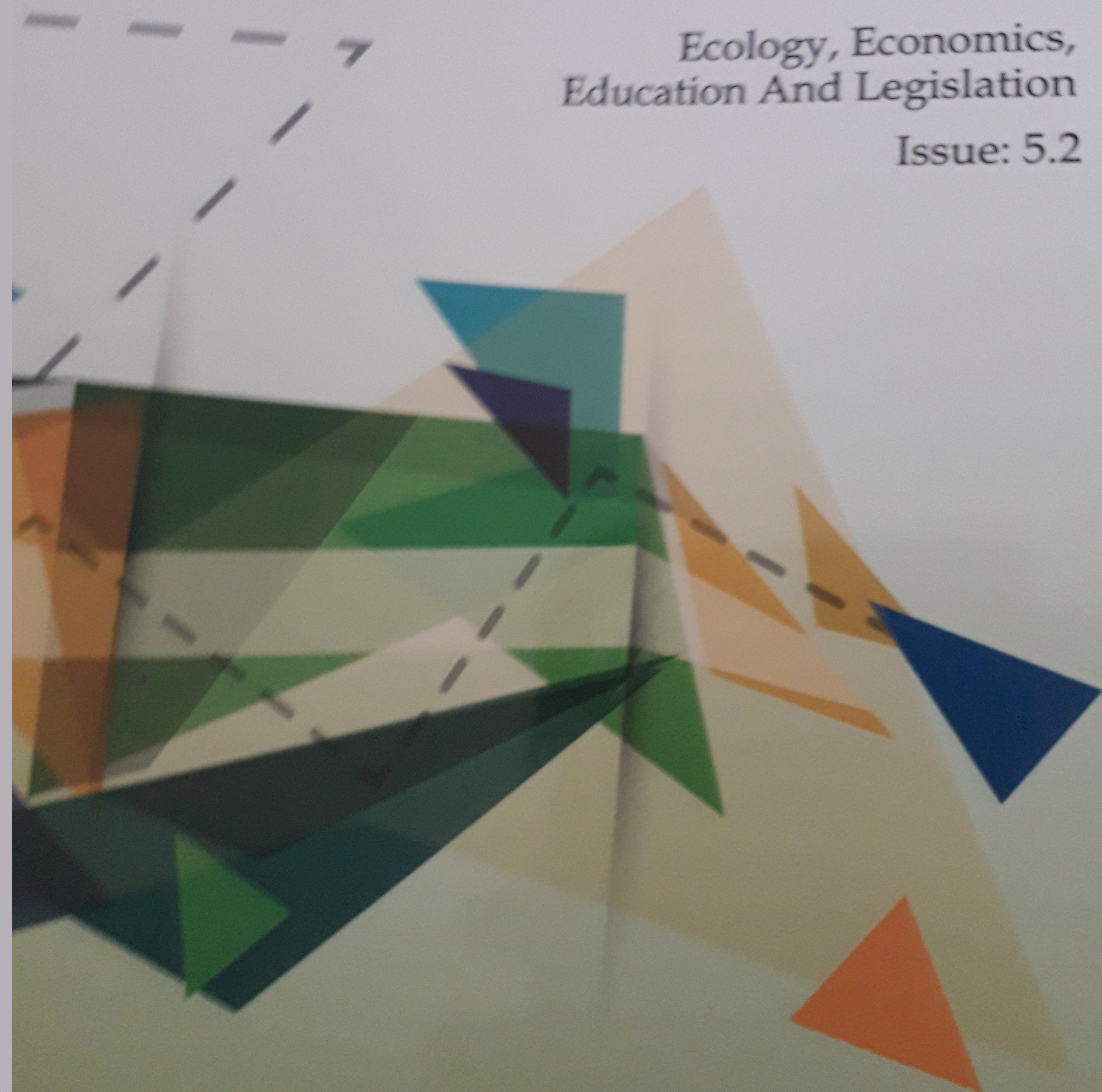


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EXPERIMENTAL STUDY OF NATURE OF PLANT CONTAMINATION BY ROCKET FUEL – HEPTYL

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Abstract. The paper presents the results of the study of the formation and accumulation of heptyl in wild plants from soil, contaminated by rocket fuel, at the sites of emergency falling of «Proton-M» launch vehicles in Central Kazakhstan. It has been experimentally proved that certain concentrations of heptyl in gray-brown sandy soils are not phytotoxic for *Agropyron pectiniformee* (1-5 mg/kg) and *Artemisia dracunculus* L. (1-25 mg/kg), however it can cause anatomical morphological changes of roots and leaves. The revealed signs increase with an increase in the dose of contamination of the soil by heptyl above 25 mg/kg. The obtained experimental data are intended for further development of environmental standards for chemical contamination of plants by rocket fuel components.

