



Transformation products of 1,1-dimethylhydrazine and their distribution in soils of fall places of rocket carriers in Central Kazakhstan

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ARTICLE INFO

Article history:

Received 11 November 2011

Received in revised form 10 March 2012

Accepted 5 April 2012

Available online 1 May 2012

Keywords:

1,1-Dimethylhydrazine

Transformation

1-Methyl-1H-1,2,4-triazole

Distribution

Soil

Solid phase microextraction

ABSTRACT

In our research, three fall places of first stages of Proton rockets have been studied for the presence and distribution of transformation products of 1,1-dimethylhydrazine (1,1-DMH). Results of identification of transformation products of 1,1-DMH in real soil samples polluted due to rocket fuel spills allowed to detect 18 earlier unknown metabolites of 1,1-DMH being formed only under field conditions. According to the results of quantitative analyses, maximum concentrations of 1-methyl-1H-1,2,4-triazole made up 57.3, 44.9 and 13.3 mg kg⁻¹, of 1-ethyl-1H-1,2,4-triazole – 5.45, 3.66 and 0.66 mg kg⁻¹, of 1,3-dimethyl-1H-1,2,4-triazole – 24.0, 17.8 and 4.9 mg kg⁻¹ in fall places 1, 2 and 3, respectively. 4-Methyl-4H-1,2,4-triazole was detected only in fall places 2 and 3 where its maximum concentrations made up 4.2 and 0.66 mg kg⁻¹, respectively. The pollution of soils with transformation products of 1,1-DMH was only detected in epicenters of fall places having a diameter of 8 to 10 m where rocket boosters landed. The results of a detailed study of distribution of 1,1-DMH transformation products along the soil profile indicate that transformation products can migrate down to the depth of 120 cm. The highest concentrations of 1,1-DMH transformation products were detected, as a rule, at the depth 20 to 60 cm. However, this index can vary depending on the compound, humidity and physical properties of soil, landscape features and other conditions. In the surface layer, as a rule, only semi-volatile products of transformation were detected which was caused by fast evaporation and biodegradation of volatile metabolites.

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1. Introduction

Baikonur is one of the rocket launching centers in the world playing a major role in development of the space industry in Kazakhstan. Launches of heavy rockets like Proton and Dnepr from Baikonur may constitute major risks to the environment and human health in Kazakhstan, Russia, Uzbekistan and other neighboring countries (Adushkin et al., 2000). These rockets use fuel based on the highly toxic 1,1-dimethylhydrazine (1,1-DMH) with strong carcinogenic, mutagenic, teratogenic and embryotoxic properties (ATSDR, 1997; Carlsen et al., 2009a,b). Following a successful launch, up to 2 t of unburned fuel are still present in the burned out first stage after separation and is discharged into the environment in specially designated regions (Adushkin et al., 2000; Kassimov et al., 1996). In a case of accident that can happen at any part of the rocket route including major cities of Kazakhstan like Astana, Ust-Kamenogorsk, Semipalatinsk and Dzhezkazgan, up to 200 t of unburned fuel may be discharged

creating unpredictable consequences (Nakanune, 2007a). The last accidental fall of a Proton rocket happened 50 km from Dzhezkazgan (Nakanune, 2007b). In July, 2006, a 45-m diameter and 20-m depth crater was formed after contingency with Dnepr rocket carrying 16 satellites. The crater can be seen from space using Google Earth software at coordinates 44°34'24.4" N, 62°58'15.5" E.

1,1-DMH is a highly reactive compound with strong reducing properties. After its discharge in the environment, 1,1-DMH undergoes a series of complex chemical transformations. A study of these transformations, which was documented by several researchers (Buryak et al., 2004; Batyrbekova, 2008), is complicated due to their high reaction rates, low stability of intermediates; many factors playing a significant role, as well as the lack of proper analytical methods. The overall transformation is driven by oxidation processes (Alimzhanova et al., 2009).

Studies of environmental soil samples polluted with 1,1-dimethylhydrazine show the presence of the following metabolites: 1-methyl-1H-1,2,4-triazole (MTA) (Kenessov et al., 2008), N-nitrosodimethylamine (NDMA) and tetramethyltetrazene (TMT) (Kassimov et al., 1996; Batyrbekova, 2008).

The use of mass spectrometry in combination with gas chromatography (Buryak et al., 2004; Kenessov, 2008; Carlsen et al., 2008) and

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liquid chromatography (Smolenkov et al., 2007; Rodin et al., 2008, 2010) in laboratory experiments allowed identification of previously unknown transformation products of 1,1-dimethylhydrazine. Results presented in other works (Alimzhanova, 2009, 2010) describe attempts to rationalize the mechanisms of the formation of the main transformation products of 1,1-DMH.

One of the main obstacles for successful detection and identification of 1,1-DMH metabolites is sample preparation. The use of a novel sampling/sample preparation technique, solid phase microextraction (SPME), in combination with GC-MS allowed to establish structures of 27 transformation products of 1,1-DMH formed in laboratory experiments including amines, triazoles, pyrazoles, tetrazoles, hydrazones, imidazoles and others (Kenessov et al., 2010).

Experimental and theoretical studies on the environmental and human health impact (Carlsen et al., 2007, 2008, 2009a,b) report carcinogenic, mutagenic, teratogenic and embryotoxic properties of many transformation products of 1,1-DMH, especially those compounds having at least one intact N–N bond.

The distribution and fate of 1,1-DMH in soils from selected fall placed (FP) have been extensively studied by several institutions in Kazakhstan and presented in papers (Batyrbekova et al., 2005; Nauryzbaev et al., 2005) and maps of 1,1-DMH distribution in fall places were visualized (Nauryzbaev et al., 2005). It is important to note that 1,1-DMH could be detected in soils approx. 30-years after the discharge (Nauryzbaev et al., 2005) in apparent disagreement with the fact that 1,1-DMH is being predicted as rapidly biodegradable (Carlsen et al., 2008). Dry and possible anaerobic conditions may play a dominant role in this connection.

