PCDD/F determination in sewage sludge composting. Influence of aeration and the presence of PCP

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ABSTRACT

Composting of sewage sludge is a common practice for sludge disposal. Some previous studies found high levels of polychorodibenzo-p-dioxins and polychorodibenzofurans (PCDD/Fs) after composting, especially octachlorodibenzo-p-dioxin (OCDD) but also 1234678-heptachlorodibenzo-p-dioxin (1234678-HpCDD) to a lesser extent. In this work, the concentrations of OCDD, 1234678-HpCDD and the rest of the 17 toxic congeners of PCDD/Fs were determined in compost obtained under different conditions. Although the toxicity of the two compounds mentioned above is small, their generation may reach undesirable levels. The PCDD/F content was analyzed in a composting plant and in a laboratory test. In both cases, the composted material was a mixture of sewage sludge, straw and sawdust. The composting plant was a tunnel with air turbine aeration and with a turner to homogenize and move the mixture upwards. The laboratory tests were carried out with Dewar vessels (with air dispersion at the bottom and controlled temperature) and with small vessels inside a controlled oven with non-forced aeration. The laboratory runs were also carried out with the addition of pentachlorophenol in some runs, as a dioxin precursor. The highest OCDD levels were found in three samples of the composting plant (30000–90000 pg/g dry matter or dm), with toxicity values surpassing the limit level for soil amendment (17 pg I-TEQ/g dm). Their formation was analyzed considering their concentration vs. that of octachorodibenzofuran (OCDF), which is not formed during composting. In the laboratory, in experiments carried out in a vessel with non-forced aeration conditions and with the addition of pentachlorophenol, the formation of OCDD was significant (e.g. from 80 to 1500 pg/g dm). That means that these two factors, non-forced aeration and the presence of pentachlorophenol, can cause the OCDD formation.

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1. Introduction

Composting is a well-extended practice of waste reduction that consists of a microbial conversion of material in the presence of suitable amounts of air and moisture into a stabilized product, compost, with the general appearance and other characteristics of a fertile soil (Wilson et al., 1980). Composting of sewage sludge for its application to land as a soil amendment is an accepted treatment for this waste (Peltre et al., 2015).

According to the composting definition, the biodegradable organic compounds during the process should be reduced or eliminated. However, an increase in the dioxin and furan content in the final compost from sewage sludge with wood chips was previously detected, in spite of the low levels in the initial sludge (Hamann et al., 1997). The main contribution to the toxicity was due to the congeners 1234678-heptachlorodibenzo-p-dioxin (1234678-HpCDD) and octachlorodibenzo-p-dioxin (OCDD).

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), also known as PCDD/Fs, are mainly introduced into the biosphere as a by-product of the chemical manufacturing industry and as a result of the combustion processes as published in the European dioxin inventories (Quass et al., 1999). Manufacture of chlorophenols (Field and Sierra-Alvarez, 2008), pulp chlorination (Dimmel et al., 1993), incineration of wastes (Tuppurainen et al., 2003), iron ore sintering (Zhang and Bukens, 2016) and non-ferrous metals smelters and sintering plants (Pitea et al., 2008) are sources which have been previously studied.

The anthropogenic activity is considered the primary route but it is not the only one. The enzymatic formation from dioxin precursors is suspected to be another route and has been previously detected during sewage sludge treatment (Disse et al., 1995; Öberg et al., 1993) and also dosed with pentachlorophenol (PCP) (Klimm et al., 1998).

It is known that there are oxidative enzymes, present in sewage sludge, such as peroxidases that can catalyze the transformation of some dioxin precursors such as chlorophenols into PCDD/Fs by an enzymatic reaction (Öberg et al., 1990; Öberg and Rappe, 1992; Svenson et al., 1989; Muñoz et al., 2014).

Some authors found concentrations of PCDD/Fs around 56 ng I-TEQ/kg, where I-TEQ is the widely used International Toxic Equivalency (Van den Berg et al., 2006), during the composting process of the following types of waste: mixed municipal solid waste with dewatered sewage sludge; yard waste; and municipal solid waste without other additions (Malloy et al., 1993). Lahl et al. (1991) reported values of 0.8–35.7 ng I-TEQ/kg in different types of compost (from a municipal treatment plant) where HpCDDs and OCDD were the

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dominant congeners. The authors attribute the high levels to a potential formation of PCDD/Fs from PCP and to PCP containing PCDD/F by-products. On the one hand, the idea of the probable formation is supported by Wittsiepe et al. (2000), who found PCDD/F formation through the in vitro reaction of chlorophenols with myeloperoxidase enzyme. On the other hand, PCP usually contains dioxin impurities in its formulation, mainly OCDD (Holt et al., 2008; Masunaga et al., 2001).

The chlorophenols involved in the PCDD/F formation during composting could come from other ingredients of the process apart from sewage sludge. Sawdust and straw are used as bulking materials in many sewage sludge composting plants (Sanz et al., 2006), to facilitate the three phases of composting (Tuomela et al., 2000), and they could contain PCP. This compound was a widely used herbicide in the past (Masunaga et al., 2001) and even nowadays traces of it can be found in sawdust (Llerena et al., 2003; Mardones et al., 2009).

The literature regarding the increase in the PCDD/F content in compost and sewage sludge is not very recent. Most of the data were published around the 1990′s and there is a lack of information on dioxins and furans in compost from sewage sludge in the international dioxin inventories and European reports. The European dioxin inventory (Quass et al., 1999) classifies the compost from waste (mainly municipal solid waste) as a source of dioxins, with values of 13.6 g I-TEQ/year, but not paying specific attention to compost from sewage sludge.

When compost is applied to land, these contaminants (PCDD/Fs) can enter the food chain. For this reason, it is expected they will be controlled in a future revision of the current European Directive about sewage sludge disposal (CEC, 1986). The European Commission is currently assessing the potential review of the Directive but to date there are only some drafts and documents (CEC, 2000, 2009) with proposed limits for the sewage sludge dioxin content. In particular, the 3rd Draft of the Working Document on Sludge (CEC, 2000) established 100 ng TEQ/kg as a limit value for the PCDD/F content in sewage sludge applied to land (although without indicating the toxicity equivalent factor for each congener). Nevertheless, some European countries have adopted more restrictive laws for sludge disposal with lower limit values for some pollutants, such as metals and PCDD/Fs, even banning the use of sewage sludge compost to land (Kelessidis and Stasinakis, 2012). Some standards concerning the quality of sewage sludge compost are found in the literature (Amlinger et al., 2004) and a guideline concentration of 17 ng I-TEQ/kg dm for the PCDD/F content in compost from wastes and biowastes can be found elsewhere (Fiedler, 1998; UNEP Chemicals, 1999), but no very up-to date values or directives have been found.

Sewage sludge compost is an alternative and can compete with other types of compost from distinct waste (municipal, vegetable, etc.) to be used as a fertilizer for different types of crops, vegetables, grain plants, fruit trees, etc., and consequently, at the end of the food chain, the presence of pollutants can affect human health (Amlinger et al., 2004).