Keywords: rocket fuel components, heptyl, chemical pollution, plants, soil, phytotoxicity, anatomical and morphological changes, leaves, roots.

1. INTRODUCTION

Despite years of research on the effects of launches of space launch vehicles (SLV) from the Baikonur Cosmodrome (Central Kazakhstan), the nature of behavior of rocket fuel - heptyl in the air-plant-air system (unsymmetrical dimethylhydrazine and nitrogen tetroxide, UDMH) and its derivatives (including nitrosodimethylamine, NDMA) has not yet been established. The UDMH and NDMA are referred to the carcinogenic and mutagenic substances [1].

Rocket fuel gets into natural landscapes as a result of aerogenic dispersion or as a result of a land-based spill. Most of the incoming fuel burns and evaporates into the atmosphere, the smaller part penetrates the soil, dissolves in water, and is captured by vegetation. Vegetation cover is the main indicator of contamination by rocket fuel components in ecosystems at sites of emergency falling of the SLV or in areas of normal incidence of detachable launch vehicle parts. The degree of contamination of plants by heptyl depends on the type of plant, and the geochemistry of the growing areas and the intensity of the polluting effect [1-3].

Russian and Kazakhstani researchers (A.P. Vorozheikin, N.S. Kassymov, T.V. Koroleva, I.O. Baitulin, N.P. Ogar, A.M. Nurusheva et al., 1991-2015) have found that

the best ability to form and accumulate UDMH and NDMA in the plant organism is possessed by wild plants of the *Asteraceae* *Chenopodioideae* and *Poa* families. This feature is provided by biogeochemical specialization of plants growing in the natural conditions of the steppe and semi-desert landscape of Central Kazakhstan. Small doses of heptyl can be used by plants as an additional source of nitrogen and carbon. Large concentrations can cause morphological and anatomical changes, and chromosomal abnormalities of the plant organism [2-6].

The purpose of the experimental studies performed by the «Garysh-Ecology» National Research Center in the framework of the Republican budget program 008 «Applied Scientific Research in the Field of Space Activities» is the creation of a scientific basis for the development of maximum concentrations of UDMH and NDMA in plants. The relevance of the work carried out enables to determine the risk of damage to nature and human being from biotoxic contamination by rocket fuel - heptyl.

At the initial stage of the study in 2018, indicators of chemical pollution were identified at the sites, where the LV parts have fallen. Experiments have been performed to assess the phytotoxicity of soils contaminated by UDMH and to study the effect of heptyl on the anatomical and morphological structure of the vegetative organs of wild plants.

2. Materials and Methods

Floristic research in 2017-2018 was performed in the general system of field observations at the places of emergency falls of the «Proton-M» LV from 2013 (positional area of the Baikonur Cosmodrome) and from 2007 (part of the territory of Karaganda region). To simulate the situation with the impact of soil contaminated by UDMH on plants, samples of gray-brown sandy soil and perennial wild plants have been selected: *Agropyron pectiniforme* is a representative of the Cereals family (*Poa*); *Artemisia dracunculus* L. is a representative of the *Asteraceae* family. Cultivated cereal - Soft wheat (*Triticum aestivum*) was used for comparison.

For quantitative chemical analysis of the content of UDMH in soil and plants, methods of ion chromatography with amperometric detection were used, and methods of reverse phase high-performance liquid chromatography with spectrophotometric detection were used to determine the content of NDMA.

The assessment of soil phytotoxicity was carried out taking into account the maximum level of contamination by UDMH, at which the germination of planted seeds and the development of seedlings and roots are inhibited by 20% or more of the control. Sprouted seeds of wild plants (tarragon wormwood, crested wheat grass) and cultivated species (soft wheat), on soil (in Petri dishes) and on filter paper (for comparison), contaminated by heptyl solution in concentrations of 1, 5, 25 mg / kg (respectively, 10, 50 and 250 MCLudmh = 0.1 mg / kg of soil, according to the RK standard). There were used known methods of seed germination and seedlings in the laboratory, and studying the phytotoxicity of the soil and determining the content of toxicant in the soil [7].

