Samara (near the territory of metallurgical plant (JSC «Arkonik SMZ»)) and in the background areas. FSBI «National Park Samarskaya Luka» (30 km west of Samara) and Povolzhsky AGLOS-Branch Federal Research Center of Agroecology RAS (20 km southwest of Samara) belong to the background areas adjacent to the technogenic ones. At the background plots, 10 soil samples were taken annually. The pH$_{KCl}$ value varied from 5.9-6.7. The areas of soil contamination include the territories adjacent to JSC «Arkonik SMZ». 15 soil samples were taken annually at two sites located 0.5 and 5 km from the plant. The pH$_{KCl}$ value varied from 5.5 to 7. The predominant type of soils is chernozems with a powerful intensely colored dark gray, often almost black humus-accumulative horizon, good structure, high resistance to destruction, medium and heavy granulometric composition.

Table 1. Hazard class, MPC, background value of industrial toxicants.

| Indicator | Pollutant, mg / kg | nitrates ($NO_3^-$) | sulfates ($SO_4^{2-}$) |
|-----------|-------------------|----------------------|-----------------------|
| Background value (F) | 7 | 35 |
| Hazard Class | 3 | 3 |
| Maximum permissible concentration (MPC) | 130 | 160 |

The criterion for soil pollution with nitrates and sulfates is the maximum permissible concentration of these substances. The maximum permissible concentration of a soil polluting substance (MPC) according to Hygienic Standards (GN) 2.17.2041-06 is the maximum concentration of a soil polluting substance that does not cause negative direct or indirect impact on the natural environment and human health. It is also possible to compare soil contamination with the natural background level. The background concentration is understood as the average concentration of substances in the studied soils, which depends on the geological and soil-forming conditions, while the soils and relief elements should be analogous to the contaminated ones (table 1). According to state standard (GOST) 17.4.3.04-85, the
category of «contaminated» should include soils in which the pollutants amount is at or above the MPC. The assessment of the degree of chemical contamination of the soil is determined according to Sanitary Regulations and Standards (SanPiN) 2.1.7.1287-03.

3. Results and discussion

The Samara region is the Middle Volga region important industrial center; large enterprises of metallurgical, chemical, aerospace, energy and other industries are located here. Modern industrial production is characterized by a complex technology, a large number of operations and pollutants emissions into the environment, the wastes number emergence. Once in the natural environment, technogenic substances can be redistributed due to migration, transformation and accumulation in the biosphere various components. The Samara region territory is characterized by a high level of anthropogenic impact on natural ecosystems. Due to its properties, soil is a stable and most objective indicator of technogenic pollution, in contrast to water and air. All this necessitates the soil pollution determination by industrial toxicants. Toxicants of industrial origin include heavy metals, oil and oil products, fluorine, nitrates, sulfates, etc. Nitrates and sulfates accumulate in the upper fertile soil layer, accumulate in plant products, and through it through the food chain they enter the body of animals and humans.

Monitoring of soil contamination with nitrates in the Samara region showed that in 2014 their content in soil varied from 10 to 36 mg/kg, which was 1.4-5.1 F and did not exceed the MPC. At the same time, the largest mass fraction of nitrate ions was noted in the soils adjacent to JSC «Arkonik SMZ», the smallest in the background plot is the Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology RAS. In 2015, the content of nitrates in the analyzed soils increased by 2.1-3.7 times. The largest amount of nitrates was found in soil samples located 0.5 km from JSC «Arkonik SMZ» - 66 mg/kg (9.4 F), the least 21 mg/kg (3 F) in soils Povolzhsky AGLOS-Branch of FSC Agroecology RAS, the excess of MPC in soil samples was not observed (table 2).

| Place of sampling of soil samples | Source, distance | Content $\text{NO}_3^-$, mg / kg |
|----------------------------------|------------------|---------------------------------|
| Samara (areas of soil contamination) | JSC "Arkonik SMZ", 5 km | 36 41 7 19 7 |
|                                  | JSC "Arkonik SMZ", 0.5 km | 18 66 22 10 27 |
| Volzhsky district (background areas) | FSBI "National Park Samarskaya Luka", 30 km | 11 32 11 7 18 |
|                                  | Povolzhsky AGLOS-Branch of FSC Agroecology RAS, 20 km | 10 21 30 16 23 |

In 2016-2018 there was a decrease in the content of nitrates in the studied soils, compared to 2015. Thus, in 2016, the largest mass fraction of nitrates was noted in the soils of the background plot Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology RAS and amounted to 30 mg/kg (4.3 F), in 2017 - 2018, the largest amount of nitrates was observed in the areas of soil contamination in Samara, 19 mg/kg (2.7 F) and 27 mg/kg (3.9 F) respectively. The minimum amount of nitrates (7 mg/kg), corresponding to the background value, was found in 2017 in the soils of the background plot of the FSBI «National Park Samarskaya Luka», in 2018 in the soils located 5 km from JSC «Arkonik SMZ».

In general, over the five-year observation period, there is a tendency to decrease the nitrates content in soils, both in the background plots and in the areas adjacent to JSC «Arkonik SMZ». According to the sanitary and epidemiological requirements for soil quality and taking into account the 3rd hazard class of nitrates, the analyzed soils are characterized by an admissible category of pollution (from 2 background values to the MPC).

