# PCDD/F in sewage sludge and its post-treatment products

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## INTRODUCTION

After European Directive 91/271/CEE entered in force, all the cities in the European Union with more than 15,000 people has to treat waste water before disposing it. Therefore, in the last years, increasing amounts of sewage sludge have been generated by wastewater treatment plants (WWTP). For example, in 1998, 800,000 tonnes d.m. of sewage sludge were produced in Spain and the estimation for year 2005 is that 1,500,000 tonnes d.m. will be produced[1]. The final fate of this material is mainly agricultural: ca. 50% of sewage sludge is used as fertilizer, ca. 25% is disposed in controlled landfills and the rest is incinerated or has other minor destinations.

The application of sewage sludge in order to increase the fertility of lands is an interesting application. However, sewage sludge contains pollutants that should be monitored. At present, the sewage sludge dose to be applied to soil is limited by the concentration of heavy metals, but, since 1999, several drafts of a new European Directive[2] have been published and the level of other pollutants (such as polychlorinated dibenzodioxins/dibenzofurans, PCB, phthalates, etc.) are considered.

Nowadays, the most usual way to apply sewage sludge to soils is after a partial dehydration in the WWTP. In addition, other post-treatment processes, such as composting and thermal drying, are receiving increased importance. The advantage of composting sewage sludge with wood is the improvement of the physical and sanitary properties of the material. However, the process can be expensive and time-consuming. Thermal drying consist of sewage sludge dehydration at elevated temperature. The thermal drying plant consumes high amounts of energy, but the final product is easier and cheaper to transport and has better sanitary aspects.

In this work, we have compared the levels of dioxins (PCDD/F) in partially dehydrated sewage sludge and its post-treatment products: thermal dried sewage sludge and compost from two wastewater treatment plants where the sewage sludge was stabilized by anaerobic and aerobic digestion.

## MATERIALS AND METHODS

Sewage sludges (DSS) were collected from two municipal wastewater treatment plants of the Catalan area: Blanes (1) and Banyoles (2) (Catalonia, Spain), with an anaerobic stabilization and aerobic respectively. The water content of the dehydrated sewage sludges were approximately 80%.

Thermal dried sludges (TSS) were obtained by indirect drying of sewage sludge in the thermal drying plant in Banyoles (Catalonia, Spain) at a temperature between 110-120 ºC for 45 min, for ensuring a reduction of water content to less than 15%.

The composted sewage sludge from Blanes was obtained in the same WWTP and the other from Banyoles in the laboratory, where the process in the plant was reproduced under very controlled conditions.

The compost from Blanes (CSS1) was obtained by mixing sewage sludge and pine wood chips in a rate 1:4,5 by weight. Thermophilic aerobic stabilization was performed at a temperature of 55 ºC with a retention period of 15 days. The composting process lasted for 3 months and the water content of the final product was approximately 35 %.

To generate the compost from Banyoles (CSS2) at laboratory-scale, sewage sludge was mixed with pine wood chips from Blanes (1:4) forming a pile. The temperature and moisture were monitored in the compost pile in order to maintain optimal condition for microbial activity. Pile was mechanically turned every week to promote aerobic organic matter decomposition. Moisture level was maintained constant at 50-60% (w/w) by addition of the proper amount of water. The composting process was ended after 2 months and the water content of the final product was approximately 55 %.

The PCDD/F analysis methodology was based on previously published methods[3,4] with some modifications. Samples of sludge were dried at 50 ºC and grounded and sieved before extraction. Approximately 6 g dry weight of sludge samples were spiked with $^{13}C$-labeled solution of 2,3,7,8-PCDD/F and extracted in Soxhlet apparatus for 24 hours with toluene. Extracts were concentrated and subjected to clean-up in a multi-layer silica column, Florisil column and SPE carbon tubes. Purified extracts were analyzed by HRGC-HRMS at 10,000 resolving power in two different polarity 60 m chromatographic columns (RTX-5 and DB-Dioxin). Monitored masses were those proposed by EPA 1613 method[5].

## RESULTS AND DISCUSSION

Table 1 provides PCDD/F results of the sludge samples analysed. In all samples, the concentrations of PCDD were higher than those of PCDF. The homologues profile was very similar in all samples. It was dominated by OCDD and OCDF, and contained relatively high concentrations of HpCDD and HpCDF, which is the trend reported by other researchers for sewage sludges[6,7]. The homologues profiles are showed in the figure 1.

The concentration of PCDD/F in sludges from WWTP with aerobic digestion was slightly higher than those with anaerobic digestion. The congener profile of sewage sludge with digestion aerobic was the same as the one with anaerobic digestion. It was dominated by proportionally high amounts of HpCDD and OCDD homologues. The most important contribuitors to I-TEQ concentration were 1,2,3,4,6,7,8-HpCDD, OCDD and 1,2,3,7,8-PeCDD.

The concentration of I-TEQ for sewage sludges were low in both cases (7,68 pg ITEQ/g d.w. and 15,6 pg ITEQ/g d.w.) and far from the future limit value set at 100 pg TEQ/g d.w. for agricultural purposes.