No sewage sludge composting papers have been found considering the influence of the aeration and/or the presence of chlorinated phenols in PCDD/F formation although this problem was presented elsewhere (Gómez-Rico et al., 2007). On the other hand, differences of almost one order of magnitude have been found for TEQ values obtained in compost samples from the same plant but at different points (Muñoz et al., 2013).

The aim of the present work is to deduce the factors that can cause a significant formation of PCDD/F and some explanation to justify the different concentrations of dioxins observed in samples of the same composting plant. Two analyses have been carried out (composting plant and laboratory scale). In the composting plant, the PCDD/F levels were investigated in samples taken at different times

and sampling points inside the plant. For the laboratory conditions, three factors have been studied in the present work: the effect of the presence of a precursor, pentachlorophenol (PCP), the aeration conditions (with or without forced aeration) and the type of sewage sludge. An analysis of the influence of the PCDD/F formation on the TEQ values is also presented.

2. Materials and methods

2.1. Composting plant

Samples of compost analyzed in this work were collected from a composting plant located in Alicante (Spain) during the period 2004–2010. The plant processes sludge generated from different wastewater treatment plants (WWTPs).

The material composted is approximately a mixture (1:1 w/w on dry basis) of sewage sludge and bulking materials (sawdust and straw in a proportion of 12:1 w/w on dry basis). The composting tunnel is 3 m wide, 2 m high and 75 m long. The aeration is based on three air turbines and the homogenization of the mixture is done by a compost turner, which moves the material from one end of the tunnel to the other, thus allowing the mass to advance throughout the length of the tunnel and providing more aeration. The operating conditions of the process plant are shown in Table 1.

2.2. Laboratory runs

Two different types of runs were performed in the laboratory during the period 2010–2016 in order to study the composting process, with forced and non-forced aeration conditions by using Dewar vessels and small vessels inside an electric oven, respectively.

In the first runs, the sewage sludge used was generated in a wastewater treatment plant (WWTP) from a rural area in the province of Alicante (Spain). The sludge comes from a mixture of primary and secondary treatment and it is chemically stabilized with $Ca(OH)_2$. Subsequently, other samples from three different WWTPs (sludge B, E and R, from urban and urban-industrial areas of the same province) were used in order to observe if similar conclusions could be obtained with other sludge types.

The material composted is a mixture of sewage sludge and bulking materials: sawdust and straw. The mixture consisted of 80% sewage sludge and 20% bulking materials: 14% sawdust and 6% straw (percentages in volume of wet materials and considering a water content of 30% in the sewage sludge after previous drying from around 85% for better mixing of the ingredients). This composition is different from that used in the composting plant since previous experience indicated no fermentation with such low amounts in Dewar vessels. Therefore, the composition for the laboratory experiments was selected in order to obtain a sufficient increase of the temperature to 60 °C during the first few days and an acceptable fermentation due to the evolution of CO_2, indicated by a concentration of the inorganic material (ash).

Table 1
Operating conditions of the composting plant.

Residence time	40 days (30–35 days with fermentation)
Turnings-over per week	3
Advance per turning-over	4 m
Aeration with turbines 1st part	15 min + 15 min resting
2nd part	15 min + 30 min resting (day and night)
Temperature profile	50–70 °C (1st part)
	35–25 °C (2nd part)
Compost moisture	≤ 50%
Organic matter	50–60%

Once the initial compost mixture was prepared, its moisture content was brought up to 65% of wet weight by water spraying in order to assure a sufficient amount of water for the process to work but not too much to hinder proper aeration. Furthermore, the dioxin precursor PCP (purchased from Sigma-Aldrich, 99% certified) was added in some runs, since this can be found in the ingredients of composting. PCP was added dispersed in water in the appropriate amount to obtain a final composition of 100 mg PCP/kg dry weight of mixture. Regardless of the inherent PCP content in the initial materials, which is about 2.8–12.0 mg/kg (Mardones et al., 2008), PCP was added in excess to provide a PCP contaminated sample. This high concentration was selected according to values existing in literature for experiments of PCDD/F formation in vitro from PCP, where results of 16–60 μmol OCDD/mol PCP were obtained (Öberg and Rappe, 1992; Wittsiepe et al., 2000). From these data, it can be deduced that the OCDD formation, when adding 100 mg PCP/kg mixture could be around 2700–10,400 pg/g sample. Mixing was done manually and long enough (around 30 min) to ensure a homogeneous mixture.

Prior to the composting process, the mixtures with and without PCP were analyzed for the PCDD/F content to take into account that the presence of traces of OCDD in the precursors is a problem for researching the formation of this compound during the composting process.

Dewar vessels used for the experiments under forced aeration conditions were 7 L stainless steel containers and were therefore rust-free, anti-corrosive and strong. These Dewar vessels have a stainless steel lid with self-contained insulation. Toggle-clamps secure the lid to the body for safe and water-tight transportation. A gas dispersion tube situated at the bottom of the vessel provided the mixture with compressed air to ensure good aeration. A sponge cylinder was installed above the dispersion tube to absorb any excess moisture and support the organic mixture which was placed above it. The amount of mixture inside the Dewar vessel was around 3 kg. The temperature was monitored during the whole experiment. A scheme of the experimental set-up is shown in Fig. 1.

A temperature sensor was inserted in the middle of the compost mixture and was connected to a programmed computer to control the airflow with an electrovalve, according to the temperature inside the organic mixture. To meet the oxygen demand in the different stages of the composting process, the computer controlled the time that the electrovalves were open as a function of the temperature of the composting mixture. When the temperature of the compost mixture increased, the valves were opened longer. Therefore, this extra air provided to the mixture avoided a sudden increase of the temperature. The airflow was set at 0.9 L min^{-1} in each Dewar vessel according to

Fig. 1. Scheme with the experimental set up for the Dewar vessel experiments.

previous experience, which showed this flow as the most suitable one to achieve the required temperature profile.

For the non-forced aeration conditions, different runs were carried out using the universal oven Model UNB100 (Memmert GmbH + Co.KG, Germany) with natural convection. Several plastic vessels, open, semi-open, closed, with perforated lids (holes were homogenously distributed) were used. Portions of approximately 50 g of the initial mixture were placed in 100 mL plastic vessels. These 50 g samples can simulate the lumps which are not well mixed inside the composting tunnel. The temperature was manually adjusted to that measured for the Dewar runs. Other vessels containing water were kept inside the oven during the entire experiment in order to maintain the humidity of the atmosphere, and water was added occasionally to the samples in order to maintain a reasonable moisture level inside the plastic vessels, 55–65%, and replace the water losses due to the evaporation. The moisture content of the samples was measured during the experiment. After approximately 40 days, the maturation process started and the experiment was stopped although some samples were kept at room temperature for a few more days to consider this maturation. Methane formation was not observed and the percentage of oxygen was that of air, so the process can be considered as aerobic but with non-forced aeration. Those gases were measured by taking a portion of the air inside the oven and analysing them by gas chromatography with a thermal conductivity detector.

2.3. Description of the experiments carried out and parameters studied

Table 2 summarizes the experiments carried out in the composting plant and at laboratory scale, the nomenclature used in each case and the parameter studied (see details in the Results and discussion section).

2.4. Sample analysis

Samples were analyzed immediately after collection or stored frozen for a maximum time of one month until analysis.

