SAMPLING AND ANALYSIS OF PCDDs AND PCDFs IN SURFACE WATER AND DRINKING WATER AT 0.001 ppq LEVELS

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ABSTRACT

A series of water samples have been analyzed. They all contained PCDDs and PCDFs at very low levels. The sampling technique and analytical methods allow determination of PCDDs and PCDFs at levels below the US EPA guideline of 0.0013 pg/L.

INTRODUCTION

During recent years a series of reports have established background levels of PCDDs and PCDFs in soil samples, air particulate and total air samples, sewage sludge as well as bottom sediments from lakes, rivers and seas. Limited information is available on the levels of PCDDs and PCDFs in various types of water samples, including drinking water and surface water. The US EPA has set a maximum allowable level for 2,3,7,8-tetraCDD in drinking water as low as 0.13 to 0.0013 pg/L (ppq) based on an estimated human cancer risk of 10^{-5} to 10^{-7} (1). Most water samples analyzed so far have a detection level for above this limit. Mahle et al. recently reported on a method allowing a detection of 1-2 ppq (2).

At DIOXIN '88 in Umeå we described a sampling technique and an analytical method that allows PCDDs and PCDFs to be identified at levels as low as 0.01 - 0.02 ppq (3). In the present paper we will report on the results of some recent studies on various water and sludge samples using a slight modification of this technique. The amount of water sampled by sucking it through the sampling device is increased to up to 1500 L.

EXPERIMENTAL

Samples

At two occasions 200 L respectively 400 L of ingoing sea water and outgoing cooling water were sampled at the Swedeish nuclear power plant Ringhals. This plant uses 1000 to 2000 ton of sodium hypochlorite per year for antifouling the sea water at a concentration of 1-2 ppm.
Three samples of water from River Ljusnan in the middle of Sweden were collected. At a metal production plant, also in the middle of Sweden, 430 L of sea water was collected from a bay of the Bothnian Sea at the mouth of River Ljungan.

At a municipality in S.Sweden 1500 L of drinking water was sampled together with a sludge sample from the same plant. The amount of sludge in this plant was approximately 30 mg/m^3.

Sampling and analysis

The sampling technique using pre-spiked polyurethane foam plugs has been described earlier as well as the clean-up and HRGC/HRMS system (3).
In this study the following spiking program was used:
Eight $^{13}C_{12}$-compounds were added to the polyurethane foam plug prior to the sampling (1.25 ng of each isomer)

$^{13}C_{12}$-2,3,7,8-tetraCDF
$^{13}C_{12}$-2,3,7,8-tetraCDD
$^{13}C_{12}$-2,3,4,7,8-pentaCDF
$^{13}C_{12}$-1,2,3,7,8-pentaCDD
$^{13}C_{12}$-1,2,3,4,7,8-hexaCDF
$^{13}C_{12}$-1,2,3,4,7,8-hexaCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-heptaCDD
$^{13}C_{12}$-octaCDD

RESULTS

The results from the analyses are given in Table 1. The recovery data are not included, but all recoveries were between 58% and 110%.
Most 2,3,7,8-substituted PCDDs and PCDFs could be detected in all samples. The toxic 2,3,7,8-tetraCDD could be found in most water samples. The level of this toxic compound in these water samples was extremely low, between 0.0031 pg/L for a river water 0.0005 pg/L for the drinking water. This is at or below the lower level in the US EPA guideline for this compound (1) and this is the first example where this criteria has been fulfilled. Counted as I-TEQ/89 (International Toxic Equivalents) (4), this drinking water contained 0.0029 pg/L, the largest contribution coming from 2,3,4,7,8-pentaCDF. The sludge sample from this water plant contained 1.4 pg/g corresponding to 0.0047 pg I-TEQ/L. The highest levels were found for hexa-, hepta- and octa CDDs and CDFs, the largest contribution to the I-TEQ in the sludge was found for 2,3,4,7,8-pentaCDF as for the drinking water.
The I-TEQ level for the two samples of seawater used for cooling in the nuclear power plant was slightly higher, 0.0057 pg/L resp. 0.0083 pg/L. The outgoing water treated by sodium hypochlorite had almost the same levels, although some minor differences could be observed. The highest absolute values were found for the hepta- and octa CDDs and CDFs.
The levels found for the water from River Ljusnan and the bay of the Bothnian Sea at the mouth of River Ljungan were almost the same, between 0.0013 pg/L and 0.0017 pg/L counted as I-TEQ/89. The parallell sampling in River Ljusnan gave very good agreement, only small differences could be found between individual congeners.

