Environmental Pollution by Drilling Waste in the Arctic

M G Opekunova¹, A Yu Opekunov¹, S Yu Kukushkin¹
¹Institute of Earth Sciences, St. Petersburg State University, V.O. 10th Line, 33/35, St. Petersburg, Russia, 199178

E-mail: s.kukushkin@spbu.ru

Abstract. The article presents the results of a study of chemical pollution of landscape components (soil water and groundwater, soils and indicator species of plants) under the influence of drill cuttings dumping onto the soil surface. The studies were carried out in the forest-tundra zone of Western Siberia in two areas for two years after pollution. The lateral and radial differentiation of chemicals was studied. The dynamics of chemical pollution of water, soil and plants was shown. The extent and geochemical zoning of secondary technogenic halos are revealed. The role of geochemical barriers in reducing the migration activity of pollutants was emphasized. The main indicators of pollution, to which Sr, Ba, Na, V, Cr, Fe, Cl²⁻, NO₃⁻ are attributed, are substantiated.

1. Introduction

The development of hydrocarbon deposits is accompanied by environmental pollution. The largest volume and variety of incoming pollutants is associated with well construction. This is due to the formation of drilling waste, which is a complex mixture of drillable rock and drilling fluids, including many chemical ingredients [2, 5].

The purpose of the investigation is to study the migration and accumulation of pollutants from drilling waste in landscape components under permafrost conditions. The studies were conducted in the forest-tundra zone of Western Siberia within the Yamalo-Nenets Autonomous Okrug in two transects of drill cuttings spills for 2 years along profiles down the terrain. On each transect, 4 (transect 1) and 5 (transect 2) test sites with soil profiles at a distance of 50 m from each other were studied, in which 3-4 samples were taken from different genetic horizons. At the same time, soil water and groundwater samples were obtained. Soil solutions were taken from the peaty horizons of peat gleyzems (Histic Gleysols) (O–T–G) heavy loamy soils within the boggy slightly drained plain (transect 2), groundwater - from the lower part of the mineral horizons of the iron-illuvial podburs (Entic Podzols) (O–BH–FC–Cg) located on well-drained territory (transect 1). Water samples were separated on a CM-6M centrifuge and filtered on filter papers grade 390, then acidified with HNO₃. At test sites, indicator species of plants were selected - representatives of various life forms: lichen - Cladonia alpestris (L.) Rubh. and Ledum - Ledum decumbens (Ait.) Lod. ex Steud.

Complete acid decomposition of soil and plant samples was carried out in the laboratory. Determination of metals in soil and plant samples (Ba, Mn, Zn, Cu, Ni, Co, Pb, Cd, Cr, Fe, V, Sr, Na, K, Ca, Sc, Zr, Al), as well as in water (those with the exception of Sc, Zr, Al), it was performed by inductively coupled plasma mass spectrometry (ICP-MS) on an ELAN-6100 DRC instrument at the Central Laboratory of A.P. Karpinsky Russian Geological Research Institute (VSEGEI). The analysis of chlorides, sulfates, phosphates and nitrates was carried out by the fluorimetric method in the
Laboratory of Geoeconomic Monitoring of St. Petersburg State University. Mineralization (TDS) was studied by a conductometric method; the pH value was determined using a Horiba pH meter with a horizontal electrode for measuring solid and bulk materials and liquids.

2. Results and discussion

The pH value and mineralization of soil water and groundwater, as well as their cationic-anionic composition, are used as indicators of the degree of environmental impact. Drilling waste pollution leads to a significant transformation of these parameters. Natural waters of the north of Western Siberia have a bicarbonate-calcium and bicarbonate-sodium composition [6]. The liquid phase of drill cuttings is characterized by a chloride-calcium type found in deep (formation) waters. A large amount of anions (Cl\(^-\) and SO\(_4^{2-}\)) and cations (K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\)) enter the environment from drill cuttings, which leads to the transformation of soil water into calcium chloride and groundwater into magnesium chloride (marine) types.