The elemental analysis was carried out in a Carlo Erba CHNS-O EA 1108 apparatus. The method is based on the complete oxidation of the sample and analysis of the resultant gases by gas chromatography. The results are expressed as weight percentage with respect to dry matter (dm).

The moisture content was determined after drying the samples in a drying chamber at 105 °C for 24 h and weighing the sample before and after drying. The result is expressed as a percentage with respect to the wet sample.

The ash content was also determined. The ratio between composted material ash and the initial material ash (both on dry matter) indicates the concentration degree of the organic material. The ash content was determined in a Heron 12PR/300 muffle furnace at 900 °C for 8 h, and the result is expressed as a percentage with respect to the dry sample.

Approximately 10–20 g of each wet sample were taken for the determination of the content of the 17 toxic tetra- through octa-chlorinated 2378-substituted PCDD/Fs and according to the US EPA method 1613 (US EPA, 1994). The wet samples were spiked with the internal standard solution containing the $^{13}C_{12}$ labeled congeners, 10 μL of EPA-1613 LCS (Wellington Laboratories Inc., Canada), and were kept with anhydride sodium sulfate for at least 3 h. Then the samples were extracted in toluene using an accelerated solvent extraction with a Dionex 100 apparatus (Dionex Corp., CA, USA). After the extraction, the samples were concentrated and changed to hexane for clean-up and purification processes, consisting of an acid-basic wash followed by a multi-column clean-up to remove interfer-
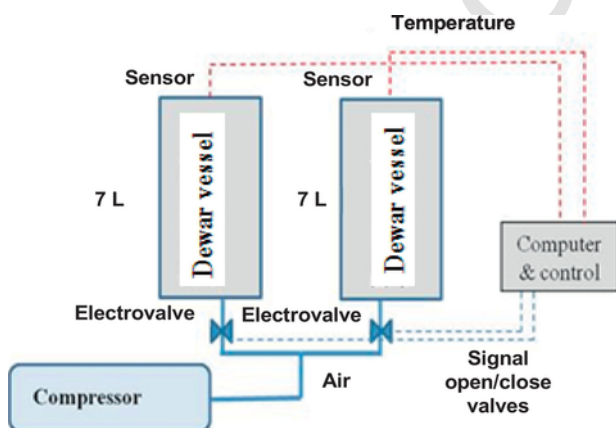
Table 2
Experiments in plant and laboratory.

Experiment	Description	Parameter studied
COMPOST PLANT 1	Plant, final compost (2004)	Year of sampling
COMPOST PLANT 2	Plant, final compost (2004)	
COMPOST PLANT 3	Plant, final compost (2006)	
COMPOST PLANT 4	Plant, final compost (2010)	
COMPOST PLANT 5	Plant, final compost (2010), replicate	
RUN CP-1	Plant, initial mixture and final compost taken with 40 days of difference (2006)	Differences with position inside the tunnel
RUN CP-2	Plant, 5 samples every 15 m along the tunnel taken from the plant the same day (2010, March)	
RUN CP-3	Plant, 8 samples every 10 m along the tunnel taken from the plant the same day (2010, September)	
DEWAR 1	Laboratory with forced aeration inside Dewar, initial mixture, intermediate sample after 7 days and final compost	Differences between initial and final sample, possible formation
DEWAR 2	Laboratory with forced aeration inside Dewar, initial mixture, intermediate sample after 7 days and final compost, replicate	
DEWAR 3	Laboratory with forced aeration inside Dewar, initial mixture and final compost, different sludge	
OVEN 1	Laboratory, non-forced aeration inside oven, vessels with perforated lids, from now on always analysing initial and final compost	Possible formation under different aeration conditions (compared to DEWAR 3)
OVEN 2	Laboratory, non-forced aeration inside oven, vessels with perforated lids, initial and final compost analysing different layers	
OVEN 3	Laboratory, non-forced aeration inside oven, vessels with perforated lids, initial and final compost analysing different layers, replicate	
OVEN 4	Laboratory, different oxygenation inside oven, open, semi-open and closed vessels	
OVEN 5	Laboratory, non-forced aeration inside oven, vessels with perforated lids, different sludge (the same as in DEWAR 3)	
DEWAR-PCP	Laboratory with forced aeration inside Dewar, with PCP added (for comparison, experiment DEWAR 3 corresponds to that without PCP)	Effect of adding PCP under different aeration conditions
Oven–PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, with PCP (for comparison, OVEN 5 corresponds to that without PCP)	
Oven-Compost Sludge B without PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, sludge B	Effect of adding PCP to different sludge samples
Oven-Compost Sludge B with PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, sludge B with PCP	

Table 2 (*Continued*)

Experiment	Description	Parameter studied
Oven-Compost Sludge E without PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, sludge E	
Oven-Compost Sludge E with PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, sludge E with PCP	
Oven-Compost Sludge R without PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, sludge R	
Oven-Compost Sludge R with PCP	Laboratory, non-forced aeration inside oven, vessels with perforated lids, sludge R with PCP	

ences and fractionate analytes. The multi-column clean-up was performed using an FMS Power Prep TM System (FMS Inc., Boston, MA, US) with silica, alumina and carbon columns. The purified extracts were concentrated with a gentle nitrogen flow and prior to the analysis, the recovery standard containing the $^{13}C_{12}$ labeled congeners 1234-TCDD and 123789-HxCDD was added, 5 μL of EPA-1613 ISS (Wellington Laboratories Inc., Canada). An Autospec Ultima High Resolution Mass Spectrometer (Micromass, UK), with a positive electron impact (EI +) source and coupled to an Agilent HP6890 Gas Chromatography apparatus (Palo Alto, CA, USA), was used for the PCDD/F analysis. The apparatus was equipped with a PTV inlet and an Agilent DB-5MS column (60 m × 0.25 mm × 0.25 μm) was employed for the separation of the specific isomers.

The toxicity values are expressed as TEQ-WHO$_{2005}$ in accordance with the toxicity factors currently proposed (Van den Berg et al., 2006).

2.5. QA/QC

A blank was prepared for each set of experiments to identify possible interferences. This consisted of an anhydride sodium sulfate matrix and followed the same procedure as for the samples. In most cases, PCDD/F levels of the blanks were much smaller than those of the samples, except for some samples with very low levels. Nevertheless in all cases the values of the blanks were subtracted. For OCDD, HpCDD and OCDF, the concentrations in the blanks were always much smaller than in the samples. Quality assurance and quality control (QA/QC) criteria for a positive identification of the congener also included the recovery percentage of the internal standards, the relative retention time of the target compound compared to the internal standard, and the chlorine isotope ratio falling within 15% of the theoretical chlorine isotope ratio when the two most abundant ions were measured. All congeners had their recovery percentages within the limits specified by the US EPA Method 1613 (US EPA, 1994); most of them were > 80–90%. Considering the limit of detection (LOD) as the minimum amount of target analyte producing a chromatographic peak with a signal-to-noise ratio of 3, and taking into account the values of LOD and the sample amounts, the minimum concentration of PCDD/Fs detected was 0.1 pg/g sample.

