

### PCDD/Fs IN EMISSIONS OF DIRT VOLCANO

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#### Introduction

Geochemical processes and volcanic activity are known to be a source of halogenated hydrocarbons such as dichloroethanes, chlorofluorometanes, chlopophorme and others<sup>1, 2</sup>. Volcanic deposits are also supposed to be one of the sources of PCDD/Fs in cores of sediment layers samples formed long before industrialization period<sup>3, 4, 5</sup>. But it should be noted that no studies demonstrating formation of CDD/Fs by volcanoes have been published. Takizawa analyzed PCDD/Fs in dust fall and volcanic ash from the active volcano Sakurajima<sup>6</sup>. The study was not designed to determine whether the PCDD/Fs observed were formed by the volcanoes or were scavenged from the atmosphere by the falling dust and ash.

However, there are "dirt volcanoes" erupting mixture of hot water, clay and gases. Analysis of this freshly erupted material may clarify the question of dioxin formation during volcanic activity. Moreover, clay samples are often found to be PCDD/F contaminated<sup>7</sup>.

This investigation shows results of PCDD/Fs determination in two samples of volcanic deposition from volcanoes of Kuril islands (Russia) and one sample of active dirt volcano from Sakhalin Island.

#### Materials and Methods

Samples have been collected and furnished to the laboratory for analysis by expedition of Institute of Marine Geology and Geophysics RAS in august 2005. The sampling locations are shown at fig. 1.

Sample **S-1** is volcanic ash horizon from depth 1.5 m; approximate age 2000-3000 y.o.; sampled on Shikotan Island.

Sample **S-2** is mixture of sand, volcanic ash and pyroclastic material; was collected in 1 month after eruption from fumarolic field of Mendeleev volcano (Kunashir Island).

Sample **S-3** is freshly erupted mixture of clay and water from dirt volcano Yuzhno-Sakhalinsky located in 20 km towards northwest from Yuzhno-Sakhalinsk; sample material erupted from depth approximately 20 m, its temperature was +11°C.

All samples were air dried at room temperature.

Samples (15-20g) were spiked with a PCDD/Fs <sup>13</sup>C<sub>12</sub>-labeled standard mixture (Wellington Laboratories) and extracted with 150 ml acetone:toluen (10:90 v:v) at 95°C in high-performance solvent extraction system<sup>8</sup>.

Extracts was cleared by acid-basic multilayer, carbon and alumina column as described previously<sup>9</sup>. Each analytical run contained a method blank. All solvents, sorbents and reusable glassware were tested to ensure the absence of contaminants and interference. Analyses were performed on GC-HRMS (Hewlett Packard HP 6890 Plus, Finnigan MAT 95XP) at resolution near 10000; SGE ID-BPX5 (30 m length, 0.22 mm id, 0.25 µm film thickness); splitless mode; oven temperature, 140°C for 1 min, 14°C/min ramp to 240°C, followed by second ramp of 20°C/min to 270°C for 15 min hold; injector temperature, 280°C; constant flow of carrier gas (He), 0.8 ml/min. Congeners identify was confirmed from the ratio of the base peak and a second molecular ion.

#### Results and Discussion

Results of PCDD/Fs measurements in volcanic samples are given in table 1. Its congener profile is showed at fig. 2.

All samples are shown to contain PCDD/Fs. No 2,3,7,8-substituted congeners with less than 7 chlorines were detected. Levels of 1,2,3,4,6,7,8-HpXDD and OCDD are in good correlation with those reported by Takizawa and amount to 0.09-1.02 and 0.7-3.35 pg/g dry weight. Sample **S-2** also showed presence of 1,2,3,4,6,7,8-HpCDF at level 0,29 pg/g dry weight which appeared to be lower than one for volcanic ash measured by Takizawa<sup>6</sup>. In the same time no heptachlorinated furans were found neither in old volcanic depositions (sample **S-1**) nor in sample from dirt volcano **S-3** (tab.1, fig. 2).

