Analysis of some chemical indicators of soils of industrial-oil-polluted territories

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Abstract. The object of the research is the territory of the military unit (Technical missile base). The subject of the research is chemical pollution of soil and structures on the territory of the former military unit. There remained destroyed structures for various purposes on the territory and there is visible soil pollution with various chemicals, presumably oil products and rocket fuel components. Methods of instrumental and titrimetric analysis of water extraction of soil samples were used to assess the pollution. A total of 13 soil samples and a control sample were analyzed. All samples were subjected to multicomponent complex analysis, during which acidity - pH, salinity, electrical conductivity, alkalinity, Ca, Mg, Cl ion content were determined in each sample. An attempt is made to answer the question about the composition and danger of such anthropogenic pollution, as well as about the possibility of further use of these lands.

1. Introduction

Human life is inseparably connected with soil. Plants that give people food, animal feed, and raw materials for industry can grow only on the soil. This greatest natural wealth has been created for centuries and millennia, and one should use it wisely. [1]

In modern life, there are various kinds of environmental impacts that do not always affect the organisms living in the area in a positive way. The problem of eliminating local pollution caused by oil spills in the areas of fuel and lubricants bases and warehouses is acute all over the world. Characteristic features of such pollution are: proximity to settlements, long-term oil pollution, lack of full-fledged soil cover in the place of spillages. For example, during the exploitation of a land plot allocated to the Ministry of Defense, there occurred technogenic pollution of the soil with various chemicals, presumably oil products and rocket fuel components. Destroyed buildings that had been used for various purposes and visible contamination remained on the territory of the plot. After the military unit has been disbanded, the object is subject to reclamation with further use of land for forest planting. [2] The question about the composition and danger of such technogenic pollution, as well as about the possibility of further use of these lands remains open, which determines the relevance of this research. [3]
2. Object, subject, goals and objectives of the research

The object of the research is the territory of the disbanded military unit (Technical missile base). The territory is an area intended for storing components of rocket fuel of one of the reduced missile divisions of the strategic missile forces, and the adjacent areas. The storage zone is a plot of 7000 m² where the typical structures for these facilities are located: building No. 1 - ADMH storage (asymmetric dimethylhydrazine); building No. 2 is a treatment station; building No. 3 is a neutralization station; building No. 4 is oxidizer storage; building No. 5 is a laboratory. There is a railway line for the transportation of rocket fuel components as well as technological platforms for tanker parking [4, 5].

The subject of the research: assessment of chemical pollution of the soil of the former military unit territory.

To achieve these goals, the following tasks were set:

- prepare soil samples collected at the research object;
- determine the acidity, electrical conductivity, salinity of the water extract and analyze the results;
- determine alkalinity, the content of chlorine, calcium and magnesium ions in soils by titration.

3. Theoretical basis

According to most scientists, the deterioration in public health observed over the past decades is associated with the negative influence of chemical environmental factors. Analysis of cause and effect relationships indicates the significant role of chemical soil pollution in the deterioration of public health. This is because the soil occupies a central place in the cycle of matter in the biosphere. In addition, it is the main depot where persistent chemicals accumulate in the natural environment, and also acts as the initial link in their migration from the source of pollution to the human body along short and long trophic chains. [6-9]

The soil acidity is one of the main characteristics that determine the course of all processes in the soil. In addition to mobilizing heavy metal ions and other pollutants, soil pH determines the ability to grow certain varieties of agricultural plants. It is known that plants poorly absorb elements of mineral nutrition on acidic soils. The pH of the soil extract can be measured using a pH meter. The neutral reaction of the soil corresponds to pH 7. If the pH is above 7, then the soil reaction is alkaline, if it is below the reaction is acidic. [10]

The increased soil acidity negatively affects vegetable crops. The only way to eliminate excess soil acidity is liming. It sharply shifts biological processes in a direction favorable for plant growth.

Electrical conductivity. Measurement of the electrical conductivity of water-saturated soil pastes allows approximate estimating the salt concentration, since the electrical conductivity is functionally related to the concentration of dissolved salts. It should be born in mind that for salts with different compositions, there are quite large differences in the dependences between the specific conductivity and concentration, sometimes reaching 30-50%. This is due to the different shares of singly charged and doubly charged ions in the filtrates from soils of different types of salinization. Therefore, one should be careful when converting electrical conductivity to total salt concentration. Traditionally, soils are considered to be saline if the specific conductivity of the filtrates from their pastes are higher than 4 mS / cm. Soils with specific electrical conductivity of the filtrates from pastes of 4-8 mS / cm are classified as slightly saline, 8-15 mS / cm - as medium-saline, more than 15 mS / cm - as highly saline. The conductivity is measured by the conductometric method. [9, 10]

