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ECOLOGY AND ENVIRONMENTAL PROTECTION

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GEOGRAPHIC AND ENVIRONMENTAL ASSESSMENT OF THE EFFECTS OF HEPTYL POLLUTION IN KAZAKHSTAN STEPPE REGIONS

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ABSTRACT

The toxic heptyl gets into the desert and steppe soils of Kazakhstan when rockets flights from the Baikonur cosmodrome. The Baikonur cosmodrome is located in the desert to the east from the Aral Sea. It has been operating since June 1955, i.e. 62 years. The desert and steppe areas are generally considered as fragile unstable ecosystems. The launch vehicles leave behind damaged phytocenoces and landscapes, and impoverished soils after falling. We found out the landscape sites, where under the influence of longterm contamination the topsoil has turned into a mechanical and chemical mixture of fine soil with toxic wastes and rocket fuel emissions. Soil sampling on the heptyl content was made on the overlapping of rockets falling areas No. 15 and 25 in the Karaganda region. In the results of the field researches we discovered geochemical anomalies of heptyl: accumulation level in steppe soils was about 250-400 maximum permissible concentrations. The soil samples were tested on changes in the composition of the steppe microbial communities. We found that heptyl led to microscopic fungi dominance. Bacterial community was suppressed, demonstrating sensitivity to the toxic heptyl. This fact gave evidence of the high toxicity of the soil, which is contaminated by heptyl.

Keywords: heptyl, geochemical and microbiological characteristics

INTRODUCTION

The ecological assessment of environment and soil cover conditions is based on the soil and geochemical researches. They are aimed at determination of the contamination sources, and also the changes in the physic-chemical and biological features of soil during the accumulation of contaminants.

The rockets launching from the "Baikonur" cosmodrome (Kazakhstan) leads to a soil contamination by used rocket fuel. The most toxic liquid rocket fuel is a combustible unsymmetrical dimethyl hydrazine (UDMH) or heptyl ($C_2N_8N_2$), which is used for the heavy launch vehicles. Heptyl – is a toxic substance of the1st class of hygienic hazard and the 2nd category of carcinogenicity. UDMH is a clear, colorless, steaming in the air, and highly toxic liquid with an ammonia smell [1]. UDMH can persist in soil for a long

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time (months and years) (Carlsen et al., 2008). Heptyl has the properties of a high volatility, unlimited solubility in a water, and ability to migrate. UDMH is usually accumulated in the deep soil layers, plants and silt ponds that is why it has significant distribution when going into the environment. Consequently, the falling of the launch vehicles with residues of toxic rocket fuel significantly contaminates Kazakhstani environment with heptyl.

The aim of the study: to carry out the soil-geochemical and microbiological researches of contamination of Central Kazakhstan's steppes soil cover with heptyl (UDMH). The objectives: to identify the most heptyl contaminated parts of Kazakhstan's steppe landscapes, to assess the state of soil's geochemistry, to study the microbiocenoces structure of soil sites contaminated with UDMH.

OBJECTS AND METHODS OF INVESTIGATION

Contaminated with heptyl rocket-vehicle detachable parts (RVDP) fall to the Karaganda region, which is the central part of the Republic of Kazakhstan, the northwest of the Balkhash lake. The Kazakhskiy melkosopochnik occupies most of the Karaganda region territory, among which the relict mountain massifs are overlooked: the Kyzylray in the east, the Karkaralinsky mountains in the northeast and the Ulutau mountains in the west. In the south the Kazakhskiy melkosopochnik goes into the Betpak-Dala clay desert and in the west – to the Turan lowland area and the Aral Kara Kum.

Geochemical researches in the rockets falling areas (RFA) were carried out by local method on the most typical landscape elements of the selected territory. During the field studies we made the grids at a pitch of 50-100 m, in order to determine the quantitative content of heptyl in soil, and it's horizontal and vertical migration. For the purpose of laboratory research we laid soil profile cuts according to the "envelope" method.

We took 60 soil samples in order to determine the content of heptyl. Including 5 ecological areas (15, 16, 17, 25, and 29) and 7 background sites of RVDP rockets falling areas (71, 79, 85, 87, 91, 95, and 98). In soil samples heptyl content was determined in 10 days through the photocolorimetry method [2].

In control and contaminated soil samples number and species diversity of soil microbiota representatives were determined by sowing of soil extract (dilution $1:10^3$) of soil samples, with different content of UDMH, on selective medium [3]. The abundance of microorganisms was expressed in colony-forming units CFU/g of absolutely dry soil. Aerobe chemoorganotrophic germs were isolated on the meat-and-peptone agar (MPA), yeasts – on the wort-agar (WA), actinobacteria – on the sugar-and-peptone agar (SPA). Nitrogen-fixing bacteria were isolated on the Ashby agar nitrogen-free medium, cellulosolytic bacteria – on the Hutchinson medium, and microscopic fungi – on the Chapek medium [4] by using the manuals [5, 6, 7]. Duration of cultivation for bacteria and yeasts was 4-7 days, and for microorganisms to UDMH was estimated by the absence or presence of their growth on respective media with water extracts of soil samples and certain heptyl concentration. The degree of manifestation of above-listed parameters was estimated by the CFU number of microorganisms, their percentage composition and LD₅₀ index (50% mortality of organisms).