However, further, it should be stated that recent experiments have provided information that 1-formyl-2,2-dimethylhydrazine, present in environmental samples, may form 1,1-DMH during intensive sample preparation when determining 1,1-DMH by classic methods based on liquid chromatography, ion chromatography or photocolormetry (Smolenkov et al., 2007).

To date, no actual data on distribution of transformation products in soils of fall places exists in open literature. Due to this fact, as well as unreliable data on the distribution of 1,1-DMH obtained, applying obsolete analytical methods, the fate of 1,1-DMH and its transformation products in fall places remains unknown.

The objectives of the present study are to detect the presence of 1,1-DMH transformation products and to reveal their distribution pattern in soils at sites of the first stage of carrier rockets which are dropped over Central Kazakhstan.

2. Materials and methods

2.1. Chemicals

1-Methyl-1H-1,2,4-triazole applied for instrument calibration, was synthesized at the A.B. Bekturov Institute of Chemical Sciences of the Republic of Kazakhstan, the purity being verified to 99.5% by GC-MS. Methylene chloride (99.8% purity) was obtained from "EKOS-1" LLC (Moscow, Russia). Helium (99.995% purity) was purchased from "Tehgas" (Orenburg, Russia). Sodium chloride (Laborpharma, Kazakhstan) was of a chemically pure quality.

2.2. Materials

For SPME-GC-MS analysis, 20 mL headspace screw top vials with PTFE-silicone septa (Agilent, Santa Clara, USA) were utilized. Before analysis, all vials and septa were washed by distilled water and pre-conditioned at oven heated to 150 °C for 2 h.

For non-SPME GC-MS analyses, 2 mL clear vials with PTFE/red rubber septa (Agilent, Santa Clara, USA) were utilized.

2.3. Equipment

All analyses were performed using 6890/5973N (Agilent, Santa Clara, USA) gas chromatograph with mass selective detector. For all GC separations, a 30 m × 0.25 mm HP-Innowax column (Agilent, Santa Clara, USA) having film thickness 0.25 µm was used. The column was maintained at a constant flow of helium at 1 mL min⁻¹ and interfaced with MS detector via a transfer line kept at 240 °C. The ion source and quadrupole temperatures were 230 °C and 150 °C, respectively. All other MS parameters were determined and optimized during automatic tune. GC-MS was controlled by MSD Productivity ChemStation E.01.01.335 (Agilent, Santa Clara, USA).

SPME and liquid injection to GC-MS was carried out using a Combi-PAL autosampler (CTC Analytics AG, Switzerland) equipped with agitator and conditioning station.

For evaporative concentration of extracts, Kuderna–Danish sample concentrator (Supelco, Bellefonte, PA) was utilized.

For sampling of soils from depths more than 40 cm, Edelman augers (Eijkelkamp, The Netherlands) were applied. Sampling of soils from depths of 0–40 cm was done using 4 stainless steel core samplers produced by Valeriy Svetov in al-Farabi Kazakh National University.

2.4. Sampling

In the present study we investigated soil samples taken from three different fall places.

2.4.1. Fall places 1 and 2

Fall place 1 is located at a position 47°20'18" N, 66°53'00" E at a height of 345 m above the sea level. The fall place is situated close to the right bank of the intermittent river Kyryksai. The fall place was formed after the landing of the first stage of Proton-M rocket carrying Canadian commercial broadcast communication satellite Ciel-2 on December 10, 2008. The territory of the fall place is flat with a small crater having a depth of about 0.5 m and a diameter of about 10 m caused by the fall. Samples were taken in July 2009 and August 2010.

Fall place 2 is located at a position 47°13'47" N, 66°31'46" E at a height of 340 m above the sea level. The fall place is situated close to the right bank of the intermittent river Zharkuduk on a hill top. The fall place was formed after a landing of the first stage of Proton-K rocket carrying first Kazakhstan communication satellite KazSat-1 on June 16, 2006. The territory of the fall place has a significant height gradient of about 20–30%. The depth of a 10-m diameter crater, formed after the landing of the rocket stage, is virtually immeasurable, due to the slope of the area. Samples were taken in July 2009 and August 2010.

In the epicenter, the sides of the horizon were marked using a compass, a 10 × 10 m grid was installed with 2 m steps. Sampling was performed in the single corners of the grid. Thus, samples from in total 36 points were taken. At the single points, 4 samples were taken, using a core sampler from each 10-cm layer down to the depth of 40 cm. Totally, 144 samples each of approx. 50 g were taken from each of the 10 × 10 m grid.

Subsequently, within the epicenter of the fall place, a 2 × 2 m grid was installed with 50 cm steps. Samples were taken from the 25 corner points in the grid. At the single points, 4 samples were taken using core sampler from each 10-cm layer down to the depth of 40 cm. In the square 2 × 2 m, 100 soil samples each of approx. 50 g, were taken from these grids.

At three points of an obvious spill of rocket fuel, layer samples were taken using Edelman auger from each 20-cm horizon down to the depth of 60 cm, deeper sampling was impossible due to rocks on lower horizons.

To further check the possible wider distribution of rocket fuel residuals around the epicentre, (sampling in 2009), a 100 × 100 m grid was installed with 10 m steps. Average soil samples were taken

from the 121 corner points of the grid. Samples were taken from a depth of 0–40 cm using core sampler.

2.4.2. Fall place 3

Fall place 3 is located at a position 47°18′37.6″ N, 66°28′5.1″ E at a height of 410 m above the sea level. The fall place is situated close to the right bank of the intermittent river Zhide. The fall place was formed after the landing of the first stage of Proton-K rocket carrying American AMC-9 telecommunication satellite on June 6, 2003. The territory of the fall place is flat with a small slope in the south-eastern direction. A crater at the epicenter has a depth of about 0.5 m and a diameter of about 10 m.

In June 2003, the trench was prepared in fall place 3. At present time, the length of the trench is 10 m, width and depth are 1 m. On the walls of the trench, it is still possible to see drainage of rocket fuel into the lower horizons. A small but specific amine smell can still be detected in the trench.

The fall place 3 was examined in August 2010. Layer-specific sampling in fall place 3 was performed using Edelman auger. The holes were drilled at the distance of 10 cm from the trench where fuel spillages had been seen. Two holes were drilled on the western side and three holes were drilled on the eastern side of the trench. Totally, 5 holes with the depth of 2 m were drilled. In the course of drilling, soil samples were taken from each 20-cm horizon. Totally, 10 samples from each hole were taken. The mass of each sample was approx. 50 g.

