



PCDD/F and dioxin-like PCB concentrations during municipal solid waste biomethanation and subsequent composting



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HIGHLIGHTS

- The obtained toxic concentrations in all the fractions were low.
- 2,3,4,7,8-PeCDF, 1,2,3,6,7,8-HxCDD and HpCDD showed the highest toxic concentrations.
- OCDD and 1,2,3,4,6,7,8-HpCDD showed the higher concentrations in almost all samples.
- The contribution of PCBs to the total toxicity is high.

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ABSTRACT

PCDD/F and dioxin-like PCB concentrations were compared in different samples of a municipal solid waste (MSW) treatment plant: the initial MSW fraction that enters the biomethanation from the digester, the semi-solid digestate obtained after biomethanation of MSW, and the solids after composting the digestate since the final product is destined for land application and special attention must be paid to these compounds for environmental considerations. The initial MSW sample showed low concentrations of PCDD/Fs, although in the biomethanation output sample the concentration was more than ten times higher. The difference was even more significant for PCBs. In compost samples concentrations for both PCDD/Fs and PCBs were in the same range as in biomethanation or lower. Nevertheless, concentrations found for all samples were low and these treatments do not pose a major problem for the environment in the working conditions used.

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1. Introduction

In recent years, a great effort has been made to reduce the amount of municipal solid waste (MSW) that is landfilled. According to the EU Landfill Directive (Council Directive 1999/31/EC of 26 April 1999), by 2013 biodegradable municipal waste landfilled must be reduced to 50% of that produced in 1995, and by 2020 to 35% of the amount produced in 1995. Two alternatives are biomethanation and composting from the biodegradable fraction.

Biomethanation, or anaerobic digestion, is a complex microbial process in which organic compounds are degraded into methane and carbon dioxide by a variety of anaerobes. This biogas can be used as a fuel after desulfuration of the biogas with hydrogen sulfide, and the fermented solid residue can be used as a fertilizer or raw material for composting. When organic compounds are maintained at 5–70 °C and neutral pH under anaerobic conditions, spontaneous biomethanation will occur. Biogas is produced in this

way in landfills but, in addition to this, biomethanation plants exist to treat some fractions of MSW to obtain biogas.

Aerobic 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. Composting can be performed either directly from the residue or after biomethanation.

The literature concerning PCDD/F concentrations in MSW and its treatment is scarce so far, and the discussion of PCDD/F emissions from MSW treatments usually refers to incineration. First of all, untreated MSW has very changeable PCDD/F concentrations. While in the UK an average concentration of 6.3 ng I-TEQ kg⁻¹ was found (Eduljee et al., 1997) in Germany around 73 ng I-TEQ kg⁻¹ was obtained (Landesumweltamt Nordrheinwestfalen, 1997). However, PCDD/F concentrations in different stages of the MSW treatment have been reported. PCDD/F concentrations of 5–117 pg I-TEQ N m⁻³ have been found in the biogas produced spontaneously (before its combustion), when MSW is landfilled (Cernuschi, 2001). Nevertheless, the biogas flow coming out from the landfill

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body is very low. Flue gases from combustion of MSW have been found to show higher concentrations of PCDD/Fs than those found in biogas. Zhang et al. (2008) reported 1160–3190 pg I-TEQ N m⁻³ in combustion of MSW, Lonati et al. (2007) showed values of 1300 pg I-TEQ N m⁻³ for old plants and 3.2 pg I-TEQ N m⁻³ for new plants of MSW combustion and 100–5000 pg I-TEQ N m⁻³ were also reported by Fiedler (1998). Regarding landfill leachate, Concejero et al. (2008) showed that nearly all the congeners were below the detection limit and only OCDD had significant levels, with a total PCDD/F content from 0.01 to 5.22 ppq I-TEQ.

Apart from the PCDD/F concentrations obtained in biogas, when biomethanation is used as a treatment for MSW, special attention must be paid to the concentrations resulting in the liquid sludge or semi-solid residue, since its final destination is sometimes the application to land as a fertilizer after composting. No studies have been found on PCDD/Fs in this waste produced anaerobically, although there is evidence of dechlorination of PCDD/Fs by anaerobic cultures and sediments (Adriaens and Grbic'-Galic, 1994). However, lesser chlorinated PCDD/Fs (2,3,7,8-substituted ones) have been found as the accumulating products resulting from reductive dechlorination under anaerobic methanogenic conditions, that could be a matter of environmental concern. Furthermore, during anaerobic treatment of another waste, sewage sludge, an increase of PCDD/Fs was observed mainly due to the rise of 1,2,3,4,6,7,8-HpCDD and OCDD (Weber et al., 1997).

