# Study of evolution of PCDD/F in sewage sludge-amended soils for land restauration purposes.

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## INTRODUCTION

The increasing amounts of sewage sludge produced by waste water treatment plants (WWTP) in our country and the restrictions in the final fate of them (e.g., the banning of sewage sludge discharges into the sea from 1998) have produced an increase in the search of new possibilities to use these kind of material. On the other hand, the extractive activities, like quarries, that produce big extensions of land without vegetation, constitute an environmental problem that should be solved. The application of sewage sludge-amended soils in order to increase the fertility of these lands can be a solution for this problem and also an interesting fate to sewage sludge (1). However, sewage sludges could contain pollutants whose evolution in the amended soils should be monitorised, mainly considering the high amounts of sludge used compaired to those for agricultural purposes. Our research group has already carried out studies about the fate of hydrocarbons, PCB and PAH (2). This work faces on PCDD/F in sewage sludge-amended soils in two experiments, one in the laboratory, under controlled conditions, and one in a quarry near Girona (Spain).

## EXPERIMENTAL

*Experiment design:*

*1) Laboratory experiment:*

Anaerobically estabilised sewage sludge was obtained from DARGISA, a sewage aerobic treatment plant in Girona (Spain). The sludge was air-dried and ground to less than 0.4 mm before soil addition. The sludge was mixed with a limy soil (previously ground and sieved to less than 2 mm) and 12 kg of mixtures were placed in polyethylene lysimeters. The experience consisted of studying the evolution of PCDD/F in a control soil (0% of sludge) and two soils with different additions of sewage sludge (7.5% and 15 %). Lysimeters were watered when necessary to maintain a 20% of moisture in order to assure half the water holding capacity, appropriate to have best microbiological activity. Soils were sampled at the beginning of the experiment and after 1 year. Homogeneous samples were guaranteed by sampling and mixing through all the container depth. The samples were stored in the dark at in the freezer.

*2) Land experiment:*

The experience was carried out in a quarry from RUBAU S.A. in Girona (Spain), near the WWTP of the city. Five plots were arranged on the quarry: one was used as control and, in the other four, the soil was mixed with different amounts of sewage sludge. The doses of sewage sludge added were the same as explained above (7.5% and 15%), but on these experiment two different applications were studied for each amount: (a) *direct application*, where the sludge was directly applied on the soil and then it was plowed to mix it and (b) *previous mix*, where the sludge and the soil were mixed previously to the application on the quarry. Each plot was 20 m long, 6 m wide and 40 cm deep. Soils were sampled at the beginning of the experiment and after 4 years.

*Reagents and Materials*

Hexane and dichloromethane (Pestipur) were obtained from SDS (Peypin, France) and toluene (glass distilled grade) was supplied by Rathburn (Walkerburn, Scotland). Sodium sulphate (GR) and silica were from Merck (Darmstadt, Germany), sulphuric acid (GR) from Scharlau (Barcelona, Spain), silver nitrate and sodium hydroxide from Panreac (Barcelona, Spain) and Florisil from Supelco (Bellefonte, PA, USA).

*Analysis of sewage slduge and sewage sludge-amended soils.*

The samples were freeze-dried, ground and sieved (2 mm) before extraction. Six grams of sludge or soil, spiked with a mixture of $^{13}C_{12}$ labeled 2378-PCDD/F, were Soxhlet extracted with toluene for 24 h. Then, extracts were transferred to hexane and cleaned-up with concentrated sulphuric acid. This step was followed by a purification in a multilayer silica column (from bottom to top: glass wool, silver nitrate-silica, silica, sodium hydroxide-silica, silica, sulphuric acid-silica, silica, sodium sulphate) eluted with hexane and a purification in a Florisil column eluted with hexane and dichloromethane/hexane (95:5) (PCB elution) and dichloromethane (PCDD/F analysis). Purified extracts were concentrated under nitrogen stream until 15 μl and the injection standards ($^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD) were added. Finally, the samples were analysed with HRGC-HRMS in a CE 8000 gas chromatograph coupled to an AutoSpec-Ultima (Micromass, Manchester, UK) mass spectrometer, operating in EI ionization (32 eV) at 10,000 resolving power. The samples were analysed in a DB-5 capillary column (60 m x 0.25 mm, 0.25 μm) and in a DB-DIOXIN in order to separate those 2,3,7,8-congeners that were not resolved in DB-5 column. Monitorised masses were those proposed by EPA 1613 method (3).