2.5. Analytical approach

To optimize the analysis of 730 soil samples in 2009 and 550 soil samples in 2010 and to gain the highest amount of data, samples were analyzed according to the following scheme:

- 1) Analysis of all soil samples by SPME-GC with MS detection in SIM mode (Table 1) to discover polluted soil samples;
- 2) Analysis of the detected polluted samples by SPME-GC with MS detection in “Scan” mode in the range of m/z 34–200 for identification of all the transformation products in the polluted samples;

Stages 3 and 4 were only performed during the 2010 samplings:

- 3) Quantitative determination of the main products of 1,1-DMH transformation in the detected polluted soil samples by the method of solvent extraction in combination with GC with MS detection in SIM-mode;
- 4) Quantitative determination of formaldehyde dimethylhydrazone (FADMH) and NDMA in aqueous extracts from 5 most contaminated soil samples found from each fall place.

2.6. Screening of 1,1-DMH transformation products in soil samples using SPME-GC-MS

Analyses were carried out according to the method described in the paper (Kenessov et al., 2010) based on SPME-GC-MS with some

modifications. Soil samples (2.0 g) were weighed into 20 mL vials and extracted using 85 μ m Carboxen/polydimethylsiloxane fiber at 40 °C for 30 min without agitation. SPME fiber was conditioned using conditioning station at 250 °C before each extraction stage for 2 min and after each desorption stage for 5 min. Desorption was carried out in a split/splitless GC inlet equipped with 0.7 mm direct SPME liner (Supelco, Bellefonte, PA) at 240 °C for 10 min. GC oven program was: 40 °C for 5 min, followed by 5 °C min^{−1} ramping to 100 °C and 10 °C min^{−1} ramping to 240 °C, where the column was held for 10 min before cooling. Each run was 41 min.

Detection in “selected ion monitoring” mode was carried out using the program given in Table 1.

The program was prepared on the basis of preliminary identification of major transformation products of 1,1-DMH in laboratory and field samples.

2.7. Quantitative determination of triazoles in soil samples

To date, the methods based on SPME-GC-MS cannot be used for quantitative determination of 1,1-DMH transformation products in soils. For quantitative determination of the concentrations of 1,1-DMH transformation products, a previously developed method (Kenessov et al., 2008), based on GC-MS following an extraction of analytes from soil by methylene chloride was applied. For extraction, 10.0 g of soil sample was placed into a 100 mL glass flask, and 30 mL of methylene chloride was added. The flask was sealed and shaken for 30 min. Obtained extracts were filtered and evaporated to a volume of 1.0 mL and injected to the GC inlet kept at 180 °C in splitless mode. For separation, we used the same GC oven program as described in Section 2.3. MS detection was carried out in SIM mode using the program given in Table 1 starting from 8.00 min due to a corresponding solvent delay. On the collected chromatograms, 1,1-DMH transformation products were identified using their retention times, their peaks subsequently being integrated.

Due to the fact that standards of 1-ethyl-1H-1,2,4-triazole, 1,3-dimethyl-1H-1,2,4-triazole and 4-methyl-4H-1,2,4-triazole were not available, their quantitative determination was carried out using external standard calibration obtained for 1-methyl-1H-1,2,4-triazole. The difference in MS sensitivity between these substances is assumed to be minimal due to the close resemblance in structure and physical chemical properties. The relative standard deviation of the method for 1-methyl-1H-1,2,4-triazole concentration in soils was below 28%.

2.8. Analyses of aqueous extracts from soils

To prepare aqueous extracts from soils, soil samples (10 g) were placed into 250 mL conical flasks where 50 mL of distilled water was added. Then flasks were shaken for 30 min, followed by filtrations of samples through paper filters “Yellow Tape” (Russia).

Quantitative determination of FADMH in aqueous extracts from soils was performed using the method based on SPME-GC-MS described in the paper (Kenessov et al., 2011). Determination of NDMA in aqueous extracts was carried out according to the method (Grebel et al., 2006) with some modification described previously (Kenessov, 2009). Sixty five micron polydimethylsiloxane/divinylbenzene fiber coating was applied for SPME of both analytes at 30 °C.

3. Results and discussion

The results of identification of 1,1-DMH transformation products obtained by analyses of soil samples from the 3 fall places included in the present studied are given in Table 2.

It is seen from the obtained data that the main products of 1,1-DMH transformation (pyrazoles, triazoles and nitrosodimethylamine) are detected in all the fall places where discharge of rocket fuel was registered. Formation of other products of transformation

Table 1
Program of SIM MS detection of major transformation products of 1,1-dimethylhydrazine.

Target compounds	Retention time, min	Ions monitored, a.m.u.
Trimethyl amine	0.00–2.00	58
Tetramethyl hydrazine	2.00–2.50	88
Formaldehyde dimethylhydrazone	2.50–8.00	72
Tetramethyl tetrazene	8.00–11.50	116
Dimethylamino acetonitrile	11.50–13.50	83
N-nitrosodimethylamine	13.50–16.00	74
1-Methyl-1H-1,2,4-triazole	16.00–21.50	83
1,3-Dimethyl-1H-1,2,4-triazole; 1-formyl-2,2-dimethylhydrazine	21.50–41.00	59 and 97

Table 2

Products of 1,1-dimethylhydrazine transformation qualitatively identified in soils from fall places examined in 2009 and 2010.