## Formation, sources and source inventories

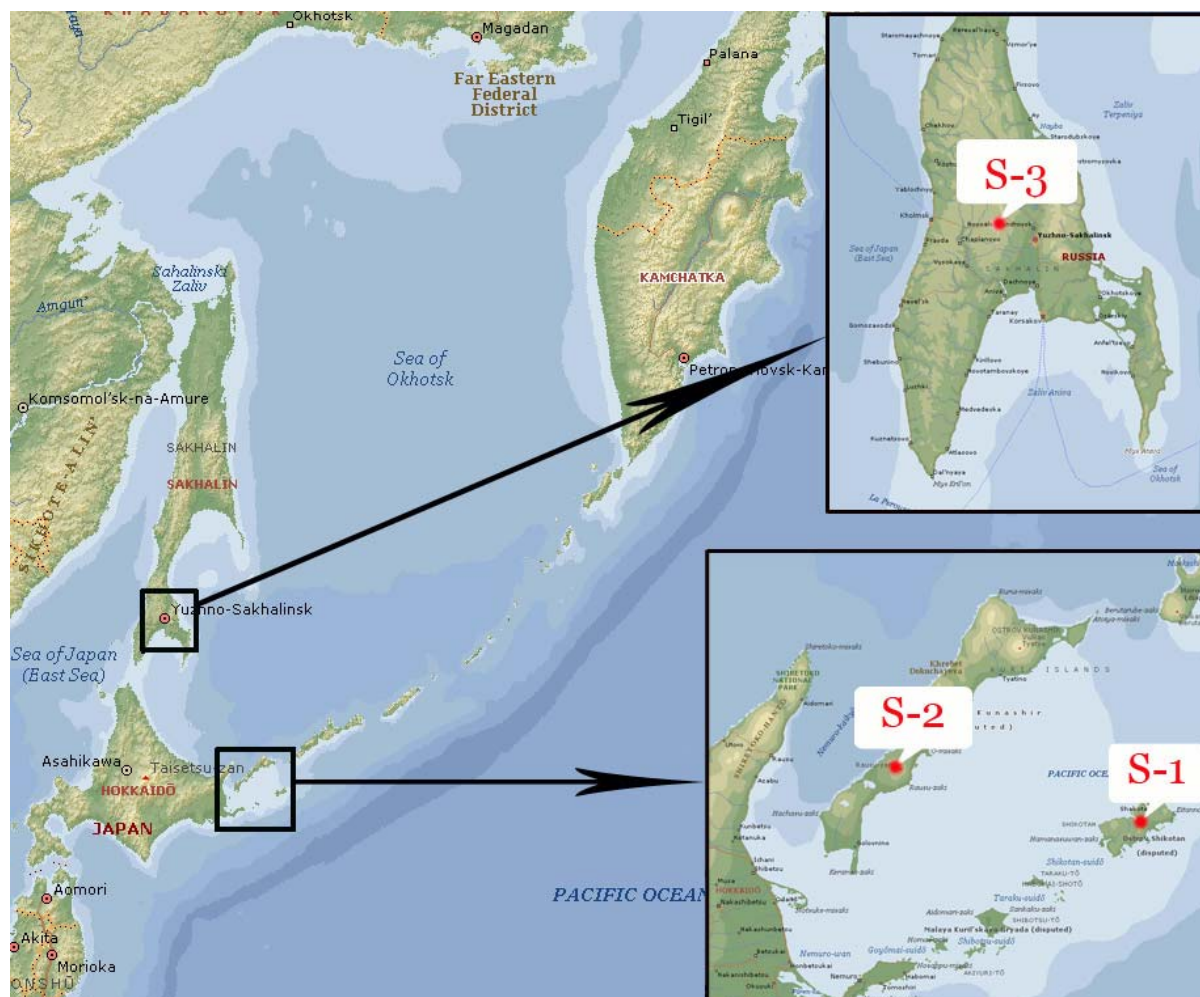


Fig. 1. Samples location map<sup>A</sup>.

The profile difference between **S-1** and **S-2** samples may be caused by several reasons:

- biochemical or washout processes as well as natural destruction of dioxins could change congener profile in 2000-3000 y.o. sample **S-1**;
- sample **S-2** could scavenged some amount of PCDD/Fs from the atmosphere.

In the same time it can be seen that sample **S-3** that didn't have a long contact with atmosphere doesn't contain 1,2,3,4,6,7,8-HpCDF. **S-1** and **S-3** PCDD/Fs congener profiles appeared to be similar. But total levels of 1,2,3,4,6,7,8-HpXDD and OCDD are lower in sample from dirt volcano **S-3**.

Dirt volcanoes are not displaying volcanic activity in usual understanding (there are no active volcanoes on Sakhalin island). Its rather kind of indicators of contemporary tectonic activity. We found trace amount of PCDDs in freshly erupted clay from dirt volcano Yuzhno-Sakhalinsky (tab. 1).

<sup>A</sup> This picture was created by using Microsoft Encarta reference library 2002.

Tab.1. PCDD/F levels in volcanic samples.

