

## *De novo* formation of PCDD/Fs in compost and sewage sludge – a status report

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### Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are formed *de novo* when non-contaminated garden waste with low levels of PCDD/Fs is composted. There is a two- to tenfold increase in higher chlorinated PCDD/Fs, depending on the congener and the individual compost. Not all isomers are affected, some new isomers appear. The detailed pattern differs from compost to compost. The toxicity (I-TEQ) typically increased two- to threefold. Similarly, PCDD/Fs are formed during the active sewage sludge process; <sup>13</sup>C-labelled PCDD/Fs, mainly octachlorodibenzo-*p*-dioxin (OCDD), was formed from added <sup>13</sup>C-pentachlorophenol.

### Introduction

The potential spreading of and exposure to PCDD/Fs of sewage sludge and compost is of concern since the organic waste preferably should be used as fertiliser<sup>1-3</sup>. It has been established that chlorophenols can be enzymatically transformed *in vitro* to PCDD/Fs by peroxidases<sup>4-9</sup>, and that PCDD/Fs are formed from chlorophenols in sewage sludge<sup>10</sup>. The objective of this study was to find out if the concentrations of PCDD/Fs increased in compost and if chloroorganic xenobiotics could act as precursors in this process.

### Experimental

<sup>13</sup>C-labelled hexachlorobenzene (HxCBz) and pentachlorophenol (PeCP), <sup>12</sup>C- and <sup>13</sup>C-PCDD/F standards, organic solvents, and all other chemicals were of the highest quality available. <sup>13</sup>C-PeCP was solvent extracted to avoid possible contamination with OCDD.

A compost (#1) was started in July 1991. Four samples were taken during its active period, and an additional sample was taken the next summer. In June 1992 two new composts (#2, #3) were started and short term experiments were performed. Later two additional composts were started (#4, #5). During the two months of active composting several samples were taken from #4 and #5, and additional samples will be taken in the summer 1993. The composts were conventional outdoor garden composts. To avoid dry and wet deposition the top of the composts were covered. Organic material and tap water was added when necessary to maintain a high biological activity. The composts consisted of fresh cut grass and twigs, some old clematis, and finely cut branches and leaves from birch, willow, and mountain ash. All input was analysed for

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background levels of PCDD/Fs. The composting process was started with fresh material in #2 and #3, while in the three other composts the pre-composting process was allowed to occur for four to six weeks to establish an active composting culture. Then the whole compost was mixed and homogenised, adding fresh composting material. A loosely netted bag with a known amount of compost was placed in the centre of the compost. The hotbeds of #1 and #5 were spiked with 9 mg  $^{13}\text{C}$ -PeCP each, the one in #4 was spiked with 9 mg  $^{13}\text{C}$ -HxCBz.

Samples were taken from the hotbeds, slowly dried, and finely ground in a ballmill. The dry weight was measured as residual mass after drying at 130 °C for 18 hours. We followed a protocol for good laboratory practice<sup>11</sup> to extract, clean up and analyse the PCDD/Fs.

## Results

The results are given in Figures 1 – 8.

Composts are heterogeneous, which makes sampling strategy important and adequate sampling difficult. When the hexa- hepta- and octa-PCDD/F data is expressed as international toxic equivalents (I-TEQ) the increase in toxicity is 0 – 300%; two- to threefold for a typical composting event. The increased toxicity corresponds to an elevation by 0.2 – 0.5 ng I-TEQ / kg dry weight. In the HxCBz-spiked compost there is a weak, unquantifiable and unsteady appearance of  $^{13}\text{C}$ -OCDF. When compared to the bioformation of OCDD from  $^{13}\text{C}$ -PeCP in activated sewage sludge<sup>10</sup>, the maximal expected formation of  $^{13}\text{C}$ -PCDD/Fs from  $^{13}\text{C}$ -PeCP in the compost would have been ten times the actual detection limit, assuming conditions are alike.

The divergent starting levels of PCDD/Fs in the parallel but distinct #4 and #5 (Figs. 5 and 7) are explained by different content of PCDD/Fs in the material added to the composts. To #5 was added some grass that had 5 – 20 times the PCDD/F concentration of the other samples. That sample was taken from the deposition area of a local MSW incinerator, and it was of the first cut of the season. A small increase in the percentage of dry matter to total wet weight (from 19% to 28%) is seen, concomitant with a decrease in total dry weight (18 – 32% loss). Accordingly, the pronounced decrease in compost volume is mainly due increased density.