Elemental analysis. Elemental soil analysis is a set of methods for determining the elemental composition of the soil, i.e. it allows getting an idea of the total content of chemical elements in the soil, regardless of their location. The majority of currently used methods for the quantitative measurement of the concentration of elements involve the analysis of a liquid sample. Therefore, before using these methods, the determined elements must be transformed into a solution, i.e. it is
necessary to decompose the soil. Currently, either concentrated nitric acid or aqua regia (a mixture of nitric and hydrochloric acid 1 HNO₃: 3 HCl) is used to decompose soils when heated in a microwave. [9, 10, 11]

- **Exchangeable cations.** Exchangeable cations are cations that are parts of the soil adsorption complex (SAC), which can be replaced by other cations from the liquid phase in contact with the SAC. These include: Ca²⁺, Mg²⁺, K⁺, Na⁺, H⁺, Al³⁺. [12]

There is total, temporary and permanent hardness.

Temporary, or carbonate, or disposable hardness is hardness due to the content of calcium, magnesium (sometimes iron) bicarbonates in the water. Permanent (non-carbonate) water hardness is caused by sulfate, chloride, phosphate and other soluble salts, most often calcium and magnesium. The sum of temporary and permanent hardness gives the total hardness of the water. There is no single unit for measuring water hardness. [10]

In the Russian Federation, water hardness is estimated by the sum of milligram equivalents of Ca²⁺, Mg²⁺ ions in 1 liter of water. 1 mEq/l corresponds to 20.04 mg/l of Ca²⁺ ions or 12.16 mg/l of Mg²⁺ ions [13].

Various compounds determine the alkaline reaction of soil solutions: carbonates and carbonates of alkaline and alkaline earth elements, sodium silicates and humates.

Alkalinity also appears as a result of the activity of sulfate-reducing bacteria. This activity forms soda. There is actual and potential alkalinity of soils.

Actual alkalinity is associated with the presence of solution of alkaline salts - Na₂CO₃, NaHCO₃, Ca (HCO₃)₂ in the soil, upon dissociation of which hydroxyl ions are formed.

Potential alkalinity is found in soils containing absorbed sodium. As a result of the interaction of the SAC with carbon dioxide contained in the soil solution, Na⁺ is replaced by hydrogen to form soda (Na₂CO₃), which alkalizes the soil solution. [12]

The amount of chlorine in the soil is about 0.01%, it is mostly found in well-soluble compounds and easily enters plants. The high chlorine content in the soil and its easy entry into plants can have a negative effect on the intake of other important anions, and very high concentrations of chlorides can also have a direct toxic effect on plants. The accumulation of chlorine in the surface layers during the evaporation of moisture in dry areas leads to chloride salinization of soils. [12, 14]

**Calcium** has a many-sided positive effect on plants: it influences the growth and development of the root system, enhances the metabolism in plants, affects the activity of enzymes; calcium prevents the flow of excess amount of other cations to plants. The presence of other cations of hydrogen (H⁺), sodium (Na⁺), and potassium (K⁺) in the soil prevents calcium from entering the plants. On acidic sandy and sandy loamy soils, as well as on solonetzes, applying lime (Ca(OH)₂) and gypsum (CaSO₄ x 2H₂O) improves not only the physicochemical properties of the soil due to the neutralization of excess acidity or alkalinity, but also plant nutrition by calcium. The gross content of calcium in soils is high, since in podzolic soils its content is 0.73% of the dry matter of the soil, in Chernozem it is 1.44%. [12, 15]

**Magnesium** plays an important physiological role in the process of photosynthesis, it is a part of chlorophyll, and also affects redox processes. With a lack of magnesium, peroxidase activity increases, oxidation processes in plants intensify, and the content of ascorbic acid decreases. Lack of magnesium inhibits the synthesis of nitrogen-containing compounds. An external sign of deficiency of this element is leaf chlorosis. The average gross magnesium content in various types of soils (% in dry matter): in Podzolic soils - 0.5, in Chernozems - 0.9. With the content of exchangeable magnesium in the soil at the level of 2 mg / 100 g and lower, its sharp deficiency is observed. First of all, this is manifested on sod-podzolic acid soils of light texture. [9, 10, 14, 15]

3.1. Research methods

**Soil sampling.** Sampling at the research stage was carried out during the growing period in August. Samples were taken in accordance with GOST 17.4.4.02-84. At the studied object, 13 test sites with a size of 2x2 meters were selected. [16]
Sites No. 1-9 were located in building No. 1. Sites No. 1a, 2a were located near buildings No. 2, 3. Site No. 3a was on the destroyed railway line. Site number 4a was in building number 5. A control sample (designated “K”) was taken 10 km from the object of study in the forest. Point samples were taken at test sites from a 0-20 cm layer using the envelope method. Combined samples were made by mixing 5 point samples taken at the same test site. [17]

Further, an aqueous extract was prepared from all soil samples for the chemical analysis. 
Instrument analysis of water extract:

- PH meter pocket HI 98106 Champ is a pocket (portable) pH meter with an updated surface of the reference electrode. The manufacturer is HannaInstruments.
- Conductometer HI 98308 PWT DiST is a means for monitoring conductivity, a measure of total mineralization, a tester of distillate quality (pure water determinant, salinometer). It checks for the presence of salts by the method of electrical conductivity.
- ORP meter Model HI 98201. The manufacturer is HannaInstruments.