3. Results and discussion

3.1. Overall results of parameters indicating the quality of the composting process

Fig. 2 shows the temperature profiles for the experiments in the plant and laboratory. Specifically, Fig. 2a shows the profile at different points inside the tunnel corresponding to different stages of the process measured the same day as run CP-3 was carried out, observing the rise of temperature in accordance with the exothermic aerobic process. The X-axis is expressed in days after calculating the time corresponding to the distance inside the tunnel. Fig. 2b shows the variation of temperature corresponding to the three laboratory experiments in DEWAR vessels. For the DEWAR 1 run, the maximum temperature reached was 62 °C, which is lower than the other runs. For the DEWAR 2 run, the maximum temperature was 68 °C after stopping the process and mixing all the contents of the vessel again. For the DE-WAR 3 run, the increase of temperature was delayed with respect to the other runs, and the run lasted 70 days to ensure adequate composting. Fig. 2c shows the temperature for the oven experiments, which in this case was manually modified in order to simulate the temperatures achieved in the composting process maintaining, at least, 10 days at a temperature higher than 65 °C, afterwards decreasing gradually until 40 days and finally maintaining an ambient temperature up to 70 days for maturation. In Fig. 2d, the profile for the DEWAR-PCP experiment is presented, which is similar to that achieved in the DEWAR 3 run.

The results of elemental analysis and ash content are shown in Table 3, and they are all in accordance with the common values for compost. More details can be found in Table 1 of Supporting Information (SI). In the same table, the composting ratio (c.r.) is pre-sented, which is defined as the ash content of the composted sample divided by the ash content of the initial sample, indicating the concentration of ash and other remaining components in the aerobic fermentation, where there is a loss of CO_2, NH_3 and dry matter, in addition to H_2O (Lim et al., 2017). Note that c.r. is normally around 1.5–2.0 in these experiments, thus indicating that fermentation is produced, although for two samples taken from the oven a c.r. 1 was observed and therefore the composting process was not produced.

3.2. Composting plant: variation of the PCDD/F levels with time

Several samples (COMPOST PLANT 1 to 5) obtained from the end of the tunnel in different years have been analyzed. Furthermore, for COMPOST PLANT 5, five replicates were taken at the end of the tunnel the same day.

The concentration profile of all congeners, considering relative concentration, is similar to that observed in Fig. 3 which shows the results of the most significant congeners OCDF, 1234678-HpCDD and OCDD. They represent 90–99% of the total concentration, and the same behavior was observed for all samples analyzed in this work. The levels of all congeners are presented in Table 2 of SI.

Considering Fig. 3, a high concentration of 1234678-HpCDD and OCDD in comparison with OCDF can be observed in three samples and this was also outlined by some researchers (Malloy et al., 1993; Lahl et al., 1991; Wittsiepe et al., 2000). The levels of 1234678-HpCDD were around 10 times higher than those for OCDF, and in the case of OCDD they were around 60 times higher. Nevertheless, there are two other samples where the differences are less pronounced, so 1234678-HpCDD levels were similar to OCDF levels and OCDD values 15 times higher than OCDF values. Specifically, the lower differences correspond to lower absolute levels. On the other hand, it can be observed that the values of the standard devia-
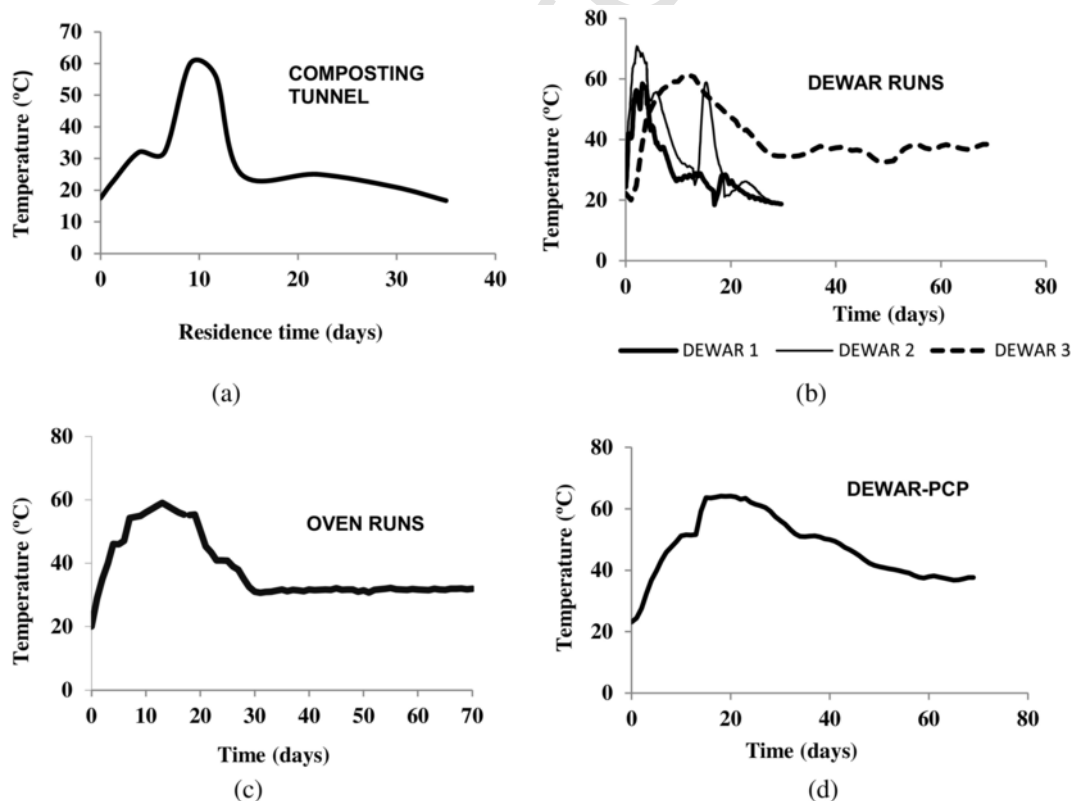

Fig. 2. Variation of temperature vs. time: a) composting tunnel, b) Dewar runs, c) Oven runs, d) Dewar-PCP run.

Table 3
Elemental analysis, ash content and concentration ratio of samples as ranges for each set of experiments.