RESULTS

RVDP falling areas are showed on Kazakhstan map control which were made "cographical binds" to geochemical research of the area heptyl contamination (Fig. 1).



Figure 1. Map of the RVDP falling areas on the territory of the Republic of Kazakhstan

We detected the landscape areas, where under the influence of long-term contamination the topsoil has turned into a mixture of fine soil with toxic wastes and rocket fuel emissions, which has mechanical and chemical nature. In general, the rocket fuel spillages with the formation of local high-contrast geochemical heptyl anomalies were registered at numerous RVDP falling areas. But there were pieces with maximum permissible level (MPL) of UDMH, it's equal to 0.00001 mg/cm² or 0.01 mg/m² [8].

Researched territory was classified as fragile unstable ecosystem with weak hydrographic net, humus-poor soils, and also landscapes, damaged by wreckages of rocket-vehicles. In all 60 soil samples UDMH was detected in concentrations from 0.02 to 40.00 mg/kg. On the average the maximum concentration of UDMH was 250-400 MPC, by comparison with heptyl MPC in soils equal 0.1 mg/kg [8]. The heptyl concentration that equals to 0.02-25.5 mg/kg was detected in 12 soil samples at 9 RVDP falling areas. Local surface and vertical soil contamination with heptyl (0,02-40,0 mg/kg) was elicited in 38 soil samples at 19 RVDP falling areas on the genetic horizons (A, B, BC, C) to 1.0 m depth.

We had been chosen RFA No. 15 and 25 for geochemical and microbiological researches. In this territory 6 zones that are at equal distances from each other were selected The UDMH content for future possible mapping of the studied territory was defined in soil samples collected in the 5 replications of these zones, in the sampling points (P).

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The maximum UDMH content was noted at P.5 (110 mg/kg), which overshoot the MPC in 1100 times, the minimum content – at P.3 and P.6 with 125 MPC. On the average the topsoil of IA No. 15 and 25 had a significant contamination throughout the whole territory: 52.25 mg/kg or 522.5 MPC. Consequently, the greater contamination degree was presented in central zone of RFA (P.5), with a decrease in the perimeter zone (P.3 and P.6).

Layer by layer soil profile research showed a decrease in the UDMH concentration, while soil depth increases. We noted in the 0-5 cm soil layer at 50 mg/kg concentration, at the maximum sampling depth (100 cm) UDMH had not been detected, its residual concentration 0.39 mg/kg was noted at 70 cm soil depth.

Thus, the researches in RFA No. 15 and 25 allowed concluding that the soil is contaminated with UDMH in various concentrations from 0.02 to 40.0 mg/kg. Areas with high contamination level (P/5) and low (P/3 and P/6) were marked.

Observed facts of a soil-geochemical condition's destruction around RVDP rockets falling areas indicate that the vapor emission of rocket fuel components and the spread of heptyl contaminated SPLV fragments arise from the explosion. Corresponding high geochemical background of NDMG contamination arises. Creation of the regional contamination takes place because of the wind, water translocation, and the secondary reallocation on the landscape components. Particularly clearly we had observed it in the north-eastern part of the territory of the RVDP RFA No. 15 and 25. In this case, the quantitative heptyl content was high in the analyzed soil samples of steppe and semidesertic zones. It is connected with a significant content in them of a thin silt fraction, which had a large absorption capacity.

Consequently, Kazakhstani steppe and semi-desert landscapes soils had a different ability to resist the anthropogenic loads in the form of liquid heptyl, which is slopping over while RVDP fall onto the soil surface.

Initial heptyl penetration into a sodic soil and brown alkaline soils occurred in the 1970-1975s. The current heptyl content (1-26 MPC) shows its prolonged presence. The typical heptyl accumulation was noted in the brown usual and incompletely developed soils, in concentrations ranging from 0.2 to 49 MPC (Table 1).

| Soil name | UDMH MPC | Soil name | UDMH MPC |
|------------------------------------|----------|----------------------------------|----------|
| Browns | 0.2 | Meadow browns undeveloped | 105 |
| Browns solonetzic | 26 | Meadow-boggy browns saline | 38 |
| Browns solonetzic and solonchakous | 15 | Solonetzes browns cortical | 317 |
| Browns solonchakous | 18 | Solonetzes browns small | 251 |
| Brown solonchak | 29 | Solonetzes browns average | 390 |
| Browns immaturate | 134 | Solonetzes meadow-browns small | 256 |
| Browns undeveloped | 48 | Solonetzes meadow-browns average | 273 |
| Browns primitive | 400 | Solonetzes meadow-browns small | 318 |

Table 1 - The UDMH content in different soils of RFA No. 15 and 25

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| Meadow-browns | 77 | Solonetzes meadow-browns | 129 |
|----------------------------|-----|--------------------------|-----|
| Menter | | average | |
| Meadow-browns solonchak | 161 | Solonchaks tipycal | 20 |
| Meadow-browns mmaturate | 49 | Solonchaks meadow | 15 |

RFA No. 15 and 25 were characterized by the UDMH accumulation in brown desertsteppe, meadow-chestnut and meadow-brown soils, in sodic and alkaline soils. Its maximum content was noted in the primitive brown and alkaline soils: from 14 to 400 MPC. Heptyl concentration depended on the time of RVDP falling; it means heptyl migration processes affected to its content in the environment.