Substances containing K, Na, Ca are widely used in the formulation of drilling fluids [2]. Hydroxides and salts of these metals are used to regulate alkalinity, the rigidity of the liquid phase. Slaked lime (Ca(OH)\(_2\)) is used as a thinner for most water-based solutions. Chalk (CaCO\(_3\)) is used to increase the density of the drilling fluid. Sodium sulfite (Na\(_2\)SO\(_3\)) is used as an oxygen scavenger. The concentration of alkali metals in the water of sludge pits studied within the licensed areas reaches 1.5-3 g/l. In solid drilling waste, their content is 0.5-1.0%. A high concentration of K\(^+\), Ca\(^{2+}\) and Na\(^+\) was measured in soil water and groundwater formed under the influence of drilling waste, especially Na\(^+\) (up to 0.53 g/l). With increasing distance from the source of pollution, the metal concentration decreases, however, even at a distance of 200 m, the Na\(^+\) content exceeds background values.

In the organogenic horizon of peat gleyzems at the place where drilling waste was discharged, the Ca content exceeds the background value by 6–7 times, gradually decreasing with distance from the source. The concentration of Na exceeds the background level by 12.5 times. Metals in the soil reach background values at a distance of 100 m from the source of pollution. The content of Ca in the iron-illuvial podburs near the source of pollution exceeds the background concentration by about 6 times. The metal migration down the transect is limited mainly to 50 m. Natrium is characterized by high concentrations at a distance of 50 and 100 m, showing a high tendency to lateral migration.

Chlorides and sulfates are part of drilling fluids. Chlorides of alkali metals are used in drilling fluids when drilling permafrost. In addition, the influx of mineralized water from aquifers is significant, therefore, their concentration in sludge and sludge water depends on the chemical composition of rocks and groundwater [5]. The content of Cl-ions in drilling waste in the research area is 2500 mg/kg and more, SO\(_4^{2-}\) ions - up to 400 mg / kg; in sludge waters, their concentrations reach 7000 and 100 mg/l, respectively. In soil waters at the site of sludge spill, the Cl-ions concentration is 1912 mg/l; at a distance of 200 m, it significantly decreases, but exceeds background values by 8–10 times. In groundwater, the content of Cl-ions is lower than in soil water, and at a distance of 200 m it is close to the background concentration (1.0-1.5 mg/l). The sulfate content in ground and soil waters is at the level of background values.

In general, a high concentration of the main cations and anions in drilling fluids leads to an increase in the salinity of soil water and groundwater, which have low background values in the forest-tundra landscapes (18-80 mg/l, depending on the type of soil). TDS of soil water increases to 2020 mg/l (transect 2), groundwater - up to 1750 mg/l (transect 1). Mineralization rapidly decreases with distance from the source of pollution. Already at a distance of 200 m, it has a value of 137 and 124 mg/l, respectively, but the excess over background values remains. The acid-base indicator of drilling waste varies widely (7.0-10.5). In general, landscape contamination with drill cuttings leads to alkalization of soils, soil water and groundwater, the death of oligotrophic and acidophilic vegetation. The death of plants during the spill of sludge is noted at a distance of 50 m; up to 100 m, a change in the species composition of plant communities is recorded. At the site of the drill cuttings spill, the pH of the soil water rises to 7.15 (transect 2) and is restored to background values (3.4-3.6) at a distance of 100 m. In groundwater, the pH value remains within the background level.
Drilling fluids contain nitrogen compounds. Nitrolignin is used to control the viscosity and structural-mechanical properties of the drilling fluid. In drilling waste, nitrogen is mainly in the form of NO₃-, to a lesser extent - NH₄⁺. Due to the high mobility, nitrates are found in significant concentrations in soil waters (more than 100 mg/l), and only at a distance of 200 m down the transect their content in water approaches the background values. The concentration of NH₄⁺ also increases mainly in soil waters, however, it is an order of magnitude lower than the nitrate content. In soils, an increased content and active lateral migration of NO₃⁻ have been established.

Surfactants are currently added to all types of drilling fluids to perform various functions. The concentration of surfactants in drilling fluids can be both very low (for example, detergents) and exceed 30 g/l [5]. In this regard, there is an increased surfactant content in drilling waste and their entry into the landscape components during the breakthrough of the walls of sludge pits. As an anionic surfactant, it most often uses lignosulfonate, which is a moderator for cement mortars. The concentration of anionic surfactants in the drill cuttings of the studied sludge pits is 2.5-3.1 mg/kg, and in the sludge water it is 0.40-0.42 mg/l. The level of surfactants in polluted soils increases in the humus horizon to 45 mg/kg. In peat gleyzems, this concentration was kept at a distance of 200 m from the site of contamination; in the iron-illuvial podburs, such a surfactant content was found only at the point of discharge of drill cuts, at a distance of 50 m it decreases by an order of magnitude.