| Sample	%C	%H	%N	%S	% Ash	c.r.
COMPOST PLANT	31.6–35.1	4.4–4.8	2.6–2.8	0–0.6	23.7–30.6	–
RUN CP (initial samples)	38.2–42.4	4.9–6.0	2.4–4.2	0–0.7	9.5–22.7	–
(final compost)	31.6–35.1	4.4–4.8	2.6–2.8	0–0.6	23.7–30.6	1.4–2.5
DEWAR (initial samples)	41.6–43.0	6.2	3.6–6.3	0.6–0.7	13.5–16.5	–
(final compost)	37.2–39.1	5.5–5.9	2.8–5.4	0.7–1.3	20.8–29.3	1.5–1.8
OVEN (initial samples)	43.0	6.2	3.6	0.7	16.5	–
(final compost)	42.2	6.1	3.1	0.9	30.2	1.0–2.6
DEWAR AND OVEN WITH PCP (initial samples)	43.1	6.3	3.7	0.9	19.6	–
(final compost)	35.8–42.7	5.2–6.2	3.0–3.2	1.0–1.2	29.0–32.6	1.5–1.7
OVEN WITH AND WITHOUT PCP AND WITH DIFFERENT KINDS OF SLUDGE (initial samples)	38.5–40.6	5.4–6.1	1.8–4.6	0–1.0	19.6–24.9	–
(final compost)					27.5–51.0	1.1–2.1
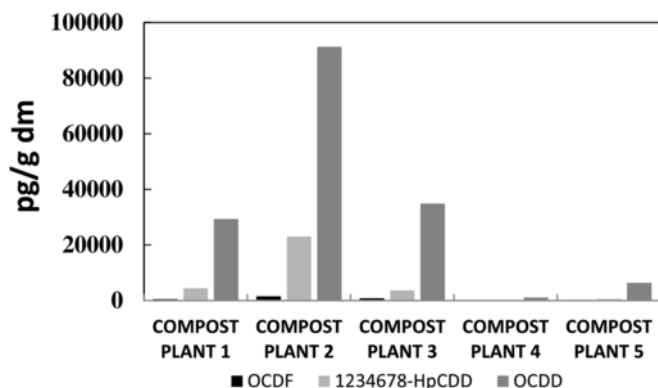
Fig. 3. Analysis of the most abundant congeners in compost plant samples.

tion of the five samples analyzed for COMPOST PLANT 5 is around 60%, much greater than the 5–10% obtained from the analysis only of the extracts by the apparatus of High Resolution Gas Chromatography with High Resolution Mass Spectrometry, indicating a heterogeneity.

The toxicity values of the different compost samples were 71.6 pg TEQ-WHO$_{2005}$/g dm for COMPOST PLANT 1, 300.5 pgTEQ-WHO$_{2005}$/g dm for COMPOST PLANT 2, 64.5 pg TEQ-WHO$_{2005}$/g dm for COMPOST PLANT 3, 7.4 pg TEQ-WHO$_{2005}$/g dm for COMPOST PLANT 4 and 23.9 pg TEQ-WHO$_{2005}$/g dm for COMPOST PLANT 5. For the last one, the standard deviation of the five replicates was 7.7 pg TEQ-WHO$_{2005}$/g. A significant variation of concentration can be observed probably due to the heterogeneity of samples and the process. Note that there is one sample that exceeds the recommended limit of 100 pg TE/g for the use of sludge for soil amendment (CEC, 2000) and another three samples exceed the guideline concentration of 17 pg/g with units of I-TEQ (Fiedler, 1998; UNEP Chemicals, 1999). Most of the values found in this section are higher than those obtained by Brändli et al. (2007) in compost from green waste with/without crude organic kitchen waste, who found a mean value of 3.0 pg TEQ-WHO$_{2005}$/g dw and ranging from 0.5 to 20 pg TEQ-WHO$_{2005}$/g dw. However, the values obtained by these authors are in accordance with our most recent results obtained for COMPOST PLANT 4 and 5.

They mentioned that there was no indication (e.g. different process, input material) as to why OCDD should be formed in the sample with the highest value of 20 pg TEQ-WHO$_{2005}$/g dw only. Therefore, heterogeneity plays an important role.

Our highest values are in agreement with those obtained by Malloy et al. (1994) for compost from municipal solid waste mixed with sewage sludge, ranging from 37 to 87 pg TEQ/g dw.

3.3. Composting plant: initial and final values

In this section, the results of three runs (CP-1, CP-2 and CP-3) are presented.

In the first run CP-1, a sample of the initial mixture of the composting plant was collected and analyzed, and a sample of the compost obtained after 40 days, which is the residence time inside the tunnel, was also collected. It was tested that the ash content of the composted sample was higher than the ash content in the initial mixture, as discussed elsewhere (Grigatti et al., 2004). In the second and third runs, CP-2 and CP-3 respectively, samples at the initial step, intermediate steps and final step were taken the same day. The intermediate samples were taken at different positions along the tunnel, spaced 15 and 10 m for runs CP-2 and CP-3, respectively.

Fig. 4 shows the concentration of the most abundant congeners: OCDF, 1234678-HpCDD and OCDD. From now on, the data of the composted samples are referred to as the initial ones (pg of PCDD/F in composted sample divided by kg of initial mixture), in order to avoid the concentration effect that makes it difficult to observe a PCDD/F formation. The reduction of volume and mass during the fermentation process produces a concentration of the remaining hardly degradable compounds (such as PCDD/Fs). Note that the values presented in Fig. 4 have been calculated from the experimental ones divided by c.r. For run CP-1, a high increase in 1234678-HpCDD and OCDD levels can be observed, whereas the OCDF concentration remains nearly constant, thus suggesting a formation of the mentioned compounds. Other congeners remain in the same order as for the initial sample, as can be seen in Table 3 of SI.

With respect to runs CP-2 and CP-3, the results corresponding to the intermediate step samples are average values and they show an erratic variation, without any variation tendency. Again, the high values of standard deviations of the 5 samples of run CP-2 and 8 samples of run CP-3 are probably a consequence of the heterogeneity of the samples. In all intermediate and final step samples the concentration of 1234678-HpCDD and OCDD are in the range of the initial values.

With regard to the TEQ-WHO$_{2005}$ toxicity values, these were 14.1 pg/g dm for the initial mixture and 30.2 pg/g dm for the final compost corresponding to run CP-1, 34.0 and 5.4 pg/g dm for the first step and final steps of run CP-2 respectively, and 12.6 and 2.7 pg/g dm for run CP-3. It can be observed that there is no trend. The literature is also contradictory. On the one hand some authors did not find PCDD/F formation during composting in spite of having high concentrations of chlorophenols (Laine et al., 1997) and on the other hand some samples from composting plants gave sometimes high levels without a clear explanation (Brändli et al., 2007).

From the previous results, no clear conclusions can be obtained, probably due to the heterogeneity of the samples, so it was decided to carry out laboratory runs with uniform mixtures controlling the composition.

