Polychemical pollution of surface waters and permafrost-affected soils in Central and North Yakutia and in North-West Siberia

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Abstract. The concentration of main organic and inorganic pollutants (heavy metals, polyaromatic hydrocarbons, radionuclides) in surface waters and in water-soil solutions was analysed on three keysites within the permafrost zone: Tazovsky Peninsula (North-West Siberia), Kolyma Lowland (North Yakutia) and adjacent to Yakutsk (Central Yakutia). In the majority of sampling points that are not directly impacted by human activity, the pollutants accumulate in the uppermost organogenic and organo-mineral horizons of natural soils. At the human-affected keysites the major pollutants may accumulate not only in the superficial horizons of the disturbed soils due to the surface runoff but also in the central parts of the profile, in the material buried by cryogenic, solifluction or fluvial processes and in some cases – in the suprapermafrost horizons and in the upper layer of permafrost transported via suprapermafrost water runoff.

1 Introduction

Nowadays Russia experiences the new wave of increasing exploration in the Arctic: oil and gas production, coal mining, building and reconservation of military objects, Arctic Ocean sea-pass development, etc. All these activities are strongly connected with the hydrocarbon consumption mechanical impact and chemical pollution due to the high rate of environmental risks. In some cases, the ecological damage can be partly recovered by bioremediation and recultivation measures [1, 2]. Still unknown is the fate of large part of pollutants’ volume, which can potentially migrate via surface and suprapermafrost water runoff as well as downwards to the soil profile due to the active processes of cryogenic

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mass-exchange and then laterally redistribute over the surface of permafrost and even penetrate into it [3, 4]. Geochemical evolution of these contaminants in polar ecosystems under global climate change and local impacts is poorly studied. Besides the local pollutants, the supertoxicants can also be accumulated in polar ecosystems: heavy metals, polyaromatic hydrocarbons (PAHs), radionuclides etc. Some of them migrate via atmosphere and hydrosphere [5], some via trophic chains [6]. However, the same as local pollutants, these toxicants’ fate in surface waters and cryogenic soils as well as in the polar ecosystems themselves within the permafrost zone is very poorly studied [7-9]. Arctic region have already become the depo of global pollutants from other regions of the planet.

2 Objects and methods

2.1 Objects and field methods

Field observations and sampling were conducted during the period of maximum active layer thawing depth and suprapermafrost water runoff (August and September 2019) on three keysites within the permafrost zone (Fig.): Tazovsky Peninsula (North-West Siberia), adjacent to Yakutsk (Central Yakutia) and on the Kolyma Lowland (North Yakutia). Soils at “Tazovsky Peninsula” (forest-tundra) and “Yakutsk” (taiga) keysites are mainly developing on the sandy and silty-sandy light-textured deposits, active layer depths here often exceed 150-200 cm. Only in the overmoistured soils of boggy depressions active layer varies within 100 cm. These two keysites are situated within relatively strong human-affected regions with intensive hydrocarbon mining and consumption, abundant infrastructure objects and relatively dense population. Autonomous soils of “Kolyma Lowland” (arctic tundra) keysite are developing on silty loams with the average active layer depth around 60-80 cm. In the overmoistured depressions active layer does not exceed 50 cm.

Surface waters and suprapermafrost soil-water solutions as well as the material of soil horizons were sampled from soil pits in the human-affected and background (directly unaffected) sites on the watersheds, slope transition zones and in the runoff accumulation zones in the depressions. Soils were identified using the IUSS World Reference Base for Soil Resources [10]. Active layer depth was measured using mechanical probing with steel rod.

2.2 Laboratory methods

Measuring of $^{137}$Cs activity was carried out by $\gamma$-spectrometry using semiconducting Ge(Li) and NaI(Tl) detectors. Bulk volume of heavy metals was measured using X-ray-fluorescentic spectrometry (Spectroscan Max GV). Acid-soluble forms of heavy metals were measured by Analytik Jena novaA 350 atom-absorbing spectrometer. Analysis of PAHs was carried out using spectrofluorimetric method (Dionex ASE 350 Accelerated Solvent Extractor and Lumachrome chromatograph). Bulk concentrations of oil hydrocarbons were measured using infrared photometry by AN-2, KN-2m and Lumex analyzers.
3 Results and Discussion

The analysis of oil hydrocarbon contamination of the surface and suprapermafrost waters and the 1:5 soil-water solutions at the sampling points within the human-affected areas of all three keysites have mostly shown the low and sometimes medium-danger levels of contamination of soils. The surface waters that partly supply the moisture regime of the soil profiles were analyzed for the oil hydrocarbon content and the study have shown the relatively low level of surface waters contamination (0.05-0.09 ml/l except for one sample that contained 0.96 ml/l of oil hydrocarbons). However, besides the obvious contamination of the superficial soil horizons (5.6-25.9 mg/kg at the “Yakutsk” keysite and 166.3-8950.0 mg/kg at “Tazovsky” keysite), the increasing concentrations of hydrocarbons in the organo-mineral mid-profile soil horizons buried by solifluction and fluvial processes (12.4-18.8 mg/kg) and in the suprapermafrost soil material (166.3-407.5 mg/kg) should be also taken into account.