To study the anatomical structure of the vegetative organs of *Agropyron pectiniforme* in comparison with the cultivated wheat species, 14 day old seedlings of plants grown in soil samples contaminated by heptyl and control (uncontaminated) were taken. For structural analysis, the aboveground and underground vegetative organs of the wild

plant of crested wheat grass (leaf and root) and wheat (leaf and root) were recorded in 70% alcohol. Anatomical preparations were prepared using a microtome with a TOC-2 freezing device. Anatomical sections with a thickness of 10 μ m were enclosed in glycerin. More than 50 temporary preparations were prepared in accordance with the generally accepted methods of M.N. Prozinoy (1960), and R.P. Barykina (2004) [8-9].

Measurement of morphometric parameters was performed by application of a computer program. Micrographs were taken on an MS-300 microscope (magnification $\times$ 180). Statistical processing of morphometric parameters was carried out using the Statistica v.10 computer program [10].

3. Results and discussion

3.1 Analysis of the dynamics of heptyl pollution in the soils and wild plants at the places of launch vehicle «Proton» emergency falling in the Central Kazakhstan

According to the degree of load on plants and related biota, UDMH concentrations are classified as low (less than 0.1 g / kg), moderate (1.0, 2.5 and 5.0 g / kg), high (10-50 g / kg) and very high (100 g / kg soil) (E.I. Yermakov, G.G. Panova et al., 1996). At low levels of UDMH in the soil, stimulation of growth, development, increase in plant productivity is observed. The nature of the effects of moderate and high doses of UDMH on plants is similar to the observed effect with an excess of nitrogen in the soil. At moderate levels, there is a short-term slowdown in the growth and development of plants, and a decrease in some productivity indicators. High levels of soil contamination are accompanied by a significant slowdown in plant development, and a decrease in their growth and productivity. The plants die at the maximum concentration of UDMH in the soil [11].

According to the results of joint Kazakhstan-Russian investigations at the accident sites, the SLV- RS-20 «Dnepr» (of 27.07.2006 in Kyzylorda region) and the «Proton-M» (from 06.09.2007 in Karaganda region), it was established that 2-3 years after repeated detoxification, the UDMH derivatives (including nitrosodimethylamine and nitrogen oxides) appear in the soil cover, and often - UDMH. The area of contamination of the vegetation cover of the UDMH and the NDMA during the spill of heptyl significantly exceeds the area of contaminated soil.

In accordance with the table, two years after the accident (in 2009), 0.16-1.9 mg / kg of the UDMH was detected in 50% samples of plants. In 2010, the UDMH was not recorded in plants, but in 83% of samples 0.1-6.9 mg / kg of the NDMA was detected. After 6-7 years after the emergency falling of the «Proton-M» PH, the UDMH and the NDMA were again found in the plant samples, but without contaminating the soil. The area of polluted vegetation exceeded the size of the site with emergency soil contamination several times.

Table - Results of the quantitative chemical analysis of samples of plants taken at the sites of the emergency fall of parts of the «Proton-M» launch vehicle (06.09.07) in 2007-2011.

Survey Year	The upper part of the booster modules and the transitional compartment of the spacecraft		«Briz-M» upper stage and part of the spacecraft		The second stage of the PH «Proton-M»	
	total samples	UDMH, NDMA (mg / kg)	total samples	samples with UDMH and NDMA (mg / kg)	total samples	samples with UDMH and NDMA (mg / kg)
2007	4	<u>3 (0,14-0,21)</u> n/a	12	n/a	11	n/a
2009	45	<u>23 (0,16-1,9)</u> 3 (0,30-1,00)	33	<u>7 (0,22-1,9)</u> n/a	37	<u>1 (0,30)</u> 2 (0,30-0,37)
2010	56	<u>56 (0,1-6,9)</u> n/a	13	<u>9 (0,10-2,2)</u> 2 (0,50-0,57)	8	<u>n/a</u> 8 (0,11-1,44)
2011	12	<u>n/a</u> 12 (0,11-0,21)	51	-	-	-

Note: in the numerator - data of laboratory studies of the Kazakhstani side, in the denominator – of the Russian side

In 2017, four years after the accident and detoxification, in the soil, up to 1.1 MPC UDMH (MPC UDMH = 0.1) were found in the soil in the area of the emergency fall of the «Proton-M» LV (dated July 2, 2013 in Kyzylorda region). mg / kg), 5-8.4 MPC NDMA (MPC NDMA = 0.01 mg / kg), and in plants 0.12-4.025 mg / kg NDMA (53% of samples). Pollution of vegetation around the site of an emergency fall has spread to the background, uncontaminated area, and it is located at a distance of 790 m.

