# LEVELS, PATTERNS AND PROFILES OF PCDDs AND PCDFs IN SAMPLES RELATED TO THE PRODUCTION AND USE OF CHLORINE

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## ABSTRACT

Analyses of electrode sludge from the chloralkali process show total levels of PCDFs as high as 300 000 pg/g sludge. The dominating congeners are hepta- and octaCDF, the so called "chlorine cluster". This "chlorine cluster" can also be identified in a solution of ferric chloride and in sludge from the chlorination of drinking water.

## INTRODUCTION

In connection with an extensive program on the formation of PCDDs and PCDFs during pulp bleaching using chlorine gas, it was observed that treatment of tap water or double distilled water with chlorine resulted in the formation of a series of PCDFs, primarily the higher chlorinated congeners (1,2). At the same time very low levels of PCDDs could be found. This specific pattern was named the "chlorine pattern".

During DIOXIN '89 in Toronto it was reported that pulp samples and also effluents from pulp mills not using chlorine bleaching were contaminated by low levels of hepta- and octaCDF, the dominating congeners in the "chlorine pattern". It was suggested that this contamination was the result of the use of other chemicals in the mills (3). At the same time it was also reported that total levels of PCDFs exceeding 200 000 pg/g could be found in a sample originating in a landfill for sludge from carbon electrodes used in chlorine production. It was assumed that the alarming levels of PCDFs were related to the chloralkali process (3).

In the present communication we will report on the analyses of other sludge samples from the same landfill as well as on a sludge sample from the treatment of drinking water with chlorine and a solution of ferric chloride used in a water treatment plant in Sweden.

## EXPERIMENTAL

### Samples

Four samples were collected in a landfill where sludge from the chloralkali process has been dumped. Two samples, completely black and collected at the surface were sludge from the carbon electrodes. Two other samples were collected at different depths in the same landfill. One of these samples was carbon sludge, the other had a green colour and consisted of chromate sludge.

Table 1:

**Results of PCDD/F in Drinking water, Ferric chloride, Electrode sludge and Chromate sludge.**

| Swedish EPA code: | 330S009 | 402S001 | 330S012 | 330S013 | 330S014 | 330S015 |
|---|---|---|---|---|---|---|
| Unit | pg/g * | pg/L * | pg/g * | pg/g * | pg/g * | pg/g * |
| Type | Drinking water sludge | Ferric chloride 12 % | Electrode sludge surface | Electrode sludge surface | Electrode sludge depth | Chromate sludge depth |
| 2,3,7,8-TCDF | 3.2 | 41 | 26000 | 56000 | 57000 | 610 |
| Tot. TCDF's | 12 | 110 | 64000 | 150000 | 140000 | 1700 |
| 2,3,7,8-TCDD | ND(.2) | ND(1.7) | ND(6) | ND(9) | ND(9) | ND(2) |
| Tot. TCDD's | 0.9 | ND | NA | NA | NA | NA |
| 1,2,3,4,8-/ | | | | | | |
| 1,2,3,7,8-PeCDF | 2.2 | 14 | 25000 | 55000 | 56000 | 1200 |
| 2,3,4,7,8-PeCDF | 1.7 | 15 | 12000 | 25000 | 24000 | 570 |
| Tot. PeCDF's | 12 | 37 | 75000 | 240000 | 240000 | 3700 |
| 1,2,3,7,8-PeCDD | ND(.3) | ND(2.7) | ND(7) | ND(9) | ND(9) | ND(3) |
| Tot. PeCDD's | 3.5 | 12 | NA | NA | NA | NA |
| 1,2,3,4,7,9-/ | | | | | | |
| 1,2,3,4,7,8-HxCDF | 2.5 | ND(2.7) | 32000 | 71000 | 73000 | 2700 |
| 1,2,3,6,7,8-HxCDF | 1.2 | 210 | 7000 | 16000 | 15000 | 530 |
| 1,2,3,7,8,9-HxCDF | ND(.3) | ND(1.4) | 1300 | 2800 | 2600 | 81 |
| 2,3,4,6,7,8-HxCDF | 0.8 | ND(1.3) | 870 | 1900 | 2000 | 54 |
| Tot. HxCDF's | 10 | 280 | 68000 | 140000 | 140000 | 5000 |
| 1,2,3,4,7,8-HxCDD | 1.1 | ND(6.4) | ND(18) | ND(26) | ND(29) | ND(8) |
| 1,2,3,6,7,8-HxCDD | ND(.4) | ND(5.8) | ND(12) | ND(16) | ND(19) | ND(5) |
| 1,2,3,7,8,9-HxCDD | ND(.4) | ND(5.8) | ND(16) | ND(22) | ND(25) | ND(7) |
| Tot. HxCDD's | 7.5 | ND | NA | NA | NA | NA |
| 1,2,3,4,6,7,8-HpCDF | 8.4 | 680 | 9100 | 19000 | 19000 | 1100 |
| 1,2,3,4,7,8,9-HpCDF | ND(.4) | ND(2.4) | 8100 | 19000 | 20000 | 960 |
| Tot. HpCDF's | 12 | 1040 | 24000 | 53000 | 54000 | 3100 |
| 1,2,3,4,6,7,8-HpCDD | 7.9 | ND(3.3) | 95 | 210 | 250 | 10 |
| Tot. HpCDD's | 16 | 180 | 220 | 480 | 560 | 20 |
| OCDF | 15 | 250 | 31000 | 76000 | 71000 | 3400 |
| OCDD | 28 | 29 | 920 | 2000 | 2200 | 130 |
| (NTEQ) | 7.0 | 40 | 13000 | 28000 | 28000 | 720 |