No	RT, min	Compound	2009		2010		
			FP 1	FP2	FP 1	FP 2	FP 3
1	4.491	Acetonitrile	+	+	+	+	+
2	11.692	Dimethylaminoacetonitrile	+	–	+	–	–
3	12.039	1-Methyl-1H-pyrazole	+	+	+	+	+
4	13.587	1,3-Methyl-1H-pyrazole	+	+	+	+	+
5	13.985	N-nitrosodimethylamine	+	+	+	+	+
6	14.323	N,N-dimethylformamide	+	–	+	+	+
7	14.928	1,4-Dimethyl-1H-pyrazole	+	+	+	+	+
8	15.450	Dimethylcyanamide	+	–	–	–	–
9	15.630	5-Amino-1,3-dimethyl-1H-pyrazole	+	+	–	–	–
10	15.934	1,5-Dimethyl-1H-pyrazole	+	+	+	+	+
11	16.455	2-Methyl-2H-tetrazole	–	+	+	+	–
12	16.724	3,4,5-Trimethyl-1H-pyrazole	+	+	+	+	+
13	17.284	1,3,5-Trimethyl-1H-pyrazole	+	+	+	+	–
14	17.425	2,5-Dimethyl-2H-tetrazole	–	–	+	+	+
15	18.373	2-Methyl-1,2,3-oxadiazole	+	–	+	–	+
16	18.797	[1,3,4]-Oxadiazole	–	–	+	+	+
17	18.880	4-Acetyl-3-methyl-1H-pyrazole	+	–	–	–	–
18	19.580	4-Benzylamine	+	–	–	–	–
19	19.602	N-Methyl-N-nitro-methanamine	–	–	–	–	+
20	19.650	4-Acetyl-1,5-dimethyl-1H-pyrazole	+	–	–	–	–
21	19.706	Tetrazoboroline, 5-ethyl-1,4-dimethyl-	+	+	–	+	–
22	20.188	1-Methyl-1H-1,2,4-triazole	+	+	+	+	+
23	20.584	1-Ethyl-1H-1,2,4-triazole	+	–	+	+	+
24	20.773	1,3-Dimethyl-1H-1,2,4-triazole	+	+	+	+	+
25	21.395	2-Methyl-propanenitrile-2,2'-azobis	+	–	–	–	–
26	21.450	1-Formyl-2,2-dimethylhydrazine	+	–	–	–	–
27	21.652	4-Methyl-4H-1,2,4-triazole	+	+	+	+	+
28	23.290	4,5-Dimethyl-4-imidazoline-2-one	–	+	–	+	+
29	23.335	1H-Pyrazole	–	+	+	+	+
30	24.164	1-Methyl-1H-1,2,4-triazole-3-amine	–	+	–	+	+
31	25.357	1-Methyl-2-amino-1H-imidazole	+	–	–	+	–
32	26.528	2,4-Dimethylbenzeneamine	–	–	–	+	–

most likely depends on the characteristics of the fall places (chemical and mechanical composition of soil, moisture content, season, the amount of spilled fuel). Many of the transformation products have further been identified as being more or less readily biodegradable (Carlsen et al., 2008). Thus, with time, many transformation products have degraded and are consequently not detected.

It is worthwhile noting that the same transformation products were identified in the soils at the oldest studied fall places (FP 3, fall in 2003) as were found in other fall places (FP 1, fall in 2008 and FP 2, fall in 2006). Dimethylaminoacetonitrile was detected only in soils of the most recent fall place (FP 1, fall in 2008).

Comparison of the results of qualitative identification of 1,1-DMH transformation products in laboratory and field investigations (Table 3) confirmed most of the results obtained in earlier laboratory experiments (Carlsen et al., 2008; Kenessov et al., 2010; Kenessov, 2009). However, in the course of examination of the fall places, the presence of trimethylamine, acetaldehyde, methyl formate, tetramethylhydrazine, the dimethylhydrazones of formaldehyde and acetaldehyde, and tetramethyltetrazene in soil were not confirmed probably due to their relatively low stability. Previous laboratory experiments have shown that these compounds may be preserved in soils of the fall places for up to 1 month only (Alimzhanova, 2010). High volatility as well as an extended period of time between the discharge of the residual rocket fuel and sampling (2 to 9 years) also affects the presence of these compounds in field samples.

To confirm formation of other products of 1,1-DMH transformation, it is necessary to examine further fall places characterized by different soils, seasons of the falls, the amount of discharged fuel and oxidant etc.

In 2009, analyses of samples by a screening method revealed 170 soil samples contaminated by transformation products of 1,1-dimethylhydrazine (Table 2), which corresponds to 23% of the total number of

Table 3

Comparison of the results of the qualitative identification of 1,1-dimethylhydrazine transformation in laboratory and real samples.

No	Compound	CAS no.
<i>Compounds detected in laboratory and real samples</i>		
1	Acetonitrile ^a	75-05-8
2	Pyrazine	290-37-9
3	Dimethylaminoacetonitrile	926-64-7
4	1-Methyl-1H-pyrazole ^a	930-36-9
5	N-Nitrosodimethylamine ^a	62-75-9
6	1,3-Dimethyl-1H-pyrazole ^a	694-48-4
7	N,N-dimethylformamide	68-12-2
8	1,4-Dimethyl-1H-pyrazole ^a	1072-68-0
9	Dimethylcyanamide	1467-79-4
10	1,5-Dimethyl-1H-pyrazole ^a	694-31-5
11	N,N-Dimethylacetamide	127-19-5
12	1-Methyl-1H-1,2,4-triazole ^a	6086-21-1
13	1,3-Dimethyl-1H-1,2,4-triazole ^a	16778-76-0
14	1-Formyl-2,2-dimethylhydrazine	3298-49-5
15	2-Methyl-2H-tetrazole	16681-78-0
16	3-Methyl-1H-1,2,4-triazole	7170-01-6
17	4-Methyl-4H-1,2,4-triazole ^a	10570-40-8
<i>Compounds detected only in real samples</i>		
18	5-Amino-1,3-dimethyl-1H-pyrazole	3524-32-1
19	3,4,5-Trimethyl-1H-pyrazole	11072-91-9
20	1,3,5-Trimethyl-1H-pyrazole	1072-91-9
21	2,5-Dimethyl-2H-tetrazole	16681-78-0
22	2-Methyl-1,2,3-oxadiazole	3451-51-2
23	[1,3,4]-Oxadiazole	288-99-3
24	4-Acetyl-3-methyl-1H-pyrazole	105224-04-2
25	p-Toluidine	106-49-0
26	N-Methyl-N-nitro-methanamine	4164-28-7
27	4-Acetyl-1,5-dimethyl-1H-pyrazole	21686-05-5
28	Tetrazoboroline, 5-ethyl-1,4-dimethyl-	20534-01-4
29	1-Ethyl-1H-1,2,4-triazole	16778-70-4
30	2-Methyl-propanenitrile-2,2'-azobis	78-67-1
31	N-Ethylidene-1-pyrrolidineamine	60144-27-6
32	4,5-Dimethyl-4-imidazoline-2-one	1072-89-5
33	1H-Pyrazole	288-13-1
34	1-Methyl-1H-1,2,4-triazole-3-amine	49607-51-4
35	1-Methyl-2-amine-1H-imidazole	6646-51-1
<i>Compounds detected only in laboratory samples</i>		
36	Trimethylamine ^b	75-50-3
37	Acetaldehyde ^b	75-07-0
38	Methyl formate ^b	107-31-3
39	Tetramethylhydrazine ^b	6415-12-9
40	Formaldehyde dimethylhydrazone ^b	2035-89-4
41	2-Butanone	78-93-3
42	Acetaldehyde dimethylhydrazone ^b	7422-90-4
43	1,1,4,4-Tetramethyl-2-tetrazene ^b	6130-87-6
44	1-Methyl-1H-imidazole	616-47-7
45	Formamide	75-12-7
46	Benzyl alcohol	100-51-6
47	1H-Imidazole	288-32-4
48	1H-1,2,4-Triazole	288-88-00
49	Dimethyldiazene	503-28-6
50	Ethaneamine, 2,2'-oxibis [N,N-dimethyl-]	3033-62-3
51	Methyldimethylcarbamate	7541-16-4
52	Propiolactam	930-21-2
53	4-Amino-3-pentene-2-one	1118-66-7
54	Methanal-N-methyl-N-formylhydrazone	61748-05-8