3.4. Dewar runs in laboratory with forced aeration

In this section, the results of three Dewar runs are presented (see Fig. 5). All the concentrations are referred to the initial mixture as mentioned previously. The purpose of these experiments was to as-
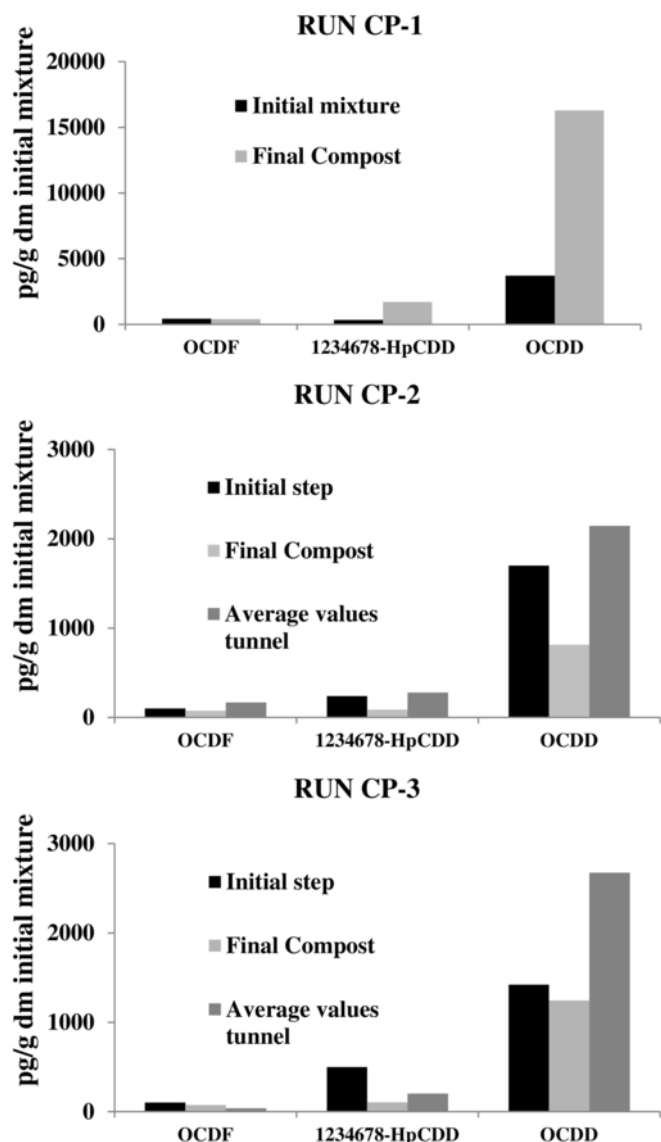
Fig. 4. Concentrations of OCDF, 1234678-HpCDD and OCDD corresponding to samples of the composting tunnel.

Fig. 5. Concentrations of OCDF, 1234678-HpCDD and OCDD corresponding to samples of the DEWAR runs.

sure a PCDD/F formation under specific conditions in case of an increase in the levels of the final compost compared to the initial mixture since the heterogeneity is lower than for the composting plant and the process is better controlled.

In the first two runs, the initial mixture was the same and the concentration at 7 days (intermediate sample taken after the increase of temperature) is also presented.

In the DEWAR 1 and DEWAR 2 runs, it can be observed that the congener concentrations of the partially composted materials and the final composted materials are similar to the initial mixture, indicating that there was no formation of PCDD/Fs. For DEWAR 3, only a slight increase in OCDD can be observed. Therefore, the aerobic composting process does not necessarily lead to a significant formation of PCDD/Fs.

Considering the TEQ-WHO$_{2005}$ toxicity values, these were 11.1 pg/g for the initial mixture and 9.3 pg/g for the final compost from the DEWAR 1 experiment, 13.4 and 11.7 pg/g for the initial and final values of DEWAR 2 respectively, and 2.8 and 2.0 pg/g for DEWAR 3 on dry basis. After comparing 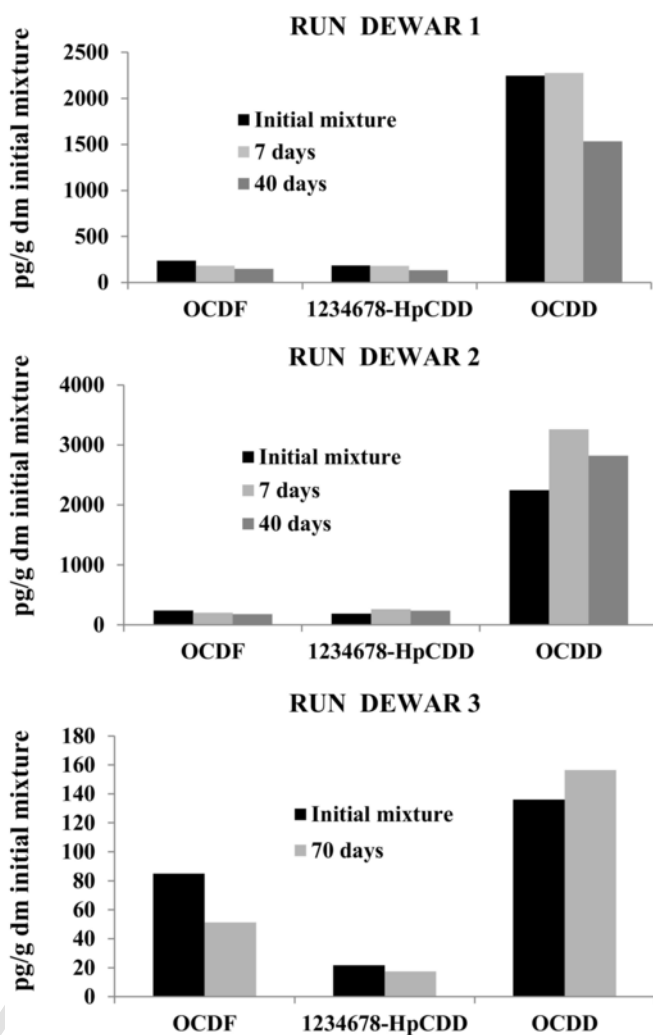the final samples to the initial ones, no increase is observed for any experiment in these conditions of good aeration (see details in Table 4 of SI). Our results are in agreement with those obtained by Klimm et al. (1998), who observed no formation of OCDD or HpCDD during digestion of sewage sludge under strictly aerobic conditions.

3.5. Oven runs varying the aeration conditions

OVEN 1, OVEN 2 and OVEN 3 were carried out with perforated lid vessels to allow a small entrance of air, so the composting could occur under non-forced conditions. In OVEN 2 and OVEN 3, three parts were considered in the final sample: the external layer (EL) at the upper part close to the lid, the medium layer (ML) and internal layer (IL) at the bottom. The objective was to observe if there was any difference considering the more difficult access of oxygen to the different layers. The runs were carried out with mixtures using different kinds of sewage sludge, but for each run the same mixture was used in all variations.

OVEN 4 corresponds to a series of three runs carried out with an open vessel OV (to favor oxygenation), a semi-open vessel SOV (intermediate oxygenation) and a closed vessel CV (to simulate anoxic or anaerobic concentration). The results of these runs are also considered, but the composting factor was 1, indicating that the composting

or decomposition process did not take place correctly in any sample. Nevertheless, the results are also presented to test if an abnormal performance of the composting process could lead to the formation of dioxins and also to test the analytical method.

OVEN 5 was carried out with a different sludge but the same as used in the DEWAR 3 run, to directly compare the composting process in these two kinds of experiments. In the case of the oven run, the vessel used had small perforated lids to ensure semi-aerobic conditions, while the DEWAR run allowed aerobic conditions.

Fig. 6 shows the concentrations of the most abundant congeners, observing similar values between the initial and final samples and between the layers and operating conditions considered for the different runs carried out. More details about the concentration of specific congeners are displayed in Table 5 of SI.

The TEQ-WHO$_{2005}$ toxicity values for the runs OVEN 1 to OVEN 5 are in the range 1.8–5.7 pg/g dm and referred to the initial sample. Comparing the OVEN and DEWAR experiments with the same initial mixture, the levels are similar although a slight increase can be observed in the OVEN experiment that is not produced in the DEWAR one. Klimm et al. (1998) also found a moderate formation of PCDD/Fs after digestion of sewage sludge for 192 days under semi-anaerobic conditions. However, under strictly anaerobic and aerobic conditions no formation was observed.

