COMPARISON OF PCDD/F LEVELS IN SEWAGE SLUDGE BEFORE AND AFTER COMPOSTING AND THERMAL DRYING PROCESSES.

E. Rullán, M.J. Montaña, R. Martí, F. Broto, L. Comellas, M.C. Rodríguez-Larena, J. Díaz-Ferrero

Institut Químic de Sarrià, Via Augusta 390, 08017 Barcelona, Spain (jdiaz@iqs.edu)

INTRODUCTION

After European Directive 91/271/CEE entered in force, all the cities in the European Union (E.U.) 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 levels 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 consists 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 (DSS) and its two follow-up products: compost (CSS) and thermal dried sewage sludge (TSS).

MATERIALS AND METHODS

Dehydrated sewage sludge (DSS): This material was obtained from the WWTP in Blanes (Catalonia, Spain), where a biological process is used. First, the sludge from the water line was treated in an aerobic process and, afterthat, it was digested in an anaerobic environment at 35.5 ºC for 25 days. Then, the sludge was dehydrated by centrifugation. The final material had ca. 80 % of water.

Composted sewage sludge (CSS): Compost was produced in two experiments: one in the same WWTP, in Blanes, (CSSa) and the other in the laboratory of the Institute (CSSb), where the process in the plant was reproduced under very controlled conditions. To generate the compost, dehydrated sewage sludge was mixed with pine wood chips (1:4.5) and introduced in forced-aired tunnels. The mix was left for 15 days (decomposition phase) and temperature increased to 58-60 ºC. In the next phase, most of wood chips were removed from the mixture and recovered to be used in other composting processes. The remaining material was piled and kept there for 3 months (stabilization phase). During this phase, anaerobic conditions were avoided by airing the material. Temperature increased due to the evolution of different compounds in the sewage sludge. When the biological processes finished, temperature decreased to room temperature (end of the process).

Thermal dried sewage sludge (TSS): This material was produced in a thermal drying plant in Banyoles (Catalonia, Spain) using dehydrated sewage sludge from Blanes WWTP as raw material. In this plant, thermal drying is carried out in a hot-wall rotary cylinder (110-120 ºC), where water is removed by evaporation, for 45 min. At the end of the cylinder, the material obtained has low amount of water (ca. 15 %).

PCDD/F analysis: The analysis methodology was based on previously published methods[3,4] with some modifications. Mainly, the method consisted of the following steps:

- Freeze-drying (for those samples with high amount of water), grinding and sieving.
- Spiking with $^{13}C_{12}$ labeled 2,3,7,8-PCDD/F.
- Extraction with toluene for 24 h in a Soxhlet equipment.
- Clean-up in a multi-layer silica column, Florisil column and SPE carbon tubes.
- Instrumental analysis 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

Composting process - Laboratory experiment

Four samples were analyzed: the initial dehydrated sewage sludge produced in the WWTP in Blanes (DSS1), the wood chips before the composting process (W1), the wood chips removed from the material after the composting process (W2) and the compost (CSSb) produced in the lab. Wood chips used for the process came from the composting plant in Blanes and had been already used for other composting processes (as it is usual in the plant). Table 1 summarized the results obtained.

Table 1.

Material	PCDD/F concentration (pg I-TEQ/g d.m.)
DSS1	8.05
CSSb	21.1
W1	22.9
W2	14.4

If levels of PCDD/F in dehydrated sludge and the corresponding compost are compared, an increase can be observed, whereas the concentration in wood decreases. Some possibilities could explain this fact. Some authors[6] reported the formation of dioxins in compost from chlorophenols. A transfer from the wood to the sewage sludge could be also occurring during the process. However, it is difficult to establish clearly the origin of dioxins in that wood.

The congener profile was very similar in all the samples. It was characterized by proportionally high amounts of HpCDD and OCDD homologues. The most important contributors to ITEQ concentration were 1,2,3,4,6,7,8-HpCDD, OCDD and 1,2,3,7,8-PeCDD. The profile of contribution to I-TEQ seems to confirm the transfer of dioxins from wood to sewage sludge mentioned above.

Composting process - Composting plant experiment

In this experiment, the initial materials for the process (dehydrated sewage sludge and wood chips) were the same as in the laboratory experiment. The composts produced in the plant were analyzed at three different times: just after the decomposition phase (15 days in the tunnel) (CSSa1), after 1.5 month in the pile (CSSa2) and the end of the process (after 3 months in the pile) (CSSa3).
The results are shown in Figure 2.

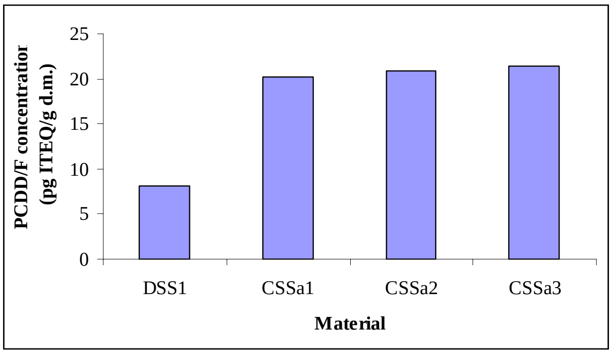

Figure 2.

PCDD/F concentration in the compost produced in the plant (21.4 pg ITEQ/g d.m.) was similar to that produced in the laboratory experiment (21.1 pg ITEQ/g). Graphic in Figure 2. shows that the concentration of PCDD/F in compost just after leaving the tunnel and after the biological stabilization process is the same. That seems to indicate that no biological formation of PCDD/F occurs during the stabilization period.

Thermal drying process
Two samples were analyzed in this experiment: a dehydrated sewage sludge sample (DSS2) from the WWTP in Blanes and the corresponding material after a thermal drying process carried out at 110-120 ºC in Banyoles plant (TSS). The results were very similar (13.1 pg I-TEQ/g d.m., for the DSS2, and 15.6 pg I-TEQ/g d.m., for TSS). Therefore, they seem to indicate that the sewage sludge treatment at 110-120ºC for 45 min does not produce dioxins in the final dried material. The profiles in both samples were also similar. Homologue profile was characterized by higher concentrations of dioxins and, specially, of the most chlorinated homologues. The most important contributor to I-TEQ in DSS and TSS was, in both samples, 1,23,7,8-PeCDD. No significant change in the profile was observed in the samples before and after the treatment.

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