^a Compounds detected in soils of all fall places, where the rocket fuel spillages were detected.

^b Unstable or volatile compounds, whose presence in real samples can be determined only in the immediate sampling and analysis after spillage of 1,1-dimethylhydrazine.

collected on-site soil samples. However, quantitative analyses of the detected contaminated samples were not carried out in 2009.

In 2010, analyses of samples by a screening method revealed 152 soil samples contaminated by transformation products of 1,1-dimethylhydrazine that correspond to 30% of the total number of field soil samples collected. In the following we describe the results of the quantitative analyses of the samples in 2010.

Using solvent extraction combined with GC-MS, only triazoles – MTA, 1-ethyl-1*H*-1,2,4-triazole; 1,3-dimethyl-1*H*-1,2,4-triazole and 4-methyl-4*H*-1,2,4-triazole were detected.

Comparison of the results of determination of transformation products by GC-MS using different sample preparations (solvent extraction and SPME) for fall places 1, 2 and 3 showed predictably that the use of SPME as sample preparation method provides much higher sensitivity of determination of volatile products of the 1,1-DMH transformation. The fact that these compounds were not detected when using the method of solvent extraction can be explained by the concentrations of volatile transformation products in soil samples of fall regions being lower than method detection limits or maybe even more obvious that they escape detection as they disappear during the concentration of the methylene chloride extract (*vide supra*).

The only product of transformation with a higher sensitivity of determination found applying the solvent extraction based sample preparation is 1,3-dimethyl-1*H*-1,2,4-triazole, likely due to its low volatility and, therefore, relative low selectivity when applying SPME.

According to the results of quantitative analysis of soil samples from the fall places, maximum concentrations of MTA were 57.3, 44.9 and 13.3 mg kg⁻¹, of 1-ethyl-1*H*-1,2,4-triazole 5.45, 3.66 and 0.66 mg kg⁻¹, and of 1,3-dimethyl-1*H*-1,2,4-triazole 24.0, 17.8 and 4.9 mg kg⁻¹ in fall places 1, 2 and 3, respectively. 4-Methyl-4*H*-1,2,4-triazole was detected only in fall places 2 and 3 where its maximum concentrations were 4.2 and 0.66 mg kg⁻¹, respectively. In 32 of 152 quantitatively analyzed soil samples, corresponding to 21%, transformation products of 1,1-dimethylhydrazine were not detected in agreement with the higher sensitivity of SPME-GC-MS based method.

Studying the aqueous soil extracts revealed that neither FADMH nor NDMA could be detected in these extracts applying SPME-GC-MS. Actually, NDMA was not even detected in aqueous extracts where it was detected after headspace analyses using SPME from contaminated soil. It can be explained by a higher recovery of NDMA from soil compared to water or its poor extraction by water from soil.

As was shown above, MTA is the main product found as a result of the transformations of 1,1-dimethylhydrazine and its concentrations in soils of fall places had the highest values. In the following we use MTA as a marker for studying the distribution pattern of the residual rocket fuel and/or its transformation products.

On the basis of the data obtained from the 2009 and 2010 sampling campaigns, distribution of MTA in fall places 1 and 2 was represented graphically. Due to the fact that the data collected using SPME-GC-MS allowed detection of higher amount of contaminated soils, peak area of MTA collected by SPME-GC-MS was plotted using the interpolation method of Barnes and its realization in 'Gri' (<http://gri.sourceforge.net>) software. The method was chosen because it provided a more exact representation of the pattern of distribution of the pollutants in the place studied.

In fall places 1 and 2, transformation products of 1,1-DMH were only detected in soil samples taken from 10×10 m grid. Therefore, distribution patterns were built only for epicenters of both fall places. Figs. 1 and 2 represent distribution pattern of MTA in fall places 1 and 2.

MTA distribution pattern obtained in 2010 confirmed the results of 2009, however, in 2010, somewhat lower responses of MTA were registered possibly due to further degradation under the effect of natural factors (microbiological processes, oxidation and evaporation).