Phenols are corrosion inhibitors, inhibiting the processes leading to the destruction of steel drill pipes. The maximum concentration of phenols measured in the study area in drilling waste is 0.30 mg/kg, in the water of drill pits this is 0.38 mg/l. Partially phenols can enter the environment, but no significant concentrations have been detected.

The migration and concentration of trace elements is of great interest in assessing the impact of drilling waste. They in various compounds are part of drilling fluids. The most important component is barite (BaSO₄), which serves as the main weighting agent for drilling fluid. As a rule, Sr, Ca, Pb, and Fe are present as impurities in barite. Strontium sulfate (SrSO₄) can be used as weighting agents. For high-density drilling fluids (5.0-7.0 g/cm³) galena, magnetite or hematite weighting agents are used [2, 9].

The Ba content in drill cuttings, even during their long-term storage (more than 2 years), reaches 5-7%, in the water of sludge pits this is 19 mg/l. In soil waters, when contaminated with sludge, the Ba²⁺ content increases to 1.15 mg/l (with a background content of 0.055 mg/l), and in ground waters it is up to 0.72 mg/l. In the upper soil horizons, the Ba concentration is 798 mg/kg (with a background value of 225 mg/kg [7]). The Sr content in drill cuttings reaches 750 mg/kg. The relatively high mobility of the metal determines its active release into environmental components: in the place of waste discharge in soil water, the Sr content is 1.41 mg/l, in ground water it is 2.36 mg/l. In soils, strontium accumulates in a peaty horizon, where its concentration is 706 mg/kg (with a background content of 21 mg/kg [7]). Pollution can be traced more than 50 m from the source. In the iron-illuvial podburs, the amount of Sr is less, but the lateral migration of the metal is high. The indicator role of Sr and Ba in soil salinization at oil production sites has been repeatedly noted in the literature [1, 3].

Metal chromates and dichromates are used in drilling fluids. Corrosion inhibitors are zinc chromate and sulfate. Zinc and copper oxides and carbonates are added to drilling fluids as absorbers of hydrogen sulfide. In addition, rocks and crude oil are sources of metals (V, Ni, Co and Cu). The concentration of these trace elements in the drill cuttings of the study area reaches: Zn - 502 mg/kg, Cu - 261, Ni - 50, Co - 21, Cr - 303, Pb - 87, V - 119 mg/kg.

Microelements contamination of soil waters occurs during spillage of drill cuttings. Their concentration is higher than the background level and amounts to: Zn - 0.099, Ni - 0.033, Co - 0.012, Cr - 0.023, Pb - 0.026, V - 0.094, Mn - 0.206, Fe - 2.120 mg/l. The content of trace elements in groundwater is much lower, with the exception of Mn (3.640 mg/l), Co (0.047mg/l), Ni (0.194 mg/l). Three groups of metals were distinguished by the distribution of tendency to migration in soil waters: an increased content of Co in the solution is observed up to 50 m from the source of pollution; Cr, Ni, Pb - up to 100 m; V, Zn, Fe, Ba, Sr - up to 150 m. Barium and strontium may also migrate over long distances as part of technogenic halos. It can also be assumed that the main form of metals in solution
under conditions of alkalization of water and high salinity are complex compounds. Anionic metals (Cr and V) can also be in the form of oxyanions ($\text{CrO}_4^{2-}$ and $\text{VO}_3^{-}$).

In the soil near the source of pollution, the maximum metal content in the organogenic horizon of soils exceeds the background values: Mn by 12.5 times, Sr by 8.9, Cr by 6.1, Ba by 3.4 times, Cu by 2.9, Ni by 2.6, Fe by 2.5, Co by 2.3, V by 1.8 times. The lateral migration of most of the studied metals does not extend beyond 50 m. The exception is V, Sr, Ba, Cr, Mn, the lateral migration of which can be traced to 100 m. In this case, $\text{Cl}^-$, $\text{NO}_3^-$ ions due to their high mobility, extend within a secondary halo to a distance of 150 m.

