ENVIRONMENTAL DISTRIBUTION OF PCDD/Fs FROM VINYLCHLORIDE MONOMER PRODUCTION: CASE SKÖLDVIK

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Introduction

Synthesis of vinylchloride monomer (VCM) is one of the chemical processes which are known to have produced PCDD/Fs as by-products (1). A chemical plant located on the southern coast of Finland produced VCM in 1973-1981. Wastewater formed in the process was concentrated in two ponds at the site, and the purified water was then led into the Gulf of Finland, a part of the Baltic Sea. The sludge that precipitated from the wastewater was transported to a landfill site, and after the discontinuation of the chemical manufacturing the rest of the sludge, 12,500 tons, was stored in one of the former wastewater ponds, which was 4-5 m deep and isolated with clay. High amounts of PCDD/Fs in the sludge were detected in the 1990's. An extensive survey on the distribution and risks of PCDD/Fs in the area was made, and the environmental levels of PCDD/Fs are reported in this paper.

Materials and Methods

Samples were collected from the sludge disposed at the site and at the landfill, aquifer below the landfill, marine and brook sediments, well waters, soils, mosses, and fish. Surface sediment samples were used to study horizontal distribution of PCDD/Fs, and samples taken with a freeze corer were used to investigate contamination history. Sediment cores were dated using methods which were based on Cs-137 radionuclides and the number of spheroidal carbonaceous particles (SCPs) in sediment material. The brook sediment samples were collected in parallel, from the depth of 0-25 cm. Sampling points with steady sedimentation conditions, i.e., a slow flow rate, were chosen. Water samples were taken from four wells and from the aquifer below the sludge deposit. Sample volumes were 2 litres.

The fish species studied were perch (*Perca fluviatilis*), pike (*Esox lucius*), sculpin (*Cottida gobio*), viviparous blenny (*Zoarces viviparus*), pike perch (*Lucioperca sandra*), flounder (*Pleuronectes flesus*), and Baltic herring (*Clupea harengus membras)*. Fish were caught from the sea areas near the VCM plant, and control fish were caught from a remote area with no known sources of pollution. Fish were analysed in composite samples prepared from several individuals.

Samples from the humus layer on soil surface were taken from sampling areas located at four distances east and south-east from the manufactory. Four subsamples taken from the top 2 cm of soil were combined to obtain homogeneous composite samples. Samples were sieved to a diameter below 2 mm. Mosses (*Pleurozium schreberi*) were collected from the same areas. The newest three shoots were dissected to separate the parts representing years 1991-1993.

Acoustic sediment profiling was used to distinguish the areas where accumulation of depositing material occurred from those of erosion or transportation. The sea bottom was echo-sounded along 23 lines in the archipelago. The following parameters were determined from sediment samples: grain size distribution, water content, and loss of ignition.

PCDD/F analysis including freeze-drying, Soxhlet extraction, several clean-up steps, and sample runs by HRGC/HRMS is described in more detail in reference 2.

Results and Discussion

A summary of the PCDD/F levels detected in various samples is presented in table 1. Two different TEQ consepts are applied: I-TEQs and WHO-TEQs (3,4).

The analysis of a sludge sample confirmed that there were high concentrations, about 26 µg/g d.w, of PCDD/Fs in the production waste of the VCM plant. The concentration was about 40 times higher than what has been detected in waste sludge from chloralkali industry (5). The most dominant congener was octaCDF (19 µg/g dry weight, 73 % of the total PCDD/Fs). Less than one percent of PCDD/Fs were dioxins. The most important congeners in terms of toxicity were 1234678-heptaCDF (40 % of WHO-TEQ) and 123478-hexaCDF (33 %). The same congeners dominated in the emissions from a Russian VCM plant, even though the proportion of octaCDF was not as high as in the sludge (1).

The sample taken from the landfill contained 148 ng/g d.w of PCDD/Fs, and again, almost 99% of them were furans. Differing from the sludge composition, the landfill sample contained more 1234678-heptaCDF than octaCDF (31 % and 20 % of total PCDD/Fs, respectively). PCDD/Fs had leached into the aquifer below the landfill, resulting in a groundwater concentration of 8.4 ng/l and a congener profile similar to that of the sludge. Considering that solubilities of few nanograms per litre have been reported for hepta- and octachlorinated furans at temperatures +20-23°C (6), the detected concentration also seems to be high. However, solubilities may be considerably higher than theoretical values if PCDD/Fs are associated with an apparently dissolved fraction (7), or suitable cosolvents enhance their solubilities (8,9).

The marine sediment core taken close to the site showed an increase in PCDD/F concentrations at the depth of 20 cm. Releases from the VCM production became manifested at the depth of 70-80 cm. Maximum concentrations were as high as 914 ng/g d.w. That was nine times higher than the concentration suggested to define very heavily polluted sediments, and 4500 times higher than background values (10). The I-TEQ was about 3.5 times higher than the Finnish guideline value for contaminated soils.

The data from nine surface samples and the surface concentrations of five sediment cores showed that PCDD/F concentrations rapidly decreased with increasing distance from the site. OctaCDF concentrations reached the background level for total PCDD/Fs (<200 pg/g, ref. 10) within a distance of 3 km north from the site, and within 9 km south from the site. Total PCDD/F concentrations were still around 1500 pg/g at 9-km distance, but the PCDD/F congener profile was considerably different from the sludge profile, possibly indicating pollution from other sources.

In several fish species (perch, pike, sculpin and flounder) PCDD/F toxicities (I-TEQ and WHO-TEQ) were 2-3 times higher than in fish caught from the control area. Elevated concentrations were mainly due to the high amounts of hexa- to octachlorinated furans. Usually, only low levels of octaCDFs are found in fish (11,12).

Elevated PCDD/F levels were detected in soil and mosses. Humus layer has accumulated PCDD/F deposition over a longer period of time, which is shown in levels higher than those detected in mosses.

Table 1. PCDD/F sum concentrations, toxicity equivalents (I-TEQ and WHO-TEQ), and concentrations of octaCDF in environmental samples and the most contaminated fish, flounder (*Pleuronectes flesus*). Concentrations for fish are reported in fresh weight, otherwise in dry weight.

Sample matrix	total concentration, ng/g	conc. of octaCDF ng/g	I-TEQ, ng/g	WHO-TEQ, ng/g
Sludge at the site	26 000	19 000	81.1	64.2
Sludge at the landfill	148	29.9	3.57	3.55
Groundwater, landfill	8.43 ng/l	6.41 ng/l	0.02 ng/l	0.02 ng/l
Brook sediments	0.30-361	0.10-113	0.07-7.90	0.07-7.85
Mosses	2.95-17.1	0.46-3.24	0.05-0.77	0.05-0.77
Soil	20.6-34.9	11.4-19.3	0.44-0.62	0.43-0.59
Marine sediment core, maximum	914	851	1.82	1.07
Fish: flounder	30.4 pg/g f.w	0.57 pg/g f.w	7.79 pg/g f.w	8.94 pg/g f.w

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