The pattern found for the congener groups in all samples is quite a typical incineration pattern, with the exception of the mouth of River Ljungan, indicating incineration as the ultimate source of these compounds in water samples. This is fully expected, the incineration pattern has been found in air samples from rural areas (5), in soil samples and in sediment samples representing background contamination as well as in snow samples.

However, in a "background" sediment samples from the Bothnian Siea the PCDD and PCDF pattern is somewhat different. In these samples we can see some influence by the typical "pulp bleaching" pattern (6), stronger the closer to a pulp mill the sediment was sampled. The water sample from the mouth of River Ljungan had also a typical "bleaching" pattern, in agreement with several pulp mills in this area. In the "bleaching" pattern the 2,3,7,8- and 1,2,7,8-tetraCDF and 2,3,7,8-tetraCDD are the dominating congener within respective group of congeners (7).

CONCLUSIONS

In the present study we have used a validated sampling technique and analytical method which allows monitoring of drinking water samples at levels at or below the present US EPA guideline at 0.0013 pg/L of 2,3,7,8-tetraCDD. A sample of drinking water from Sweden was found to be below this guideline. The isomer specific analyses also allow the determination of the contamination level of all toxic PCDDs and PCDFs counted as I-TEQ/89 using the I-TEF system (4) at the pg/m^3 level (0.001 ppq) in water samples.

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Table 1. Levels of PCDDs and PCDFs in water samples (pg/m^3)

	Ringhals I		Ringhals II		River Ljusnan			River	Drinking	Water
	In	Out	In	Out	1	2	3	Ljungan	water	sludge
Sample Volume (m^3)	200	200	400	400	936	929	932	431	1500	(pg/g)
2,3,7,8-TCDF	16	13	7.2	9.1	11	11	11	26	9.6	1.0
Tot. TCDF's	160	74	32	47	110	76	120	75	94	11
2,3,7,8-TCDD	ND(5)	ND(5)	1.9	2.6	1.0	2.1	1.0	3.1	0.5	ND(.4)
Tot. TCDD's	23	20	7.6	5.9	31	17	29	7.9	25	3.8
12348/-12378-PeCDF	3.2	9.7	2.0	2.1	3.6	4.3	7.3	7.9	ND(.3)	ND(.3)
2,3,4,7,8-PeCDF	3.4	6.8	2.5	2.3	5.9	7.6	10	8.5	2.3	0.9
Tot. PeCDF's	58	69	26	29	73	60	100	60	17	8.6
1,2,3,7,8-PeCDD	ND(3)	ND(3)	0.9	0.4	4.1	4.8	3.7	ND(.4)	ND(.5)	ND(.5)
Tot. PeCDD's	23	14	11	10	86	66	77	15	8.2	3.4
123479/-123478-HxCDF	6.8	6.6	2.1	2.5	5.6	5.0	11	9.5	0.7	2.3
1,2,3,6,7,8-HxCDF	2.1	2.0	1.2	1.3	3.8	4.4	8.2	3.1	0.6	0.8
1,2,3,7,8,9-HxCDF	ND(5)	ND(6)	ND(1)	ND(1)	ND(.7)	ND(1)	ND(.7)	ND(.6)	ND(.5)	ND(.5)
2,3,4,6,7,8-HxCDF	ND(4)	ND(4)	1.9	1.2	4.7	6.6	9.1	2.0	ND(.4)	0.9
Tot. HxCDF's	33	36	16	14	56	58	100	74	5.3	13
1,2,3,4,7,8-HxCDD	11	ND(6)	1.1	ND(2)	2.0	2.2	1.8	ND(.6)	ND(0.8)	ND(.8)
1,2,3,6,7,8-HxCDD	4.7	6.7	1.5	2.3	21	20	18	4.6	1.0	1.5
1,2,3,7,8,9-HxCDD	5.4	ND(5)	ND(2)	1.2	11	17	9.3	2.7	ND(.9)	ND(.8)
Tot. HxCDD's	68	36	25	18	150	170	140	47	6.7	8.5
1234678-HpCDF	25	19	10	12	37	23	58	99	0.3	8.4
1234789-HpCDF	ND(7)	ND(7)	ND(2)	ND(2)	0.3	ND(1)	4.0	ND(.9)	ND(1)	0.8
Tot. HpCDF's	28	31	18	20	59	37	90	300	0.3	13
1234678-HpCDD	110	70	30	31	59	62	110	36	4.4	11
Tot. HpCDD's	200	120	59	63	110	120	170	68	7.2	22
OCDF	26	ND(15)	20	18	29	18	44	100	ND(6)	10
OCDD	620	240	185	154	170	150	140	140	17	48
I-TEQ	8.3	7.5	5.7	6.3	13	16	17	14	2.9	1.4