The distribution of metals in the soil section were estimated using the coefficient of radial differentiation (R), which is defined as the ratio of the substance content in the upper horizon with respect to this in the parent rock. A coefficient exceeding a value of one ($R > 1$) may indicate a surface source of the influx of metals into the humus horizon. The results showed that on the studied profiles of the substance with pronounced lateral differentiation and external sources of input ($R > 1$), they were noted only at the first sites located directly in the places of the drill cuttings spill. Metals with $R > 1$ for decreasing the coefficient values (in brackets) in the iron-illuvial podburs represent the series: Ca (2.85) > Cu (1.84) > Cr (1.53) > Zn (1.25); in peat gleizes soils: Sr (4.99) > Ca (2.2) > Mn (1.25) > Zn (1.24) > Cu (1.12) > Na (1.07).

In the studied landscape catenas, two species of indicator plants were selected that are used in assessing the state and environmental pollution during the development of oil and gas condensate fields in the north of Western Siberia [6]: lichen *Cladonia alpestris* and rosemary *Ledum decumbens*. Analysis of the chemical composition of plants showed that a group of metals is distinguished, the content of which varies depending on the position in the studied profiles. As they approach the source of pollution, their concentrations increase, and the maximum values exceed the background values. The set of indicator elements for lichen and rosemary is almost identical and includes Na, V, Cr, Fe, and Sr. The most contrasting contents are typical for Fe and Sr. The maximum extent of the halo of dispersion of elements in plants reaches 150 m from the source of pollution.

From the analysis we can conclude about the following features of the dynamics of metals in the soil. Two years after the dumping of waste onto the relief in soils, the concentration level of most of the studied metals increased in the upper organogenic soil horizon in relation to the previous year. This is due to the continued flow of pollutants from the sludge due to planar flushing. The composition and concentration of metals in peaty gleizes soils are shown in the following series: Fe (5.4), Sr (3.8), Ba (3.2), Co (3.1), Zn (2.3), Ni (2.0), V (2.0), Cr (1.8), Cu (1.3), Pb (1.2). In the iron-illuvial podburs, the level of metal accumulation in the upper horizon turned out to be somewhat lower: Cr (3.6), Cu (2.6), Ba (2.4), Na (1.8), Zn (1.7), V (1.7), Mn (1.6), Fe (1.5), Co (1.4), Ni (1.4), Zr (1.4), Pb (1.2), Sr (1.1).

It is important that the noted changes in the soil affected only the organogenic horizon and did not affect the underlying mineral ones.

The accumulation of metals in the upper organogenic soil horizon is explained by the barrier role of peat and humus horizons, which are capacious biogeochemical barriers [3, 4]. An increase in the pH of soil solutions when contaminated with drilling waste reduces the migration activity of cationogenic metals. With a planar washout from the source of pollution, metals are sorbed by the organic matter of the upper horizons of soils and accumulate there. Of certain importance in the fixation of trace elements is iron, which under the conditions of seasonal thawing of permafrost is carried out by the ascending migration of glue waters to the surface zone of oxidation and evaporation [8]. When alkalizing, Fe enters into a hydrolysis reaction, and freshly formed hydroxides adsorb trace elements. The technogenic alkaline barrier that forms at the site of drill cuttings spill additionally fixes metals and other pollutants in the surface soil layer. As noted above, under these conditions, metalloids (V, Cr) in the composition of oxyanions preserve their migratory ability, which determines their lateral migration in soils as a part of a dispersion halo up to 100 m, and in soil solutions up to 150 m.

A comparative analysis of the metal content over two years in plants shows that the changes are more pronounced on transect 2, where after two years the growth of Na, Mn, Fe, Co, Cu, Zn, Sr was measured in both indicator species. At the same time, the content of Ba and Pb decreases in lichen.
Cladonia alpestris, and Na and Pb in Ledum decumbens. On transect 1, the growth of Ba, Ni, Cr is observed in rosemary, in the lichen it is only Cr, but a decrease in the concentration of Na, V, and Sr is found.

3. Conclusion

Thus, the results of the study allow us to draw the following conclusions.