### Composting process

Although the increase was small, PCDD/F concentration in the compost of the two WWTP was higher with respect to its sewage sludge. Some authors explains this fact by the formation of dioxins in compost from chlorophenols[8]. The congener profile of the compost and its corresponding sewage sludge was very similar. In the case of samples from Banyoles the most important contributors to ITEQ were 1,2,3,4,6,7,8-HpCDD and OCDD. In the case of samples from Blanes, the most important contributor in sewage sludge was 1,2,3,7,8-PeCDD and in the compost were 1,2,3,4,6,7,8-HpCDD and OCDD.

### Thermal drying process

PCDD/F concentration in the thermal dried sewage sludge from WWTP with aerobic digestion (TSS2) was very similar to its corresponding initial material. Therefore, it seem to indicate that the sewage sludge treatment at 110-120 ºC for 45 minutes does not produce dioxins in the final dried material. The most important contributors to ITEQ in both samples were 1,2,3,4,6,7,8-HpCDD and OCDD.

In the case of thermal dried sewage sludge from WWTP with anaerobic digestion (TSS1), PCDD/F concentration was slightly higher than its corresponding sewage sludge. This can be attributed to the variability due to the origin of the samples more than to an actual increase due to the process. The congener profile was very similar in both samples and the most important contributor to ITEQ was 1,2,3,7,8-PeCDD.

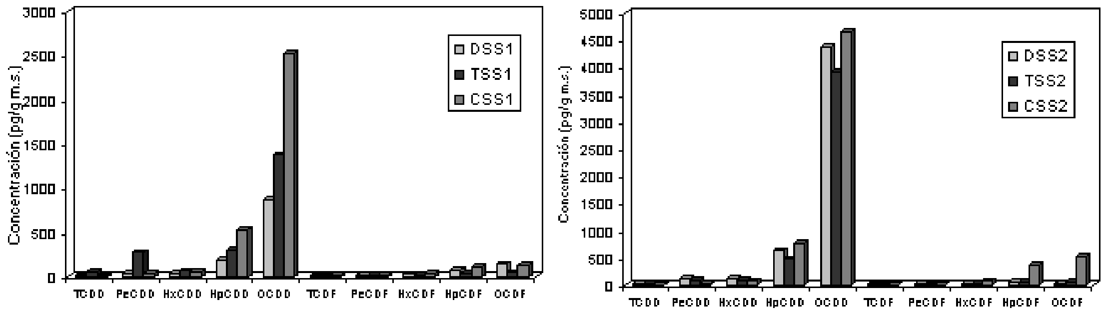


Figure 1: Homologues profiles comparing the sewage sludge with its post-treatment products from two WWTP.

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Table 1: Concentration of PCDD/F (expressed in pg/g dry weight) in sewage sludge and its post-treatment products from two WWTP.

| **PCDD/F** | **DSS1** | **TSS1** | **CSS1** | **DSS2** | **TSS2** | **CSS2** |
|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 0,39 | 0,43 | 0,40 | 0,59 | 0,57 | 0,34 |
| 1,2,3,7,8-PeCDD | 3,58 | 9,32 | 3,43 | 3,76 | 3,52 | 2,08 |
| 1,2,3,4,7,8-HxCDD | 0,86 | 1,38 | 1,77 | 3,12 | 2,62 | 3,12 |
| 1,2,3,6,7,8-HxCDD | 5,81 | 16,0 | 9,22 | 13,0 | 12,1 | 13,3 |
| 1,2,3,7,8,9-HxCDD | 2,13 | 7,63 | 4,34 | 9,43 | 8,81 | 6,21 |
| 1,2,3,4,6,7,8-HpCDD | 103,49 | 173 | 314 | 327 | 245 | 419 |
| OCDD | 875,73 | 1376 | 2522 | 4380 | 3910 | 4648 |
| 2,3,7,8-TCDF | 2,36 | 3,95 | 3,10 | 2,66 | 2,44 | 1,19 |
| 1,2,3,7,8-PeCDF | 1,56 | 2,30 | 1,58 | 1,36 | 1,23 | 0,98 |
| 2,3,4,7,8-PeCDF | 2,06 | 2,14 | 1,94 | 2,01 | 1,84 | 1,24 |
| 1,2,3,4,7,8-HxCDF | 2,22 | 2,59 | 3,27 | 2,56 | 2,42 | 4,27 |
| 1,2,3,6,7,8-HxCDF | 2,10 | 1,83 | 2,51 | 2,56 | 2,41 | 3,04 |
| 2,3,4,6,7,8-HxCDF | 2,47 | 1,93 | 3,43 | 5,56 | 3,69 | 3,16 |
| 1,2,3,7,8,9-HxCDF | 0,21 | <0,13 | <0,19 | <0,13 | <0,11 | <0,51 |
| 1,2,3,4,6,7,8-HpCDF | 49,9 | 27,1 | 59,4 | 47,7 | 46,9 | 107,9 |
| 1,2,3,4,7,8,9-HpCDF | 1,57 | 1,17 | 2,66 | 1,14 | 1,31 | 7,73 |
| OCDF | 149,5 | 56,7 | 141,5 | 37,9 | 60,8 | 526 |
| Total 2,3,7,8 | 1206 | 1683 | 3074 | 4840 | 4306 | 5748 |
| I-TEQ PCDD | 4,98 | 10,7 | 9,31 | 12,7 | 11,0 | 12,5 |
| I-TEQ PCDF | 2,71 | 2,55 | 3,04 | 2,93 | 2,62 | 3,52 |
| I-TEQ PCDD/F | 7,68 | 13,2 | 12,4 | 15,6 | 13,6 | 16,0 |

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