Observation of soil contamination with sulfates in the Samara region showed that in 2014 the sulfate content in the analyzed soils varied from 43 to 303 mg/kg (from 1.2 F to 8.7 F). In the soils of the
background plot of the FSBI «National Park Samarskaya Luka» their content exceeded the MPC by 1.4 times, in soils located 5 km from JSC «Arkonik SMZ» by 1.9 times, which corresponds to the moderately hazardous category of pollution (table 3).

Table 3. Mass fraction of sulfate anions in soil samples of the Samara region.

| Place of sampling of soil samples | Source, distance                                                                 | Content $SO_4^{2-}$, mg / kg |
|----------------------------------|---------------------------------------------------------------------------------|-------------------------------|
| Samara (areas of soil contamination) | JSC «Arkonik SMZ», 5 km                                                        | 303 149 36 188 13             |
|                                  | JSC «Arkonik SMZ», 0.5 km                                                       | 143 92 110 52 30              |
| Volzhsky district (background areas) | FSBI «National Park Samarskaya Luka», 30 km                                    | 216 64 106 38 70              |
|                                  | Povolzhsky AGLOS-Branch of FSC Agroecology RAS, 20 km                          | 43 84 47 89 173               |

In 2015, there was a decrease in the content of sulfates in the studied soil samples, compared to 2014, with the exception of the background plot Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology of the Russian Academy of Sciences, in the soils of which the sulfates content increased 2 times and amounted to 2.4 F. Sulfates were found in the soils of the National Park Samarskaya Luka background plot (64 mg/kg, 1.8 F). At the same time, the sulfate ions content in all soil samples exceeded the background value (35 mg/kg), the excess of the MPC was not observed. In 2016, the sulfates content in the soil increased by 1.2 times at sites located 0.5 km from JSC «Arkonik SMZ», by 1.7 times at the background site of the FSBI «National Park Samarskaya Luka». In the studied soil samples of 2016, the sulfate content varied from 36 to 110 mg/ha, exceeding the background value, but not exceeding the MPC. In 2017, the sulfate ions content in soils varied from 38 to 188 mg/kg (1.1-5.4 F), an excess of MPC was noted in soils located 5 km from JSC «Arkonik SMZ» (1.2 MPC) which corresponds to the moderately hazardous category of pollution. In 2018, in most soil samples, the sulfates mass fraction did not exceed the MPC, with the exception of the Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology of the Russian Academy of Sciences the background plot soils, where the sulfate content was 173 mg/kg (1.1 MPC), which corresponds to a moderately hazardous pollution category.

Monitoring of soil contamination with sulfates in 2014-2018 showed a trend towards a decrease in their content in the soil, with the exception of the background site Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology RAS, where their content increased (from 43 mg/kg in 2014 to 173 mg/kg in 2018). According to the sanitary and epidemiological requirements for soil quality and taking into account the 3rd class of sulfate hazard, all analyzed soils in 2015-2016 are characterized by an admissible category of pollution (from 2 background values to MPC). In 2014, only the soils of the background plot Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology of the Russian Academy of Sciences and soils located 0.5 km from JSC «Arkonik SMZ» can be attributed to the permissible category of pollution, in 2017 soils of the background sites and soils 0.5 km from JSC «Arkonik SMZ», in 2018 the soils located near JSC «Arkonik SMZ» and soils of the background plot of the FSBI «National Park Samarskaya Luka».

Chemical industries, metallurgical, textile and woodworking enterprises introduce a significant amount of nitrogen compounds into the environment. Natural emission of sulfates is caused by anthropogenic release into the atmosphere and deposition on the earth's surface associated with the oxidation of sulfur dioxide during the combustion of fossil fuels, smelting of ferrous and non-ferrous metals, oil refining, and production of sulfuric acid. The accumulation of nitrates and sulfates in the upper horizons can lead to an increase in soil acidity. The study of soils showed that the reaction of the medium varied from slightly acidic to neutral and amounted to pH_{KCl} 5.5-7.0.
4. Conclusion
The studies carried out to identify the dynamics and assessment of soil pollution made it possible to establish that the soil is an indicator of long-term natural and man-made impacts. In 2014-2018 the content of nitrate ions in the soils of the background plots and in the areas adjacent to metallurgical plant varied from 7 to 66 mg/kg (1-9.4 F), sulfate ions from 13 to 303 mg/kg (0.4- 8.7 F). During the studied observation period, there is a tendency to decrease the content of nitrates in soils, both in the background plots and in the plots adjacent to JSC «Arkonik SMZ», the MPCs were not exceeded, which makes it possible to refer these soils to a pollution acceptable category. Exceeding the MPC of sulfates in research certain years (2014 in soils 5 km from JSC «Arkonik SMZ» and soils of FSBI «National Park Samarskaya Luka», 2017 in soils 5 km from JSC «Arkonik SMZ», 2018 in soils of the Povolzhsky AGLOS-Branch of the Federal Research Center of Agroecology RAS) had a local character. At the same time, all soil samples where the MPC was exceeded were characterized by a moderately hazardous category of pollution.

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