Thus, based on the results of field studies, it has been established that in the soil at the sites of an emergency falling of the SLV, pollution by UDMH and NDMA persists for a long time. There is a re-pollution by UDMH and NDMA after their absence in the land cover for several years. Most of the contaminated samples are plants of the *Chenopodioidae* and *Compositae* family.

3.2 Analysis of the phytotoxicity of heptyl pollution soils to the wild plants in the Central Kazakhstan

To determine the phytotoxicity threshold of a soil contaminated by heptyl, seed germination and the intensity of seedling development on soil samples with the introduced concentration of the UDMH solution exceeding the MPC by 10, 50, 250 times were studied. In testing the sensitivity of plants to UDMH, gray-brown sandy loam soils of the «Baikonur» Cosmodrome area with low nitrogen content were used, which explains the stimulating effect of UDMH on seed germination and the intensity of seedling development.

On the third day of the experiment, after visual observation of germination and taking into account the germination of seeds of wild plants and wheat, the following was established:

- Soil with UDMH content introduced in concentrations equivalent to 1 mg / kg, 5 mg / kg and 25 mg / kg stimulates the germination of seeds of a wild plant - tarragon wormwood.
- soil with UDMH content applied in concentrations equivalent to 1 mg / kg and 5 mg / kg stimulates, and 25 mg / kg does not alter the germination of seeds of wild-growing cereal – crested wheat grass.
- soil with UDMH content applied in concentrations equivalent to 1 mg / kg does not affect, and 5 mg / kg and 25 mg / kg inhibits the germination of soft wheat seeds.

Thus, the phytotoxicity threshold of wild plants (wormwood and crested wheat grass) is 25 mg / kg UDMH in the soil, which exceeds the phytotoxicity threshold of cultivated grass - soft wheat (5-25 mg / kg UDMH in the soil). Concentrations of UDMH in the soil, equivalent to 1-5 mg / kg, stimulate the germination of seeds, as well as the growth of aboveground and underground parts of wild and cultivated plants.

3.3 Analysis of the anatomic-morphological changes in wild plants due to heptyl pollution soils

Under the experimental conditions, the effect of UDMH on the anatomical and morphological structure of a wild-growing plant (crested wheat grass) and a cultivated species (soft wheat) was studied. The wormwood Estragon did not participate in the study, due to the weak development of the seedlings of the plant, which did not allow anatomical sections of the stem to be made.

According to the data of comparative analysis, insignificant changes in the internal structure of leaf blades were found in the couch grass.

- the thickness of the upper epidermis in soil samples with excess of UDMH introduced in concentrations equivalent to 1, 5 and 25 mg / kg is increased relative to the control (0.041, 0.041, 0.036, control 0.032 μ m);
- the thickness of the lower epidermis in soil samples with the UDMH content, introduced in a concentration equivalent to 1 mg / kg higher relative to the control (0.038, 0.037 μ m); at an equivalent concentration of 25 mg / kg, remains at the same level;
- the thickness of the leaf blade in soil samples with the UDMH content deposited at a concentration equivalent to 1 mg / kg lower relative to the control (0.736 and

0.697 μm , respectively); at concentrations of equivalent 5 and 25 mg / kg higher relative to the control;

- the thickness of the mesophyll layer in soil samples with the UDMH content introduced in equivalent concentrations of 1, 5 and 25 mg / kg was reduced relative to the control (0.589, 0.545, 0.558 micron, control - 0.594 micron);
- an area of conductive beams in soil samples with the UDMH content introduced in concentrations equivalent to 1.5 mg / kg remained at the same level; at an equivalent concentration of 25 mg / kg reduced (0.178 μm , control 0.181 μm).

The samples of the crested wheat grass, contaminated by the UDMH in concentrations equivalent to 1 mg / kg and 5 mg / kg, have a fairly even layer of exodermis, and with a pollution of 25 mg / kg, the winding structure of the root and its slight thickening are determined. In the control sample, the exodermis (integumentary tissue) and the entire root have a very winding structure.

The leaf of a soft wheat sprout is characterized by a thickness of the upper epidermis of 0.161 μm in the control, 0.165 μm - when contaminated by 25.0 mg / kg UDMH of the soil. The lower epidermis of the leaf lamina is thickened - 0.199 μm , when the UDMH is contaminated 25.0 mg / kg UDMH, 0.169 μm in the control. The thickness of the leaf blade on a soil sample with the UDMH concentration equivalent to 25 mg / kg was 1.41 μm , in the control it was 1.57 μm .