On the other hand, composting supposedly degrades some organic pollutants present in the waste, but an enzymatic formation of PCDD/Fs (polychlorinated dibenzo-p-dioxins/furans) can take place during composting under certain conditions, as studied during sewage sludge composting by Weber et al. (1997). In this case, the increase was also due to 1,2,3,4,6,7,8-HpCDD and OCDD, as for anaerobic digestion. Malloy et al. (1993) also found high concentrations of PCDD/Fs (mean value of 56 ng I-TEQ kg⁻¹) during the composting process of MSW, MSW mixed with sewage sludge and yard waste composting, where 1,2,3,4,6,7,8-HpCDD and OCDD were again the dominant congeners, probably due to a potential formation of PCDD/Fs from pentachlorophenol (PCP). However, Eduljee et al. (1997) reported a PCDD/F decrease during MSW composting. They found MSW to contain 6.3 ng I-TEQ kg⁻¹ of waste while compost contained 0.4–3.3 ng I-TEQ kg⁻¹. Therefore, the increase or decrease of the PCDD/F concentrations during composting seems to depend on the process conditions and initial materials containing PCDD/F precursors. Concejero et al. (2008) showed similar concentrations to Eduljee et al. (1997) after studying three MSW composting facilities, 1.53–5.26 ng WHO₂₀₀₅-TEQ kg⁻¹ (or 2.92–9.22 ng I-TEQ kg⁻¹). These authors completed their study with the analysis of dioxin-like PCBs, obtaining for these compounds 1.15–3.62 ng WHO₂₀₀₅-TEQ kg⁻¹, and therefore PCBs are as important as PCDD/Fs for environmental considerations.

The initial mixture necessary to carry out the composting process consists of waste and a bulking agent (e.g. straw, sawdust, leaves, woodchips, etc) to make it permeable to air. Both bulking agents and MSW could contain the precursors for the PCDD/F formation, such as pentachlorophenol. Pentachlorophenol was used for many years as a fungicide to treat wood to avoid woodworm, although nowadays its use is limited because of its relationship with the formation of PCDD/Fs. Nevertheless, chlorophenols can be still found in leachates from MSW landfills (Ozkaya, 2005). Some “in vitro” studies demonstrated the relationship between some peroxidase enzymes and chlorophenols with the dioxin formation, leading to considerable amounts of higher chlorinated PCDD/Fs (Öberg et al., 1990; Öberg and Rappe, 1992; Wittsiepe et al., 1999).

Hence, a PCDD/F formation has been suggested from anaerobic treatment and composting of waste, but the information is contradictory and some other authors reported a reduction in the dioxin

levels after these treatments. Therefore, the aim of this work was to determine PCDD/F concentrations (the 17 2,3,7,8-tetrasubstituted congeners) in different samples: MSW, after biomethanation of MSW, and after composting of the digestate obtained in biomethanation. Dioxin-like PCBs (non-ortho and mono-ortho congeners (Van den Berg et al., 1998)) were also included in this study since their contribution to the toxicity could be significant.

2. Materials and methods

MSW, biomethanation digestate and compost were provided by a MSW treatment plant located in the Southeast of Spain, which receives non-hazardous municipal waste. Five samples were analyzed:

1. MSW (biomethanation input): consists of MSW with particle size smaller than 40 mm without ferric materials, which is the most suitable fraction for the process.
2. Biomethanation output.
3. Fresh compost: compost obtained after 21 d of composting formed from the biomethanation output (particle size smaller than 40 mm) and the intermediate particle size fraction (40–80 mm).
4. Mature compost from the fraction with particle size smaller than 12 mm, after more than 1 month of maturation.
5. Rejected fraction: comprises the fraction of final compost after maturation with particle size larger than 12 mm. This fraction is separated from the mature compost, so it is not used as a fertilizer and is disposed of to landfill. It also contains plastic, glass and other non-fermentable materials.

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 weight percentage with respect to the wet mass (wm). The elemental analysis was carried out in a Carlo Erba CHNS-O EA 1108 apparatus, after drying the samples at 105 °C for 24 h. The method is based on the complete oxidation (combustion) of the sample and analysis of the resultant gases by gas chromatography. The results are expressed as weight percentage with respect to dry mass (dm). The ash content was determined in a Heron 12PR/300 muffle furnace at 900 °C for 8 h, and the result is expressed as percentage with respect to dry mass. The oxygen percentage was calculated by difference, taking into account C, H, N, S and ash contents.

In addition to this characterization, a thermogravimetric analysis (TG) of the samples was carried out in a Mettler Toledo thermobalance model TGA/SDTA851e/LF/1600, in order to obtain more information about the changes produced during the processes studied (see [Supplementary Information](#) for more details and results).

The PCDD/F and PCB analysis was carried out according to the US EPA method 1613 (US EPA, 1994). An amount of approximately 10 g of each wet sample was spiked with the internal standard solutions containing the ¹³C₁₂ labeled congeners, 1613LCS-PCDD/Fs and WP-LCS-PCBs (Wellington Laboratories Inc., Canada), and was kept for 3 h with sodium sulfate. Then the samples were extracted in toluene using accelerated solvent extraction with a Dionex 100 apparatus (Dionex Corp., CA, USA). Extraction was followed by a clean-up and purification step consisting of an acid-basic treatment and a clean-up procedure using an FMS Power Prep TM System (FMS Inc., Boston, MA, US) using silica, alumina and carbon columns. The purified extract was analyzed using an Autospec Ultima high resolution mass spectrometer (Micromass, UK), with a positive electron impact (EI+) source and interfaced with a Hewlett–Packard (Palo Alto, CA, USA) 6890 Plus

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