For the purpose of study quantitative and qualitative characteristics of soil sample's microbial structure from RFA No. 15 and 25 we selected points 1/6, 1/9 and 1/12. Earlier in these soil samples UDMH content was determined [9].

A significant number of the CFU microscopic fungi were shown compared to control in soil samples, which are contaminated by UDMH (Table 2).

Table 2 – Sustainable representatives of the microbial community in a naturally contaminated with UDMH soil samples

| Option | The CFU of Microorganisms/g in soil at UDMH application, mg/kg | | | | |
|-------------------------|---|--------|--------|--------|--|
| | control | 0.23 | 3.62 | 13.68 | |
| Yeasts | 56±4 | 52±5 | 40±4 | 39±6 | |
| Micromycetes | 125±16 | 142±20 | 175±21 | 176±24 | |
| Cellulosolytic bacteria | 4±1 | 3±1 | 2±1 | 1±1 | |
| Actinobacteria | 12±3 | 11±3 | 9±2 | 6±1 | |

The soil yeast's tolerance to heptyl was noted. Reduction of the CFU index in the empirical variants compared with the control was not significant, even when the highest UDMH concentrations.

The CFU index of cellulosolytic bacteria basically was low. Single colonies grew up on the Hutchinson medium in the Petri dishes. The general cellulolytic ability of steppe soils was low. Actinobacteria showed the LD_{50} index at high UDMH doses: 3.62 mg/kg or 36 MPC. At UDMH critical dose (13.68 mg/kg or 137 MPC) lethal result of growth and development of these cultures was noted.

Representatives of *Azotobacter* and chemoorganotrophic bacteria were sensitive microorganisms. Their CFU number (index) dropped through the floor when increasing of UDMH concentrations in soil samples (Table 3).

We had observed the LD_{50} indicator for *Azotobacter* at 2.3 MPC (0.23 mg/kg), lethal or critical dose turned out to be 3.62 mg/kg (36 MPC). Consequently, the indicator function of *Azotobacter* on technogenic contamination was confirmed [10, 11, 12, 13]. The inhibition of growth and development were noticeable for bacterial

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chemoorganotrophic communities (Table 2). Their critical dose was found to be UDMH concentration 13.68 mg/kg.

Thus the changes in qualitative and quantitative composition of microbiocenoses when the soil contamination with heptyl had been occurred. The microscopic fungi and yeasts were the most resistant representatives in microbial community structure. The degree of the soil toxicity can be determined through the number of CFU *Azotobacter*/g. A linear correlation between the UDMH concentrations in soil samples and the decrease in the CFU number (index) of *Azotobacter* was observed.

CONCLUSION

Analyzing the research materials we can maintain that soil-geochemical and microbiological characteristics of Kazakhstani territory has been worsened as a consequence of spillage of liquid heptyl, and also because of the fire when falling of rocket-vehicle residual parts. MPC overage is absent if heptyl completely burns out when RVDP falling, even if a funnel will be large. It is was noted that in those places where the upper stage and the third stage elements fall there are some excess of heptyl MPC norms within 1000-1100 times. However, at a distance of 50 meters from the point of impact MPC is not exceeding the norm. Thus marked high geochemical anomalies of heptyl content are connected with a fall of RVDP.

RFA No. 15 and 25 were characterized by the accumulation of RVDP, in the places where residual amount of rocket fuel components spills took place. Also local high contrasting geochemical UDMH anomalies were formed. Considering the closeness of the 2^{nd} level watercourses (Zhide and Zharkuduk rivers), the danger of its transferring into the flood water with subsequent flushing into the Kalmakkyrgan river arises. This river had fishery and hunting-commercial significance.

In due course time heptyl contrast anomalies decreased and after different periods, in each particular case, depending on a combination of natural, manmade factors and age, reached MPL in soils.

In the 2nd of July 2013 at the "Baikonur" cosmodrome at the start launch vehicle "Proton-M" with three satellites "Glonass" on board fell down. In the center of the funnel, which was formed after the fall, experts found excess of heptyl MPC for about 527 times [14]. The liquidation of the wreckage consequences still continues as of day.

We consider that the identification and remediation of territories, contaminated by components of rocket fuel in RFA, is an important environmental problem. Necessity of its solution requires additional research and development of rehabilitation technologies of disturbed lands.

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