* Detection limits in brackets

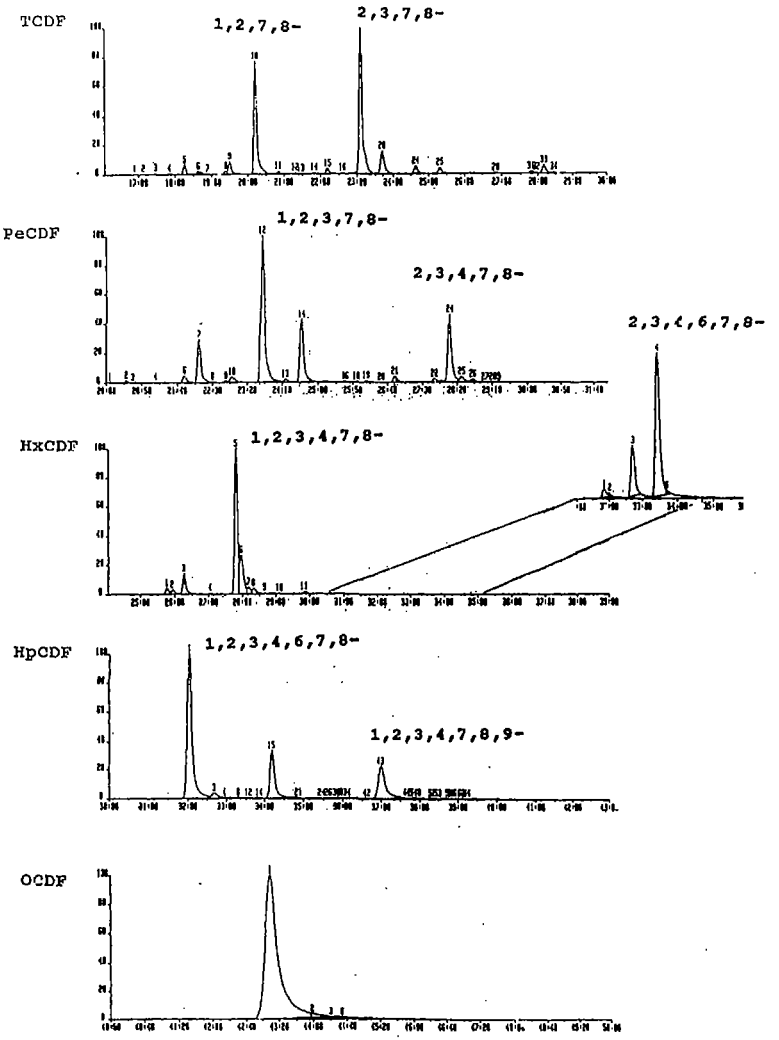


**Figure 1. Patterns of PCDFs in the electrode sludge.**

One sample was a 12% solution of a commercial sample of ferric chloride. The ferric chloride is normally prepared by burning scrap iron in a stream of chlorine gas. This solution of ferric chloride was used in a municipal water treatment plant in E. Sweden.
Another sample was a sludge sample from a municipal drinking water plant in W. Sweden. It was collected after the chlorination step.

Analyses

The extraction and clean-up was performed using methods earlier described (4,5). For the MS-analyses we used a VG 70-250 S instrument operating at 8 000 daltons equipped with a 60 m SP 2330 column.
The samples were collected by the Swedish EPA within the National Dioxin Survey and they were sent coded to the analytical laboratory. The QA/QC program includes the use of a series of $^{13}C$-labelled compounds as well as the re-analyses of known samples and blanks.

## RESULTS AND DISCUSSION

The results in the present study are collected in Table 1.
The analyses of the samples from the chloralkali mill support our earlier observation. The three samples o carbon sludge showed similar levels as in the earlier sample. The congener profiles and isomeric patterns for all samples are almost identical, see Figure 1. The chromate sludge was also very similar, although the levels are approximately 50 times lower.
We have now arrived at the conclusion that sludge from the graphite electrodes used in the chloralkali process is contaminated by PCDFs at levels up to 300 000 pg/g. The levels of PCDDs are usually below the detection limit. The levels for the Nordic Toxic Equivalents (NTEQ) in these samples could be as high as 25-30 000 pg/g sludge.
The solution of commercial ferric chloride used in the municipal water treatment plant was also found to be contaminated by the higher chlorinated PCDFs, typical for the "chlorine pattern", although the levels are quite low. This is in agreement with an earlier report by Heindl and Hutzinger (7).
We also found that the sludge from the chlorination of the municipal drinking water was contaminated by PCDFs, typical for the "chlorine pattern". In addition, hepta- and octaCDD could also be identified. There seems to be a difference between this plant and the laboratory chlorination of water, where no PCDDs could be identified (2). The major constitutents in the municipal sewage sludge are hepta- and octaCDD (3). Counted as NTEQ, the level in this sludge sample is quite low, 2 pg/g sludge.

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