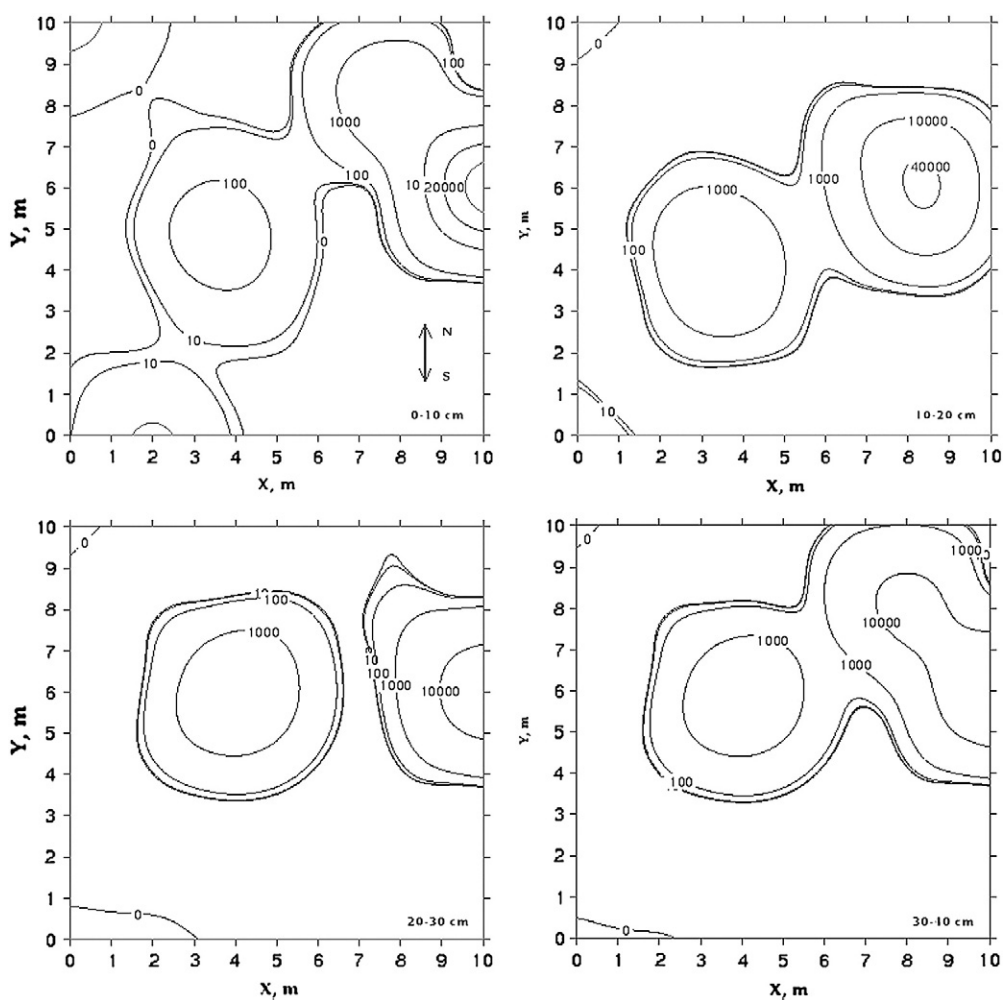


Fig. 1. Distribution of 1-methyl-1*H*-1,2,4-triazole in fall place 1 at different depths (sampling in 2010).

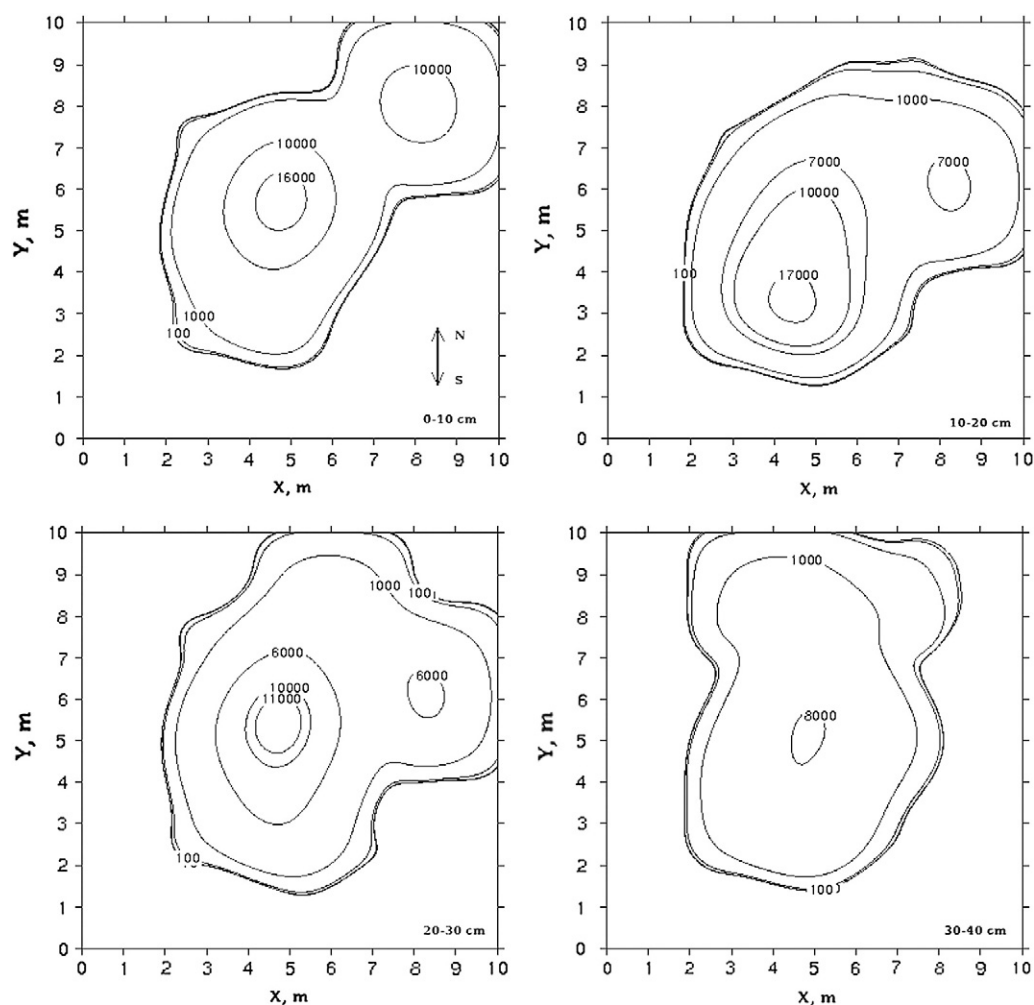


Fig. 2. Distribution of 1-methyl-1H-1,2,4-triazole in fall place 2 at different depths (sampling in 2010).