1. Chemical pollution of soils, plants, soil and groundwater occurs when the conditions for handling drilling waste are violated and dumped onto the terrain. Of the studied landscape components, the maximum changes in the chemical composition and extent of the technogenic halo were noted in soil solutions. Salinization of soils, an increase in the mineralization and pH of soil (to a lesser extent groundwater) are a serious problem due to the high concentration and active migration of alkali metals (K⁺, Ca²⁺ and Na⁺), Cl⁻ and NO₃⁻ ions.

2. Alkalization of soils and soil water under the influence of drill cuttings leads to the death of oligotrophic and acidophilic vegetation, which is observed over 50 m, and to the restructuring of plant communities at a distance of up to 100 m.

3. In the soil profile, pollution was found in the organogenic horizon; radial migration of pollutants down the section has not been established. In the upper horizon, two years after the spill, an increase in the concentration of metals is noted in relation to the previous year. The lateral migration of metals as a whole does not exceed 100 m, and it is more active in iron-illuvial podburs. In peaty gleys, the migratory activity of metals decreases due to the high buffering of the peat horizon.

4. The complex (alkaline, biogeochemical and sorption) barrier formed at the spill site reduces the lateral migration of cationogenic metals, accumulating them mainly near the source of pollution. Cryogenic conditions minimize the downward flow of matter in radial differentiation, forming during seasonal thawing of permafrost, the transfer of pollutants by ascending water flows to a complex geochemical barrier.

5. A set of indicator metals during the spill of sludge pits in the forest-tundra zone includes Sr, Ba, Na, V, Cr, Fe, of which Sr is characteristic of all the studied components. Chlorides and nitrates are reliable indicators of pollution in the abiotic components of the landscape, but due to their high mobility, soil desalinization occurs in a relatively short period of time [1].

4. References

[1] Vodyanitskii Yu N, Avetov N A, Savichev A T, Trofimov S Ya, Shishkonakova E A 2013 Influence of oil and stratal water contamination on the ash composition of oligotrophic peat soils in the oil-production area (the Ob' region) Eurasian Soil Science 46(10) pp 1032-1041
[2] Gubanov V N, Lopatin D V, Sychev V S, Tolstoukhov A A 2006 Book of a solution engineer ed. A S Dobrosmylov (M.: Garuss Publishing House) 551 p
[3] Zamotaev I V, Nikonova A N, Ivanov I V, Mikheev P V 2015 Chemical contamination and transformation of soils in hydrocarbon production regions Eurasian Soil Scienc. Vol. 48 12 pp 1370–1382 DOI: 10.1134/S1064229315120133
[4] Lodygin E D 2019 Sorption of Cu²⁺ and Zn²⁺ Ions by Humic Acids of Tundra Peat Gley Soils (Histic Reductaquic Cryosols) Eurasian Soil Science Vol. 52 7 pp 769–777 DOI: 10.1134/S1064229319070093
[5] Ovchinnikov V P, Aksenova N A 2008 Drilling flushing fluids: Textbook. Manual for universities (Tyumen: Publishing House "Oil and Gas University") 309 p
[6] Opekunova M G, Opekunov A Yu, Kukushkin S Yu, Arestova I Yu 2018 Evaluation of Environmental Transformation in Areas of Hydrocarbon Deposits in the North of Western Siberia Contemporary Problems of Ecology Vol. 11 1 pp 99–110
[7] Opekunova M G, Opekunov A Yu, Kukushkin S Yu, Ganul A G 2019 Background Contents of Heavy Metals in Soils and Bottom Sediments in the North of Western Siberia Eurasian Soil Science Vol. 52 4 pp 380–395 DOI:10.1134/S106422931902011X
[8] Tregubov O D 2017 Geochemical barriers in soils and landscapes of the Anadyr tundra Vestnik Moskovskogo Universiteta Seriya 5: Geografiya 3 pp 70-79

[9] Skipin L N, Skipin D L, Petuhova V S, Solovev D B 2019 Improvement Possibilities of the Ways of the Bore Mud Desalinization IOP Conference Series: Earth and Environmental Science 272 Paper № 032047. [Online]. Available: https://doi.org/10.1088/1755-1315/272/3/032047

Acknowledgment
This work was supported by the Russian Foundation for Basic Research (project №. 19-29-05081. Soils of oil and gas areas in the north of Western Siberia: resistance to chemical pollution and the potential for self-purification in a changing climate).