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

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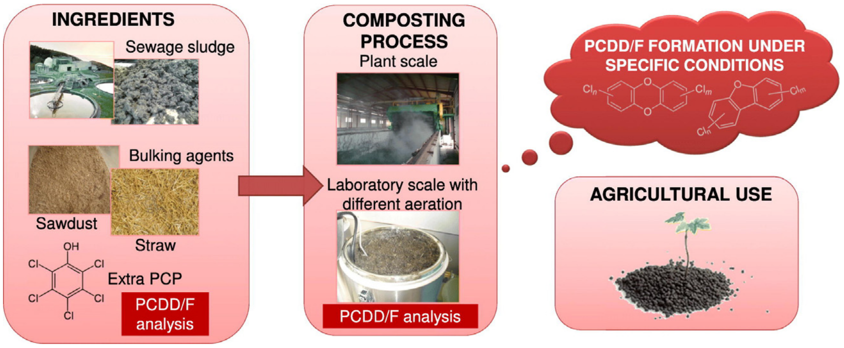
HIGHLIGHTS

- PCDD/F levels exceeded the proposed limits in three samples of the composting plant.
- OCDD formation was observed at laboratory scale with PCP and non-forced aeration.
- Toxicity due to the presence of PCDD/Fs is negligible in most cases.

GRAPHICAL ABSTRACT



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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 Buekens, 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 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.

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