The more detailed examination of the fall place epicenter with a step of 0.5 m allowed to gain a greater amount of data and to determine the pollution boundary more precisely. Detailed processing of the data of 2009 and 2010 confirmed the fact that pollution of soils in the fall place had a local character. Thus, the spots of discharge can have different sizes ranging between 10 cm and 2 m in diameter.

The first stage of “Proton” rocket has 6 fuel tanks with 1,1-DMH and 6 boosters. After separation of the first stage, the weight of boosters is significantly higher than the weight of nearly empty fuel tanks. Consequently, during landing of the first stage, rocket boosters are first to touch the land forming an 8–10 m crater. As the first stage has 6 boosters, the result may be several large (more than 50 cm) and numerous small spots of fuel at and around the fall place epicenter.

We conclude that the method of systematic grid sampling apparently is efficient for mapping the area of pollution with MTA. Despite high inhomogeneity of the pollution and some inaccuracy of the obtained distribution maps, it can be used for estimation of the area and the level of pollution for evaluation of the environmental damage and thus forming the background for possible remediation activities.

For a more elaborate analysis of the vertical distribution of 1,1-DMH transformation products in the fall place 1, we selected point 18 ($x = 10.0$, $y = 6.0$; cf. Fig. 1) in which the highest peak areas of analytes were registered (Table 4).

As shown in Table 4, responses of all 1,1-DMH transformation products significantly depend on the depth. In samples from the upper soil horizon, concentrations of most products, as a rule, are lowest which is caused by evaporation or aerobic biodegradation,

the intensity of which in the upper soil horizons is maximal. The highest concentrations of the various transformation products in point 18 are found at various depths, which can be explained by variations in mobility and downwards leaching. However, a more detailed analysis

Table 4

Responses of 1,1-dimethylhydrazine transformation products in soil samples taken from different depths (cm) in FP1 (point 18). Maximal concentrations are indicated using bold font.

RT, min	Compound	Peak area, $\times 10^{-6}$			
		0–10	10–20	20–30	30–40
11.692	Dimethylaminoacetonitrile	19	n/d	1	n/d
12.026	1-Methyl-1H-pyrazole	n/d	2	n/d	1
13.606	1,3-Methyl-1H-pyrazole	n/d	1	n/d	1
13.994	N-Nitrosodimethylamine	0.5	0.6	n/d	n/d
14.246	N,N-Dimethylformamide	22	23	9	3
14.915	1,4-Dimethyl-1H-pyrazole	n/d	1	n/d	n/d
15.906	1,5-Dimethyl-1H-pyrazole	n/d	1	n/d	n/d
16.470	2-Methyl-2H-tetrazole	1	2	n/d	2
17.275	1,3,5-Trimehtyl-1H-pyrazole	0.6	1	n/d	n/d
17.456	2,5-Dimethyl-2H-tetrazole	n/d	1	n/d	1
18.355	2-Methyl-1,2,3-oxadiazole	n/d	0.7	n/d	1
18.797	[1,3,4]-Oxadiazole	19	2	1	1
20.175	1-Methyl-1H-1,2,4-triazole	42	104	37	2
20.541	1-Ethyl-1H-1,2,4-triazole	0.3	5	2	83
20.732	1,3-Dimethyl-1H-1,2,4-triazole	7	17	8	5
21.635	4-Methyl-4H-1,2,4-triazole	n/d	3	n/d	13
22.719	N,N-Dimethyl-2-pyrazineamine	n/d	3	n/d	1
23.357	1H-Pyrazole	n/d	5	n/d	0.4

Table 5

Responses of 1,1-dimethylhydrazine transformation products in soil samples taken from different depths (cm) in FP2 (point 14b). Maximal concentrations are indicated using bold font.

RT, min	Compound	Peak area, $\times 10^{-6}$			
		0–10	10–20	20–30	30–40
10.84	1,3-Diazine	0.1	n/d	0.04	n/d
12.03	1-Methyl-1H-pyrazole	1	6	10	26
13.60	1,3-Methyl-1H-pyrazole	1	5	6	13
13.98	N-Nitrosodimethylamine	n/d	n/d	2	5
14.92	1,4-Dimethyl-1H-pyrazole	0.5	1	2	5
15.88	1,5-Dimethyl-1H-pyrazole	0.6	1	2	4
16.45	2-Methyl-2H-tetrazole	0.2	0.6	1	2
16.67	3,4,5-Trimethyl-1H-pyrazole	0.4	1	2	4
17.26	1,3,5-Trimehtyl-1H-pyrazole	0.5	0.4	0.6	0.9
17.42	2,5-Dimethyl-2H-tetrazole	0.2	1	1	3
18.33	2-Methyl-1,2,3-oxadiazole	n/d	n/d	n/d	0.4
18.78	[1,3,4]-Oxadiazole	0.5	0.5	0.7	1
19.08	3-Methyl-pyrolizidine	0.3	0.3	0.6	1
19.70	Tetrazoboroline, 5-ethyl-1,4-dimethyl	n/d	2.8	40.0	227
19.97	4H-Pyran-4-one	0.7	0.6	1	n/d
20.10	1-Methyl-1H-1,2,4-triazole	224	51	100	51
20.50	1-Ethyl-1H-1,2,4-triazole	22	2	6	3
20.70	Dimethyltriazole	70	6	12	3
21.63	4-Methyl-4H-1,2,4-triazole	22	10	20	14
23.08	N-Ethilidene-1-pyrodinamine	4	6	16	36
23.33	1H-Pyrazole	2	1	2	4
24.14	1-Methyl-1H-1,2,4-triazole-3-amine	3	2	3	6
24.40	6-Methyl-4,5-pyrimidine-amine	0.3	0.4	1	1

here would require more detailed knowledge of soil structure, possible fracture etc. Further variations in water solubility may play a significant role.