*QA/QC*

The whole analytical procedure was validated before the analysis of samples. Accuracy, precision (repeatability and reproducibility) and limit of detection were studied using a sewage sludge sample.

## RESULTS AND DISCUSSION

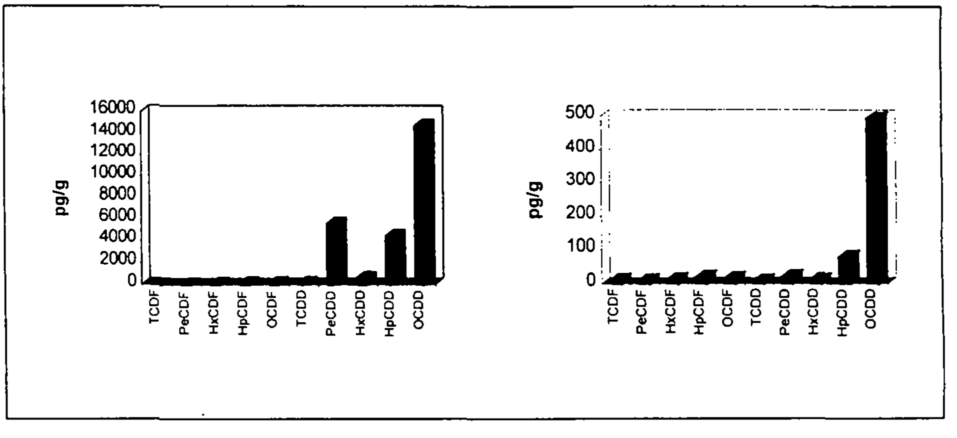
The validation of the analytical method yielded the results shown in Table 1. Values are referred to the sum of concentration of the 17 toxic congeners (values in cursive have been calculated as I-TEQ).

**Table 1.**

| Parameter | |
|---|---|
| Concentration (ng/g) | 5.5 *(0.022)* ng/g |
| Accuracy (Recovery, %) | 107 *(94)* |
| Repeatability (RSD, %) | 5.8 *(2.3)* |
| Reproducibility (RSD, %) | 1.8 *(9.0)* |
| Limit of detection | 0.013 *(0.001)* ng/g |

The PCDD/F contents of the sewage sludge used in the experiment was 68.2 pg TEQ/g (d.w.). Concentrations of PCDD (especially hepta- and octa- congeners) were higher than PCDF (Figure 1a), which is the trend reported by other authors for most sewage sludges (4, 5). The profile of sewage sludge-amended soils was similar to that of the sludge as it is shown in Figure 1b.

**Figure 1a. Sewage sludge** **Figure 1b. Sewage sludge-amended soil**




The concentrations of PCDD/F (pg TEQ/g sample d.w.) obtained in the samples of lab and land experiment are summarised in Table 2.

**Table 2.**

| | | Lab experiment | | Quarry experiment | | | |
|---|---|---|---|---|---|---|---|
| **Time (yr)** | | 0 | 1 | 0 | | 4 | |
| **Application** | | | | Direct appl. | Previous mix | Direct appl. | Previous mix |
| **Amount (%)** | 0 | 0.4 | 0.62 | 1.12 | | 0.84 | |
| | 7.5 | 2.56 | 2.38 | 1.52 | 3.14 | 12.15 | 7.68 |
| | 15 | 5.29 | 5.6 | 5.26 | 2.56 | 8.50 | 4.26 |
| **Sewage sludge** | | 68.2 | | | | | |

In the lab experiment, the PCDD/F value of amended soils is directly related to the sewage sludge dose applied. After one year, no evolution is observed in any sample: the levels remain constant in all of them.

We can conclude that PCDD/F concentrations in the control soils from the quarry experience are lower than in the amended soils. About the different kinds of application and the evolution of the amended soils, it is not possible to establish a trend due to the dispersion in the results, clearly higher than the reproducibility variation of the analysis method. It may be due to the lack of homogeneity in the plots when high amounts of soils and sewage sludge are used.

The conclusions from the two studies are that sewage sludge application increases PCDD/F concentration in soils and that these compounds are persistent in the soils after long periods of time. However, it is important to examine carefully land experiments, where the control of all the conditions is difficult and therefore the results can show higher dispersion.

## ACKNOWLEDGEMENTS

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