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# Ecological Modelling Research of Transformations of Unsymmetrical Dimethylhydrazine and N-Nitrodimethylamine

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## ABSTRACT

The article presents the results of ecological modeling of soil and plant pollution processes by toxic heptyl rocket fuel (unsymmetrical dimethylhydrazine, UDMH) and the product of its transformation by N-nitrosodymethylamine (NDMA). Experiments delivered in laboratory conditions show that in sabulous gray-brown soil (uncontaminated soil samples were taken from the Baikonur Cosmodrome zone), the reaction of transformation of UDMH in NDMA is reversible and depends on the concentrations of reacting compounds. NDMA is transferred from the soil to the stems and leaves of plants of wild-growing species by the aerogenous route. The ability to accumulate NDMA by leaves and stems of plants is more or less dependent on the plant species.

**Objective** - research on the transformation of unsymmetrical dimethylhydrazine (UDMH) and N - nitrozodymethylamine (NDMA) in a closed reservoir - an ecological model of rocket fuel pollution.

**Research methods.** The method of ecological modeling studies of UDMH and NDMA contamination in soil and plants has been developed and tested. Boxes with samples of sabulous gray-brown soil and seeds of wild plants brought from the drop zones of detachable parts of launch vehicles have been placed in hermetically sealed and transparent containers. NDMG or NDMA are introduced into the soil.

To measure the content of UDMH and NDMA in soil samples, in condensate on container walls, in the above-ground part and roots of plants, as well as in water washes from leaves, the method of quantitative chemical analysis high performance liquid chromatography has been used.

**Keywords:** aerospace activity, ecological model, unsymmetrical dimethylhydrazine, n-nitrosodymethylamine, transformation, aerogenic transmission, plants, soil.

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## INTRODUCTION

The Baikonur Cosmodrome has been launching space-mission vehicles for several decades. During this period, the designated areas of Kazakhstan's territory regularly receive separated parts of the launch vehicles. Such a long period of operation of the drop zones experiencing long-term loads of various modifications of the launch vehicle does not occur in any other spacefaring nation of the world (USA, France, etc.) [1, 9].

The main factor of anthropogenic impact on the natural ecosystem in the areas where separated launch vehicle parts fall off, is the ground spill of unprocessed rocket fuel - heptyl (unsymmetrical dimethylhydrazine, UDMH). UDMH is a volatile, highly toxic, carcinogenic and mutagenic substance. Environmental pollution problems are mainly related to the toxicity of the UDMH itself, as well as a wide range of its transformation products. The greatest hazard is N-nitrosodymethylamine (NDMA), an organic compound, which belongs to the first class of toxic hazard for humans. Relevance of studying the behavior of UDMH and NDMA in plants is associated with the risk of negative effects of rocket fuel on humans, on the natural food chain "contaminated soil, water, air, plants → herbivorous animals → food products → human" [2, 4, 6].

The results of research on the transformation of UDMH in natural conditions (performed by the research center "Garysh-Ekologiya") demonstrate the ability of wild species plants to accumulate UDMH within 0.16-1.9 mg/kg of dry weight of the plant, NDMA - 0.1-3.18 mg/kg [8, 10].

Further on, the behaviour of UDMH in plants was studied in the framework of ecological modeling studies under laboratory conditions.

## RESEARCH OBJECT

Plants of wild-growing species Bluegrass (*Agropyron pectineforme*), *Stipa sareptana*, Kentucky bluegrass (*Poa pratensis*), *Agropyron fragile*, *Artemisia terrae-albae*, Linear-leaved wormwood (*Artemisia dracunculus*), *Artemisia diffusa*).

## RESEARCH METHODS

The closed container method is used to study the effect of toxic, volatile compounds on plant growth and development. The experiment involves initially uncontaminated UDMH samples of sabulous gray-brown soil selected in areas where separating carrier rocket parts fall. The contamination of model soil samples UDMH and NDMA was performed under laboratory conditions [7, 12].