To study the vertical distribution of 1,1-DMH transformation products in fall place 2, point 14b ($x=5$; $y=5.5$, cf. Fig. 2) was chosen, in which greatest responses of analytes were registered (Table 5).

Analogous to the above discussion for fall place 1 the data given in Table 5 show that the response of all 1,1-DMH transformation products significantly depends on the soil depth. Although the majority of the compounds including the most toxic of them, i.e. NDMA, were measured at their highest concentrations in the lowest soil layer (30 to 40 cm) indicating possibly a somewhat looser structure of the soil in fall place 2 that facilitated faster leaching. It should be noted that the highest concentration found was in the lowest soil layer studied. To date, there is no verification of the true concentration maxima as they may actually be found at greater soil depths.

The vertical distribution of 1,1-DMH transformation products in fall place 3, was studied in detail applying the data from a point internally denoted w3 where the greatest concentrations of analytes were detected. The data as function of depth are presented in Table 6.

It should be noted (Table 6) that the response of all 1,1-DMH transformation products significantly depends on the depth. However, where horizons down to 160 cm have been included in the study, that

in all cases the true maximums are found within the studied profiles, i.e., between 20 and 60 cm depth. Only in a couple of cases we find detectable concentrations below 100 cm depth.

As seen in the above two examples, we found rather low concentrations in the top soil, 0–20 cm, as a result of evaporation possibly combined with a higher microbial activity than found in the deeper layers.

4. Conclusions

Comparison of the results of determination of transformation products by GC-MS using different methods of sample preparation (solvent extraction and SPME) for three different fall places of burned out first stages of heavy rockets launched from the Baikonur Cosmodrome showed that only the use of SPME as sample preparation provides the detection of volatile transformation products of 1,1-DMH. SPME also provides a higher sensitivity for detection of compounds in soils contaminated with rocket fuel residuals. For semi-volatile metabolites, both methods provide comparative sensitivity, however, at considerably higher expenses for applying solvent extraction based sample preparation.

Comparison of the results of identification of 1,1-DMH transformation products in laboratory and field investigations confirmed most of the results obtained in previous laboratory experiments. In addition to our previous studies, we found 18 previously not detected compounds that could be assigned as 1,1-DMH transformation products in the places of rocket fuel discharge.

Examination of fall places confirmed that 1-methyl-1H-1,2,4-triazole was the main product of 1,1-dimethylhydrazine transformation in the places of rocket fuel discharge and the main accumulating component. The obtained patterns of horizontal distribution show the highest concentrations of MTA in the sites of obvious discharge of rocket fuel with their gradual decrease with distance.

The method of systematic grid sampling proved to be efficient for mapping the area of pollution with MTA. Despite the high inhomogeneity of pollution and some inaccuracy of iso-concentration maps, the obtained distribution maps can be used for estimation of the area and the level of pollution, for evaluation of the damage done to the environment and as background information for possible remediation activities.

The results of a detailed study of distribution of 1,1-DMH transformation products along the soil profile showed that transformation products can migrate down to the depth of approx. 120 cm. However, the migration rate appears rather slow. Thus, after 2–3 years following the fall studied, the highest concentrations of 1,1-DMH transformation products are registered, as a rule of thumb, at the depth 20–60 cm, however, this index can vary significantly depending on the type, humidity and physical properties of soil, the features of the relief and other conditions. In the surface layer, again as a rule

Table 6

Responses of 1,1-dimethylhydrazine transformation products in soil samples taken from different depths (cm) in FP2 (point w3). Maximal concentrations are indicated using bold font.

RT, min	Compound	Peak area, $\times 10^{-6}$							
		0–20	20–40	40–60	60–80	80–100	100–120	120–140	140–160
12.03	1-Methyl-1H-pyrazole	n/d	10	14	12	0.4	0.2	n/d	n/d
13.61	1,3-Methyl-1H-pyrazole	1	5	5	42	0.1	n/d	n/d	n/d
14.02	N-Nitrosodimethylamine	n/d	2	3	3	0.4	n/d	n/d	n/d
18.78	[1,3,4]-Oxadiazole	0.07	0.2	0.5	0.2	0.06	n/d	n/d	n/d
19.08	3-Methyl-1H-pyrolizidine	n/d	0.3	0.3	0.3	0.07	n/d	n/d	n/d
20.10	1-Methyl-1H-1,2,4-triazole	2	9	8	4	1	0.1	n/d	n/d
20.50	1-Ethyl-1H-1,2,4-triazole	0.1	0.6	0.9	0.5	n/d	n/d	n/d	n/d
20.70	1,3-Dimethyl-1H-1,2,4-triazole	0.4	1	0.9	0.6	0.1	0.06	n/d	n/d
21.63	4-Methyl-4H-1,2,4-triazole	1	0.2	2	2	0.7	n/d	n/d	n/d
23.09	N-Ethilidene-1-pyrodinamine	0.08	0.7	2	1	0.2	n/d	n/d	n/d
23.33	1H-Pyrazole	0.1	0.7	1	1	0.3	n/d	n/d	n/d
24.16	1-Methyl-1H-1,2,4-triazole-3-amine	0.1	0.5	1	0.9	0.3	0.1	n/d	n/d

of thumb, only semi-volatile products of transformation are registered probably as a result of fast biodegradation in combination with high evaporation rate of the volatile transformation products.

Acknowledgment

The work was performed in the framework of The International Science and Technology Center (ISTC, Moscow, Russia) K-1482 project "Development of effective methods of analysis of environmental objects contaminated with rocket fuel components and creation of a scheme of high-sensitive biosensor module for the presence of mutagens" funded by European Union.

Authors are grateful to Dr. Sergey Nechipurenko and Taiyr Abdulkarimov (both from Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, Almaty, Kazakhstan) for participation in field sampling, Dr. Nurzhan Kurmankulov (Institute of Chemical Sciences, Almaty, Kazakhstan) for the synthesis of 1-methyl-1*H*-1,2,4-triazole used for calibration and Dr. Jacek Koziel (Iowa State University, Ames, IA, USA) for assistance in preparation of the final version of the paper.

Authors are grateful to "Infrakos Ecos" LLC (Almaty, Kazakhstan) for provision data on location and origin of fall places 1 and 2 studied in the present work.

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