In the following sections, the presence of high amounts of precursors and the behavior of different sludge samples together with different aeration conditions are studied.

3.6. Dewar and oven runs with PCP

Two new runs, one with a DEWAR vessel (DEWAR-PCP) and another with a vessel inside the oven (OVEN-PCP), were performed with an initial mixture with added PCP, as explained in the Materials and methods section.

Fig. 7 shows the congener concentrations referred to the initial samples. For the DEWAR-PCP run, the levels of 1234678-HpCDD and OCDD for the initial and final sample are similar. However, for the non-forced aeration OVEN-PCP run, the concentration of OCDD increases from 630 to 2708 pg/g dm referred to the initial sample. There is also an increase of 1234678-HpCDD, from 29 to 68 pg/g dm referred to the initial sample. This means that the presence of a precursor in high amounts together with the non-aerated conditions can lead to a PCDD/F formation.

The results presented here are consistent with the different data published concerning the formation of dioxins during composting of organic wastes (Malloy et al., 1993; Öberg et al., 1993; Öberg et al., 1994); where in some cases the observed formation of 1234678-HpCDD and OCDD does not alter the TEQ toxicity. In other cases
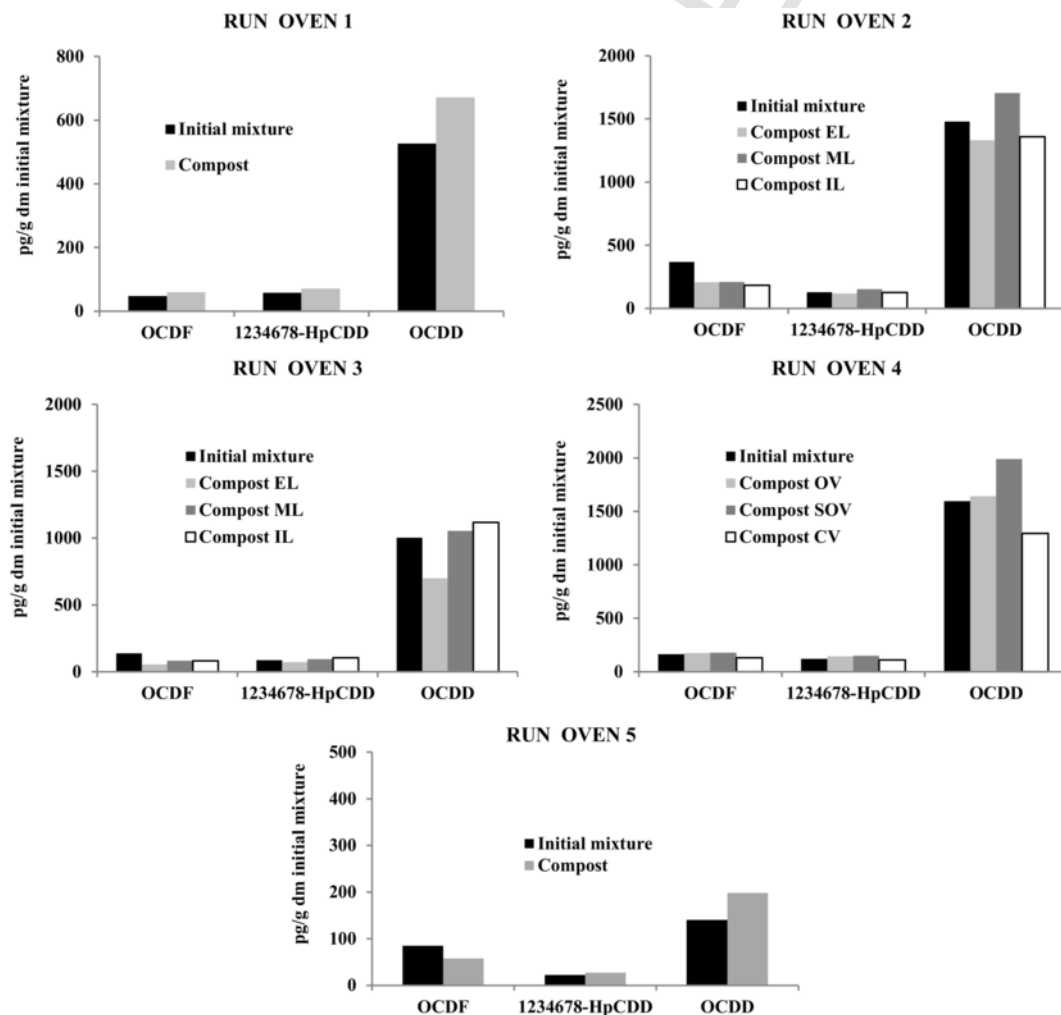

Fig. 6. Concentrations of OCDF, 1234678-HpCDD and OCDD corresponding to samples of the 1 to 5 OVEN runs.
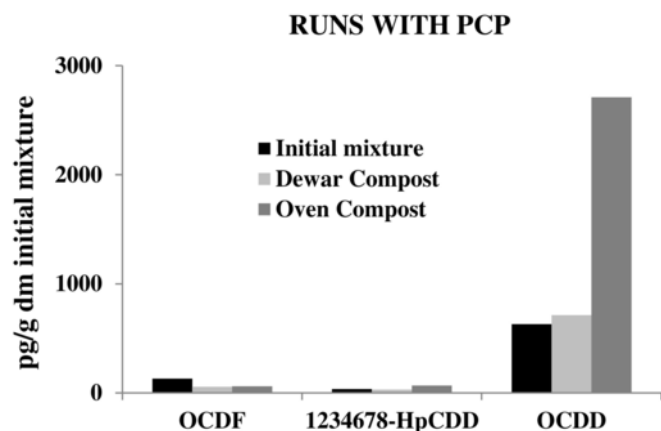
RUNS WITH PCP

Fig. 7. Concentrations of OCDF, 1234678-HpCDD and OCDD corresponding to samples of the DEWAR-PCP and OVEN-PCP runs.

however, when the formation of 1234678-HpCDD and OCDD is very high, a moderate or remarkable increase in the WHO-TEQ toxicity is observed. According to their results, a formation of PCDD/Fs occurs de novo from precursors in compost, although they did not study specifically composting from sewage sludge. In this work, the toxicity values were 2.0 pg WHO_{2005}/g for the initial mixture, 1.2 pg WHO_{2005}/g for the final sample from the DEWAR-PCP run and 4.7 pg WHO_{2005}/g for the OVEN-PCP run. Therefore the increase in toxicity is not worrying since the initial value was low. More information is detailed in Table 6 of SI.

3.7. Oven runs with and without PCP with different sludge samples

Three different sewage sludge samples B (urban plant), E (industrial/urban plant) and R (industrial/urban plant) have been employed to test if the formation of PCDD/Fs is produced under non-aerated conditions. These three mixtures were divided into two parts and in one of them, PCP was added as a precursor, thus obtaining six initial samples. To analyze the reproducibility of the results, two equal 250 mL PE vessels with taps were filled with each mixture (up to 4/5 of the total volume of the bottle), and the taps were perforated with homogeneously distributed holes and therefore non-aerated conditions were achieved. Thus, twelve vessels were placed inside the conventional oven with natural convection to carry out the different experiments. The temperature inside the oven was manually modified in order to simulate the temperatures achieved in the composting process as mentioned previously.