	S-1	S-2	S-3
2,3,7,8-TCDD	<0,05	<0,03	<0,02
1,2,3,7,8-PeCDD	<0,08	<0,05	<0,04
1,2,3,4,7,8-HxCDD	<0,12	<0,07	<0,05
1,2,3,6,7,8-HxCDD	<0,12	<0,07	<0,05
1,2,3,7,8,9-HxCDD	<0,12	<0,07	<0,05
1,2,3,4,6,7,8-HpCDD	0,30	1,02	0,09
OCDD	1,97	3,35	0,70
2,3,7,8-TCDF	<0,04	<0,03	<0,02
1,2,3,7,8-PeCDF	<0,07	<0,04	<0,03
2,3,4,7,8-PeCDF	<0,07	<0,04	<0,03
1,2,3,4,7,8-HxCDF	<0,09	<0,06	<0,04
1,2,3,6,7,8-HxCDF	<0,09	<0,06	<0,04
2,3,4,6,7,8-HxCDF	<0,09	<0,06	<0,04
1,2,3,7,8,9-HxCDF	<0,09	<0,06	<0,04
1,2,3,4,6,7,8-HpCDF	<0,14	0,29	<0,06
1,2,3,4,7,8,9-HpCDF	<0,14	<0,08	<0,06
OCDF	<0,46	<0,28	<0,2
<b><i>I-TEQ</i></b>	0,00495	0,01640	0,00164
<b><i>WHO-TEQ</i></b>	0,00317	0,01338	0,00101
Others TCDD	<0,05	<0,03	<0,02
Others PeCDD	<0,08	<0,05	<0,04
Others HxCDD	<0,12	<0,07	<0,05
Other HpCDD	<0,19	<0,11	<0,08
Others TCDF	<0,04	<0,03	<0,02
Others PeCDF	<0,07	<0,04	<0,03
Others HxCDF	<0,09	<0,06	<0,04
Others HpCDF	<0,14	<0,08	<0,06

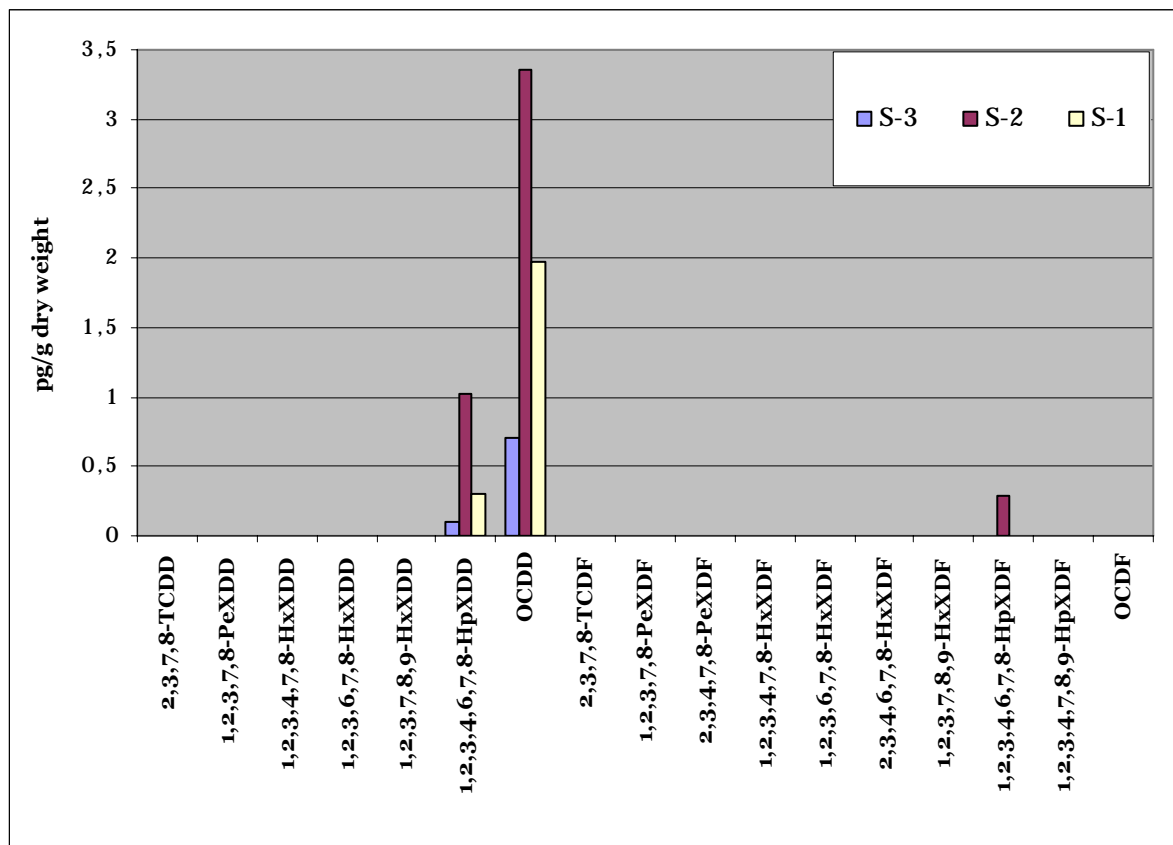


Fig. 2. PCDD/Fs congener profile in volcanic samples.

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