

**Determination of PCDF/PCDD in sludges from drinking water treatment plant.  
Influence of chlorination treatment.**

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### 1. Introduction

Much attention has been drawn to the problem of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) and their environmental effects. Every year thousands of tons of sludge are produced in drinking water treatment plant (DWTP) with presence of these contaminants<sup>1)</sup>. This study was carried out in order to establish the possible influence of chlorine treatment in WWP on the formation of PCDFs/PCDDs. Due to very low levels found in water samples, we based our work in the analysis of coagulation sludges.

Previous analyses performed in two different DWTP (Sant Joan Despí and Cardedeu), supplying drinking water to Barcelona city and its surroundings, demonstrated the presence of all 17 toxic isomers. However, in the first one, the levels found were higher. It is well known that the use of prechlorination induces the formation of trihalomethanes, chlorophenols, halogenated surfactants, etc.<sup>2,3,4)</sup>. For this reason a pilot plant without prechlorination step was installed in Sant Joan Despí.

The municipal DWTP studied (Sant Joan Despí) is located 7 Km from the mouth of Llobregat river and is able to potabilize 32 m<sup>3</sup>/s by employing several treatment processes including: prechlorination, coagulation with aluminium sulfate, settling, ozonization, filtration through granular activated carbon (GAC), and postchlorination. Llobregat river is extremely polluted due to the great concentration of industries and urban centers along its course. It receives the discharges of many different industries including textile, galvanic, pulp mill, salt mines, farms and domestic waste water and, therefore, a wide range of organic pollutants can be found in its water<sup>5)</sup>.

### 2. Sampling

PP installed in the DWTP use the same processes described above, except prechlorination. This PP permitted to test the behaviour of organic contaminants without presence of chlorine. In the same way permitted to evaluate the origin of PCDF/PCDD: raw water or formed during the chlorination treatment.

Subsequently, the sampling program was carried out in 2 different steps of treatment:

- a) suspended matter in raw water
- b) sludge from settling step: real plant and pilot plant.

Samples were collected at the same place in different days in order to compare the results obtained

with the different water qualities. Each sample consisted of 4 L of suspension sludge. All samples were collected in glass bottles, pre-washed with methanol and rinsed with organic free distilled water, and stored in freezer until analysis.

### 3. Experimental

For sludge samples, the wet solid obtained after decantation and centrifugation was first dried and then manually ground until a fine powder was obtained. Prior to analysis the samples were spiked with a range of  $^{13}\text{C}_{12}$ -labelled internal standards. The samples were then Soxhlet extracted for 48 hours with toluene. The sample extracts were transferred to hexane following by acid treatment ( $\text{H}_2\text{SO}_4$ , conc.) and finally cleaned-up. This clean-up was performed using classical methods of adsorption chromatography in open columns. Three types of columns were used: multilayer silica column, florisil and basic alumina.

Samples were analyzed for each of five chlorinated dibenzo-p-dioxin and dibenzofuran congener groups with four to eight chlorines by HRGC/HRMS with a Fisons 8060 GC equipped with a 60 m DB-5 and DB-Dioxin (J&W Scientific) fused silica capillary column (0.25 mm ID, 0.25  $\mu\text{m}$  film) coupled to a VG-AutoSpec Ultima Mass Spectrometer operating in the EI mode at 10.000 resolving power.

### 4. Results

~~A summary of the results obtained by isotope dilution method using relative response factors~~ previously obtained from five calibration standards solutions, are given in table 1. Quantitative analysis was done by spreadsheet 2020.

Results show that the concentration of PCDFs/PCDDs in these sample types are generally very low ( $< 6 \text{ pg I-TEQ/g}$ ), being dioxins predominant. These results are similar to those reported in the literature <sup>6,7,8,9</sup> in sludges. On the other hand, congener concentration increased with chlorination degree.

### 5. References

- 1) F. Pauné, J. Rivera, I. Espadaler and J. Caixach. *J. Chromatogr. A*, (1994) 684:289-296
- 2) F. Ventura and J. Rivera. *Bull. Environ. Contam. Toxicol.*, (1985) 35:73-81
- 3) F. Ventura and J. Rivera. *Bull. Environ. Contam. Toxicol.*, (1986) 36:219-225
- 4) F. Ventura, A. Figueras, J. Caixach, I. Espadaler, J. Romero, J. Guardiola and J. Rivera. *Wat. Res.*, (1988) 22:1211-1217
- 5) J. Rivera, F. Ventura, J. Caixach, M. de Torres, A. Figueres and J. Guardiola. *Intern. J. Environ. Anal. Chem.*, (1987) 29:15-35
- 6) Anthony K.W. Ho and R.E. Clement. *Chemosphere*, (1990) 20:1549-1552
- 7) N.C. Weerasinghe, M.L. Gross and D.J. Lisk. *Chemosphere*, (1985) 14:557-564
- 8) L.L. Lamparski, T.J. Nestruck and U.A. Stenger. *Chemosphere*, (1984) 13:361-365
- 9) M. Horstmann, M.S. McLachlan, M. Reissinger. *Chemosphere*, (1993) 27:113-120

Table 1. PCDFs and PCDDs in DWTPs: St. Joan Despí and Cardedeu.

	St. JOAN DESPI		CARDEDEU	
	Concentration (pg/g)	I-TEQ (pg/g)	Concentration (pg/g)	I-TEQ (pg/g)
2378-TCDD	N.D. (0.028)	-	0.21	0.210
12378-PeCDD	0.89	0.445	0.42	0.210
123478-HxCDD	1.00	0.100	0.55	0.055
123678-HxCDD	7.97	0.797	2.73	0.273
123789-HxCDD	3.30	0.330	1.31	0.131
1234678-HpCDD	121.50	1.215	48.92	0.489
OCDD	1130.60	1.131	290.14	0.290
2378-TCDF	1.17	0.117	1.18	0.118
12378-PeCDF	0.57	0.028	0.25	0.012
23478-PeCDF	0.88	0.440	0.61	0.305
123478-HxCDF	2.50	0.250	1.73	0.173
123678-HxCDF	1.45	0.145	1.73	0.173
234678-HxCDF	2.42	0.242	1.17	0.117
123789-HxCDF	0.30	0.030	0.40	0.040
1234678-HpCDF	23.96	0.240	11.34	0.113
1234789-HpCDF	2.08	0.021	1.39	0.014
OCDF	62.92	0.063	12.85	0.013
Total PCDDs	1852.16	4.018	570.26	1.658
Total PCDFs	214.80	1.576	152.74	1.078
I-TEQ TOTAL		5.594		2.736