## Conclusions

As to the formation of PCDD/Fs, the five garden composts have several characteristics in common. However, each compost show some unique features. The increase was two- to tenfold depending on the PCDD/F congener, noticeably the higher chlorinated ones. Some new congeners appear, a few disappear, and several remain unchanged. The increase in toxicity load from the higher PCDD/Fs varies from none to three times.

The increase of PCDD/F levels in the compost is not due to dry and wet deposition, as calculated on background levels and deposition of PCDD/Fs<sup>12</sup>. That will only explain a few percent of the increase over nine months in #1. Direct analyses show that this time-dependent increase cannot be explained by dioxin contamination of the PeCP used, nor by loss of organic matter (release of CO<sub>2</sub>). According to our results the formation of PCDD/Fs occurs *de novo*

from precursors in the compost. So far we have not been able to identify any chloroorganic precursors in the compost. However, we found a significant increase in  $^{13}\text{C}$ -PCDD/Fs when sewage sludge was spiked with  $^{13}\text{C}$ -chlorophenol. Other chloroorganic precursors like predioxins and diphenyl ethers might be present in the compost. When continuing compost studies along these lines, one certainly needs to find the important parameters that governs the formation of PCDD/Fs, whether the process is physico-chemical or biogenic.

Thermal and metabolic processes are the most likely to be involved in the *de novo* formation. Several peroxidase-rich lignin-degrading micro-organisms are active in composting processes e.g., bacteria like Actinomycetes (*Streptomyces*, *Rhodococcus*) and white rot fungi like Basidiomycetes (*Phanerochaete chrysosporium*). On the other hand, some of these micro-organisms are currently used to bioremediate chloroorganic pollutants in soil and ground water. Therefore, the time-weighted mass-balance of input, formation, degradation and output of environmental pollutants in sewage sludge and compost might be exceedingly complex to estimate. In conclusion, the processes has to be understood in greater detail to be able to answer the question whether the activated sewage sludge and composting processes are for the good or the bad in respect to reducing or spreading haloorganic environmental pollutants.

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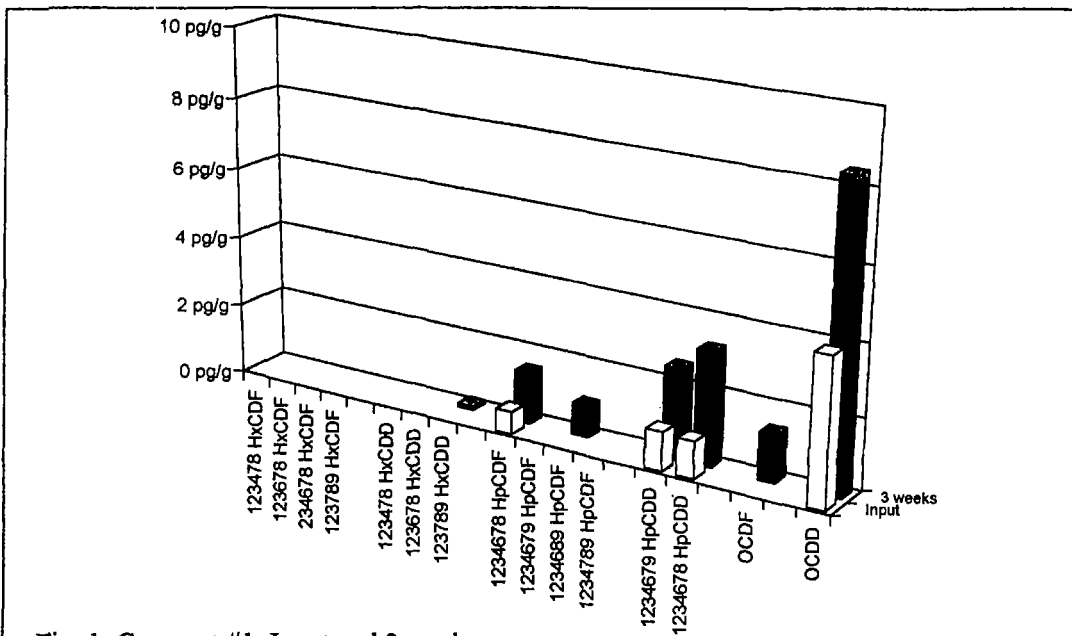