With the introduction of 25 mg / kg of the UDMH contamination into the soil, the anatomical features of the root of the seedlings of cereal changed. The thickness of the primary cortex was reduced (control 1.01 μm , contaminated by 0.865 μm), the central cylinder (endoderm cells 1.27 μm in the control, contaminated by 1.015 μm), xylem vessels were reduced.

The central cylinder of the root is formed from conductive tissues - phloem and xylem, parenchyma (stores nutrients and water) and pericycle (the root-bearing layer, from which the formation of the cylinder begins).

Thus, anatomical and morphological changes in plants grown from soil contaminated by the UDMH were found in the root and leaf sections. They are characterized by an increase in the thickness of the integumentary tissue (upper epidermis and lower epidermis), a decrease in the thickness of the leaf lamina and conducting bundles; a decrease in the thickness of the primary cortex of the root, the thickness of its central cylinder, and the area of xylem vessels. The increase in the observed signs with an increase in the dose of soil pollution by the UDMH (concentration above 25 mg / kg) can serve as an indicator of environmental pollution by the UDMH.

4. CONCLUSIONS

The obtained information in the course of carrying out of a full-scale and experimental research is necessary to form a scientific substantiation of the environmental standard - the maximum permissible concentration of rocket fuel (heptyl, UDMH) in plants of Central Kazakhstan.

According to the results of field studies, it has been determined that in the soil at the places of an emergency falling of the SLV, the pollution by UDMH and NDMA persists for a long time. There is a re-pollution by UDMH and NDMA after their absence in the

land cover for several years. Most of the contaminated plant samples belong to the plants of the *Chenopodioideae* and *Compositae* family.

It is established that the content of the UDMH in the soil of 1-25 mg / kg of the UDMH is not phytotoxic for *Artemisia dracunculus* L. wormwood and crested wheat grass *Agropyron pectiniformee*. Soil contamination of 5-25 mg / kg UDMH is phytotoxic for a cultivated plant - Soft wheat (*Triticum aestivum*).

Anatomical and morphological changes of plants grown in soil contaminated by the UDMH (25 mg / kg) are expressed as an increase in the thickness of the covering leaf tissue (upper epidermis and lower epidermis), a decrease in the thickness of the leaf lamina and conducting bundles, a decrease in the thickness of the primary cortex of the root, its central cylinder, and the areas of xylem vessels of the root system.

The results of experimental studies of soil phytotoxicity and anatomical and morphological changes of wild plants serve as a model, imitating the action of soil contaminated by the UDMH on perennial wild plants in natural conditions of Central Kazakhstan, the region in which the rocket and space activity is carried out at the Baikonur Cosmodrome.

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Fe OXYHYDROXIDES AS A REMEDIATION AGENT FOR CONTAMINATED MINE WATERS

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ABSTRACT

One of the goals of our research was the evaluation of quantitative and qualitative properties of the Fe oxyhydroxides emerging from mine waters.

Another one of the main goals of this research was the effectiveness comparison between natural and supported attenuation used as a remediation method for the removal of potentially toxic metals and metalloids from mining waters occurring on sites with sulfidic mineralization. Samples for this research were taken from abandoned mineral deposit of sulfide ores in the locality Pezinok. These abandoned deposits pose a danger to the environment in the form of increased concentrations of some potentially toxic elements (especially Sb) in waters flowing out of the abandoned adits. We managed to prove, that natural attenuation is also an effective remediation method for mining waters contaminated by potentially toxic elements but supported attenuation (by aeration) is significantly more effective considering the amount of precipitating solids – Fe oxyhydroxides.

Keywords: oxyhydroxides, attenuation, remediation method, mine waters

INTRODUCTION

Cleaning of mine waters contaminated by various potentially toxic chemical elements can be challenging, both economically and in terms of time. The source of contamination usually cannot be removed; therefore, we can only attempt to reduce its consequences, which can be long lasting. The remediation of these areas using conventional physico-chemical methods is usually costly and often involves additional environmental risks. Conventional methods of mine water purification include coagulation and flocculation, membrane separation, a few electrochemical methods, chemical extraction, ion exchange and many other methods [1,2]. Recently, not only natural and synthetic sorbents, but also industrial and agricultural wastes are used to remove contaminants from waters. This can be a cost-effective alternative to commonly used, more expensive methods for removing metals and metalloids from waters [3].

SITE DESCRIPTION

Samples for our research are represented by mine waters extracted from the abandoned mining area near Pezinok town in south-western Slovakia. This mining area is located on the east slope of the ... figure 1.