Comparing the initial samples, the PCDD/F concentration was significantly higher for those with PCP added. This increase was around 50% for the three different mixtures, mainly due to OCDD and to a lesser extent 1234678-HpCDD that corroborates the PCDD/F contamination of commercial PCP observed by other authors (Holt et al., 2008; Masunaga et al., 2001).

Fig. 8 shows the experimental results corresponding to the congeners OCDF, 1234678-HpCDD and OCDD. From this Figure, it is deduced that there is a clear formation of OCDD in the three compost experiments when PCP is added. An ANOVA test was performed with the results obtained and the same deduction was observed from the values of F calculated with the test. These were close or higher than 10.1, which corresponds to a value of α equal to 0.05, and therefore a significant difference was detected for this congener. More details can be found in Tables 7, 8 and 9 of SI.

It seems that there is also a formation of 1234678-HpCDD in the runs with and without PCP (except for the sample Final compost 1 with sludge E), However, the increase is not high enough to be significant with α = 0.05 as obtained for OCDD. These facts show the complexity of the enzymatic formation during composting. In any case, the formation of 1234678-HpCDD is much less than that of OCDD.

Taking into account the TEQ-WHO_{2005} toxicity values in the experiments without PCP, these were 0.4–0.9 pg/g for the initial mixtures with the different sludge samples and 1.2–2.1 pg/g for the final composts. For the experiments with PCP, the results were 0.4–0.9 pg/g TEQ-WHO_{2005} for the initial and final mixtures. More details are shown in Tables 7, 8 and 9 of SI. Note that the values for the final compost samples are always referred to the initial samples, and therefore the real values are slightly higher after multiplying by c.r. It can also be observed that it is difficult to distinguish the PCDD/F formation with these low levels of toxicity. Öberg et al. (1993) also obtained a low toxicity increase during composting of garden waste with ^{13}C-PCP added to some samples, ranging from 0.2–0.5 pg I-TEQ/ g dw.

Comparing all samples from a composting plant and laboratory experiments analyzed in Sections 3.2–3.7, it can easily be deduced that the TEQ-WHO toxicity values depend mainly on the 1234678-HpCDD and OCDD concentrations for the most toxic samples COMPOST 1 to 3, whereas for the less toxic samples, their small toxicity depends on the less chlorinated congeners.

4. Conclusions

From the results obtained, it can be said that compost is an ecological product and the possible formation of dioxins is negligible in most cases. However, inappropriate aeration and the presence of PCP cause a significant increase of OCDD. Therefore, these two factors should be controlled in the composting plants to prevent PCDD/F formation. In this study, with a concentration of 100 mg PCP/kg sample, the formation of OCDD was observed.

The PCDD/F levels in the plant studied have decreased over the years, which means that the process conditions are probably more appropriate and avoid the formation in this case. Nevertheless, the PCDD/F levels in composting plants should be controlled periodically to observe and analyze possible increases in the toxicity of the product obtained.

On the other hand, in order to obtain reliable values of levels of PCDD/Fs, integrated samples from different points should be considered, thus avoiding an abnormal result of any sample.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.10.249.
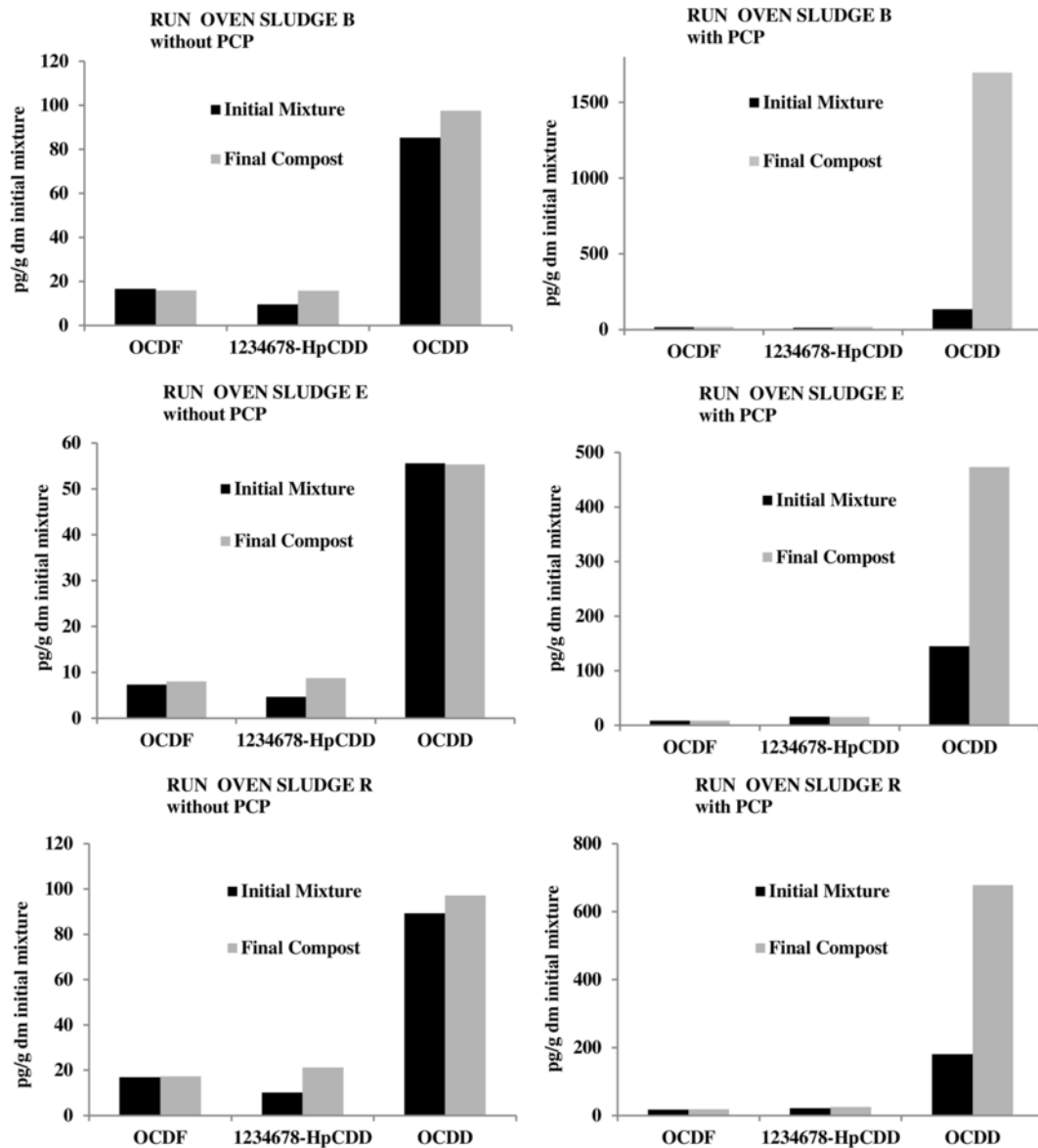
Fig. 8. Concentrations of OCDF, 1234678-HpCDD and OCDD corresponding to samples of compost in non-aerated vessel in an OVEN without and with PCP.

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