Closed containers have been used (closed and transparent containers with the following dimensions: 70 cm (width), 70 cm (length), 60 cm (height), in each of which two boxes were placed, with the dimensions 20 cm (width), 52 cm (length), 18 cm (height). One box with uncontaminated soil and a plant, the second box with contaminated UDMH or NDMA soil without plants. Distance between the boxes was 20 cm. 4 kg of soil was placed in each box.

High performance liquid chromatography methods were used to control concentrations of UDMH transformation products in experimental samples [3].

## RESEARCH FINDINGS AND THEIR DISCUSSION

In laboratory conditions, using closed containers, model studies of UDMH and NDMA contamination of soil, plants, air and water have been conducted. The following main research results have been obtained.

Samples of sabulous gray-brown soil were contaminated with UDMH in concentrations of 1.92 mg/kg, 9.95 mg/kg, 18.47 mg/kg, 21.14 mg/kg, 39.14 mg/kg. In 4-5 months after application of 1.92 and 9.95 mg/kg of UDMH, in the upper soil layer 0-1 cm its content stabilizes at the level of 0.026-0.032 mg/kg, and in the soil layer 2-10 cm - at the level of 0.054-0.058 mg/kg. Thus, the properties of sabulous gray-brown soil (low humus content (0.42 %), low absorption capacity (11.70 mg/eq. per 100 g) allow to firmly bind up to 0.058 mg/kg NDMG. The rest of the NDMG introduced into soil samples is transferred to composite, mobile forms of UDMH with high migration capacity.

Weak-alkali environment (pH 8.0), high sand content (80.5 %) of sabulous soil provides evaporation of UDMH and its oxidation derivatives from the top layer of soil. High aeration of sabulous soil provides oxidation of UDMH to NDMA. Thus, after 3 months, 0.2% of the introduced UDMH concentration (0.04 mg/kg of 18.47 mg/kg) is transformed into NDMA.

The results of the model laboratory studies are consistent with the results of geochemical studies of the space-mission vehicle RS-20 emergency fall area in 2006. ("Scientific and Research Center "Garysh-Ekologiya", 2013). It was found that 22.8 mg/kg of UDMH and 1.08 mg/kg of NDMA are transformed and decomposed in the soil to approximately the same content of 0.04 mg/kg during the first two years after the accident and remain at this level for another five years [11].

The following clarifications have been made to the ecological modeling in laboratory conditions. The content of UDMH decreases to a stable level of 0.054-0.058 mg/kg in the upper soil layer (0-10 cm) after 4 months, at a temperature of +25-30 °C. In the same conditions, the NDMA content decreases over four months from 38.61 mg/kg to a stable level of 0.027 mg/kg.

*Thus, the UDMH introduced into sabulous gray-brown soil is more decomposed than fixed sorption. Test samples of sabulous gray-brown soil have a certain limit of strong binding of UDMH to 0.058 mg/kg.*

Modeling of NDMA transmission in air as part of aqueous condensation droplets into leaves and stems of plants, as well as into soil samples previously uncontaminated with NDMA or UDMH leads to the following conclusions.

As the NDMA content of contaminated soil samples increases, the NDMA content of condensate (fine water droplets) on the tank walls increases.

In the condensate after 20 days, 0.281 mg/ $dm^3$ NDMA transformed from the soil sample with 39.14 mg/kg of UDMH is detected; after 3 months - 0.086 mg/ $dm^3$ of NDMA (transformed from the soil sample with 21.14 of UDMH), 1.796 mg/ $dm^3$ of NDMA (transformed from the soil sample with 286.99 mg/kg NDMA); in 5 months - 1.09 mg/ $dm^3$ NDMA (transformed from soil with 140.38 mg/kg NDMA); in 4 months - 0.368 mg/$dm^3$ of NDMA (transformed from soil with 71.69 NDMA), 0.01 mg/ $dm^3$of NDMA (transformed from soil with 38.61 mg/kg NDMA).