The analysis of the surface waters at the strongly human-affected sampling plot at the “Yakutsk” keysite (area adjacent to the long-term dumpsite) have shown the relatively high concentrations of some microelements that are exceeding the Russian governmental ecological maximum permissible concentrations (MPC): e.g. Ba > 2.7-4.9 MPC, Co > 3.2, Ni > 3.4, Pb > 4.9, Cu > 19.0, Fe > 50-132, Mn > 201-294, Zn > 459. Surface waters along the catena from the dumpsite at the watershed to the overmoistured boggy environment in the adjacent depression can be characterized as highly mineralized (700-1600 mg/l) and the mineralization increases downward the mesorelief. The concentrations of microelement stay high along the catena while the oil hydrocarbon concentrations fall (from 2.7 to 0.6 MPC). All of the water samples contain PAHs and phenols but within the MPC. The salt composition of the surface water here is mainly hydrocarbonate-magnesium-calcium but there is an increase of sulphates and sodium in the accumulative depressions in the mesorelief associated with the increasing of the mineralization rate.

Study of the acid-soluble forms of heavy metals at the “Tazovsky Peninsula” keysite have shown the increasing concentration of Cd (up to 3.3 mg/kg) and Pb (up to 29.2 mg/kg) in superficial organo-mineral horizons of human-affected Histic Cryosols despite the
background (unaffected) soils can be characterized by relatively high concentrations of these elements as well. The analysis of acid-soluble forms of heavy metals in the Histic Spodic Cryosols of “Yakutsk” keysite have shown the pronounced accumulation of nearly all elements in the uppermost organic and organo-mineral soil horizons of nearly all sampled soils. But concentration of heavy metals is decreasing in the background (directly unaffected) soils unlike in the human-affected Cryosols where Pb, Cd, Co and As concentrations in the organo-mineral mid-profile soil horizons buried by solifluction and fluvial processes and in the suprapermafrost soil material can reach and even exceed those in the uppermost ones. No accumulation of heavy metals was obtained in the uppermost organo-mineral material, mid-profile soil horizons buried by solifluction and fluvial processes or in the suprapermafrost parts of Turbic Cryosols at the “Kolyma Lowland” keysite.

Samples from human-affected and background Turbic Cryosols from “Kolyma Lowland” keysite were analyzed to study the specific activity of $^{137}$Cs artificial isotope. It has been shown that only few of the samples from the uppermost organic and organo-mineral soil horizons contain detectable amounts of this element (12.8-31.2 Bk kg$^{-1}$). The material of the central and lowermost soil horizons did reveal any $^{137}$Cs activity. This fact strengthens the idea that this artificial radioisotope do not migrate with soluble organic forms downwards into the middle and lowermost parts of soil profile. Suprapermafrost soil horizons here are often enriched with the water-soluble forms of biogenic elements (e.g. P, S, K, Ca, Na) which correlates with the downward increasing of total organic carbon in these soils.

The content of polyaromatic hydrocarbons (PAHs) was studied in the relatively long-term buried and frozen (more than 6 years) soils (Histic Reductaqueic Cryosols) on the keysite in North-West Siberia. The total sum of PAHs varies widely within 36.0-331.4 ng/g which is strongly connected with the genesis of the material and the total organic carbon content. Despite the total content of PAHs does not exceed the background values that are relevant for this region, the sum of “heavy” high-molecular PAHs of anthropogenic origin are presented in the samples of buried organo-mineral material and may reach 5.7% of the total PAHs (background unaffected soils contain only 0.2-0.4% of “heavy” PAHs). This fact strengthens the idea of the possible long-term conservation of these pollutants in frozen deposits and buried soils.

### 4 Conclusions

The studies of soils and water streams along the hydrologic-geomorphologic catenas from the autonomous forms of the mesorelief, where the contamination sources were detected down through the transition slope zone to the hydromorphic soils of the mesorelief depressions, have shown the pronounced environmental redistribution of pollutants: soluble salts, different forms of heavy metals, oil hydrocarbons. These elements and compounds accumulate in hydromorphic soils (with thick superficial organogenic horizon and well-expressed) that develop in the depressions of mesorelief.

Study was supported by RFBR (19-05-00071a; 19-45-090011p_a) and by the State Assignments of the IPCBPSS RAS (0191-2019-0044), IGEM RAS, IB Komi SC UrB RAS (No AAAA-A17-117122290011-5), Melnikov Permafrost Institute SB RAS (No. 0380-2019-0003).
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