ORP meter is a calibrated and reliable instrument for measuring the redox potential of a liquid.

3.2. Titrimetric (volumetric) analysis method

Hardness of the water / solution. Temporary hardness is determined by direct titrating a certain volume of water with a hydrochloric acid solution:

$$Ca(HCO_3)_2 + 2CHI = CaCl_2 + 2H_2O + 2CO_2↑,$$

$$Mg (HCO_3)_2 + 2HCl = MgCl_2 + 2H_2O + 2CO_2↑.$$

The total hardness is easier to determine by complexometric titration. The total hardness of water is due to the presence of Ca$^{2+}$ and Mg$^{2+}$ ions in it.

The constant hardness is determined by the difference by subtracting the temporary hardness from the total hardness. [10]

Alkalinity is determined by titration. Total alkalinity (HCO$_3$) is determined by titration of an aqueous extract of 0.01 n. by H$_2$SO$_4$ solution in the presence of methyl orange. Total alkalinity is expressed as a percentage of HCO$_3$ and mEq per 100 g of soil. [10]

Chlorine. The concentration of chlorine in the soil is determined by the argentometric method (titration) in an aqueous extract from the soil with 0.01 n. AgNO$_3$ solution. [10]

Calcium and magnesium. The extraction of exchangeable calcium and magnesium from the soil is carried out using ammonium acetate. The content of calcium and magnesium ions is determined by titration of a 0.05 n solution of Trilon B with subsequent conversion to the concentration of Ca and Mg. [10]

4. Research results

4.1. Analysis of acidity, conductivity and salinity of aqueous extract

The measurements were carried out with portable instruments.

According to the analysis of the acidity of the water extract, it was found that the highest acidity of the soil (8.31) was in the sample taken on the territory of the military laboratory (sample 4a, in building No. 5). This can probably be explained by the long-term storage and use of chemicals including strong alkalis in this area. At the same time, the control sample showed an almost neutral environment (7.18).

Analysis of the water extract salinity of the samples showed that the lowest salinity of all samples was in the control. The highest salinity (1000 mS) for the sample collected near the treatment and neutralization stations (sample 2a, at buildings No. 2 and No. 3), which can also be explained by the presence of residual concentrations of reagents used during the operation of these stations. Quite high salinity indicators, in comparison with other samples, were found in the sample near the railway tracks.
(sample No. 3a) – 198 mS. In the study area, the salinity of the samples varies from 29 mS to 155 mS. At the control site, the salinity is 105 mS.

When analyzing the water extract for electrical conductivity, it was revealed that the soil of sample 7, one of the samples from the rocket fuel storage (in building No. 1), has the highest electrical conductivity (140 mV) and the lowest salt content (29 mS). The electrical conductivity in the control sample is 73 mV and this is one of the lowest in the analyzed samples. This indicator characterizes the presence of redox processes in the environment, while oxidative reactions predominate on the territory of a former military unit.

4.2. Titrimetric analysis.
As a result of titration of the water extract from the presented soil samples, it was found that high alkalinity values (0.41 mEq/l) are observed in samples near the treatment station (sample 1a — building No. 2), and in samples from the ADMH storage (No. 9 and No. 7, building No. 1) - low ones (0.1 mEq/l). A control sample also showed minimal alkalinity (0.1 mEq/l).

The highest chlorine ion content (0.1065 mEq/l) was observed in the sample from the ADMH storage (No. 1, in building No. 1), and the lowest one (0.0026 mEq/l) in the laboratory sample (sample 4a, in building No. 5).

The highest content of calcium ions (1.62 mEq/l) is observed in one of the samples from the rocket fuel storage (No. 1), the lowest in the control sample (0.87 mEq/l). The maximum total content of calcium and magnesium ions (2.25 mEq/l) was determined in the control sample, and the lowest (0.185 mEq/l) in the sample taken in the area of the treatment station (No. 1a, building No. 2).

5. Conclusion
Compared to the control sample, deviations in the composition of the soil were revealed: this is an excess or deficiency in the content of such elements as: calcium, magnesium, chlorine. Anomalies in the general alkalinity of the environment, salinity, acidity and electrical conductivity were also detected.

All analyzed soil samples from the territory of the former military base showed an alkaline reaction of the environment.

At the time of the research the soils of the disbanded military unit show signs of chemical pollution and require additional measures to neutralize the territory before the start of reclamation work.

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