*Thus, NDMA is transmitted from contaminated soil to air in small droplets of water and remain in the air for up to five months, while NDMA is not detected in the air.*

NDMA was found in the stems and leaves of plants in the amount of 0.33-0.389 mg/kg - *Agropyron pectineforme*, 0.010 mg/kg - *Stipa sareptana,* 0.28 mg/kg - *Artemisia terrae-albae*; 0.014 mg/kg in flushings from leaves - *Stipa sareptana*, 0.54 mg/kg - *Poa pratensis*. The presence of NDMA has not been established in the roots of wild plant species.

The aerogenic transmission of NDMA from soil samples contaminated with NDMG to uncontaminated soil samples has been demonstrated. Thus, in the previously uncontaminated soil samples 0.017-0.021 mg/kg of NDMA (transformed from contaminated soil sample UDMH 39.14 mg/kg) was found.

The detection of 0.11 mg/kg of UDMH (in a closed container with soil sample contaminated with 39.14 mg/kg of NDMG) in previously uncontaminated soil indicates aerogenic transmission of UDMH.

For a more detailed study of UDMH and NDMA transport by air, it is necessary to simulate air flows (wind) in a closed container, taking into account the almost complete decomposition of NDMG in air within a day.

*Thus, NDMA is aerogenically transmitted from the soil to the stems and leaves of wild plant species. The ability to accumulate NDMA from leaves and stems of plants is more or less dependent on the plant species. No NDMA has been found in the roots of wild plant species, probably NDMA is not transferred from the leaves and stems to the roots by the phloem. NDMA and UDMH from contaminated soil samples are aerogenically transmitted to previously uncontaminated soil samples. The aerogenic transmission capacity of UDMH is lower than that of NDMA.*

In the framework of the ecosystem model the possibility of reversibility of the reaction of transformation of UDMH to NDMA has been studied.

The shift in the direction of the reaction NDMG↔NDMA depends on the concentrations of reacting components. Under the conditions of the model system in soil samples contaminated with 286.99 mg/kg of NDMA, after 3 months 0.011 mg/kg of UDMH in the surface soil layer (0-1 cm) and 0.013 mg/kg of UDMH in the soil layer 2-10 cm were found. No UDMH was found in soil samples with lower NDMA content.

*Thus, in samples of sabulous gray-brown soil NDMA is transformed into UDMH, in conditions of high content of NDMA (286.99 mg/kg). The reaction of transformation of UDMH in NDMA is reversible and depends on the concentrations of reactive compounds.*

The conclusion about the reversibility of the reaction of transformation of UDMH into NDMA has the following justification, according to the literature data (Handbook of toxicology..., 1999). The NDMA enters into an oxidation and reduction reaction. At oxidation, the nitroso group (—N=O) is oxidized to the nitro group (—$NO_2$). Depending on the reducing agent, the reaction can take place with the formation of unsymmetrical dimethylhydrazine, dimethylamine, ammonia, formaldehyde, and others. Weak reducing agents turn NDMA into hydrazine, and strong reducing agents into initial secondary amine [5].

Weak ($HNO_2$ - nitric acid) and strong reducing agents ($NH_3$ ammonia) are present in the used experimental soil samples of the present ecological modeling studies. In general, the chemical reactions into which NDMA may enter have not yet been sufficiently investigated.

## CONCLUSION

The ecological system of the territories of Kazakhstan polluted with unprocessed rocket fuel is complicated, so studying the processes running in the system itself requires considerable time and money. It is difficult to obtain complete information about the system. In this regard, this paper proposed and tested a methodology for the construction and study of a simulation model of soil surface contamination by heptyl propellants (UDMH) and the consequences of this contamination for the environment at the Baikonur Cosmodrome and drop zones of detachable parts of launch vehicles.

Imitation models allow studying the mechanisms of ecosystem functioning in laboratory conditions with given biotic and abiotic components.

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