Fig. 1. Compost #1. Input and 3 weeks

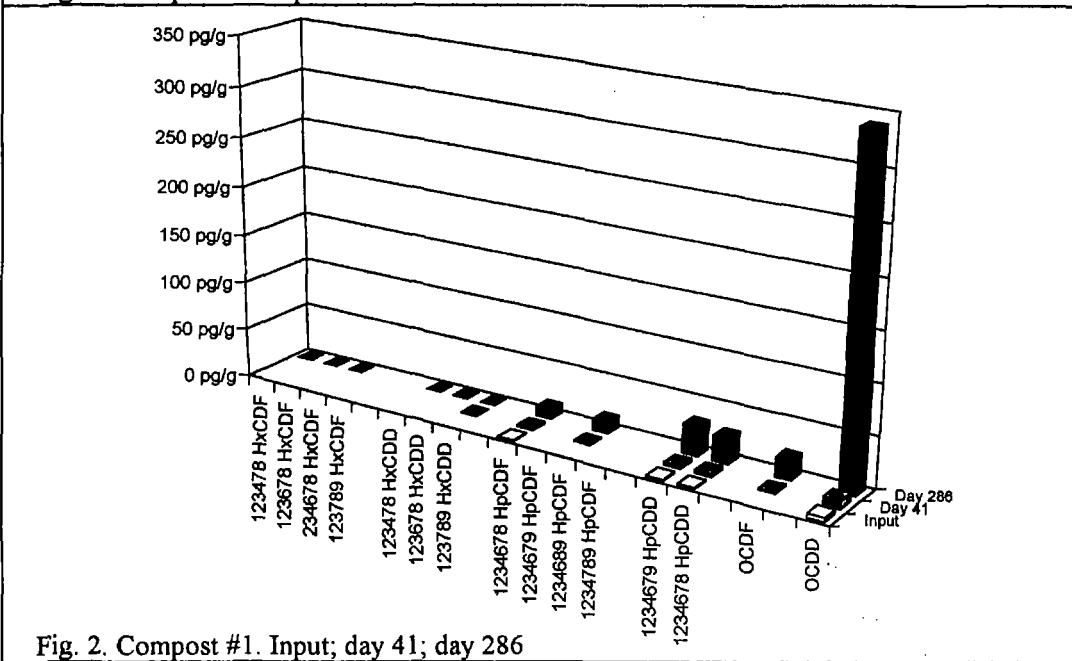


Fig. 2. Compost #1. Input; day 41; day 286

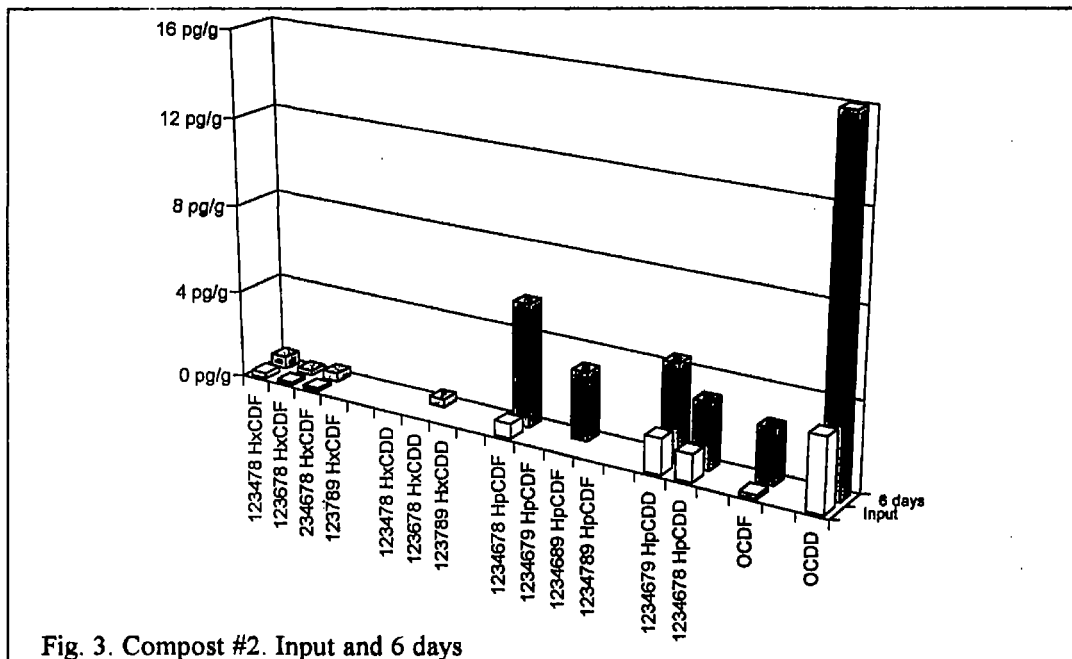


Fig. 3. Compost #2. Input and 6 days

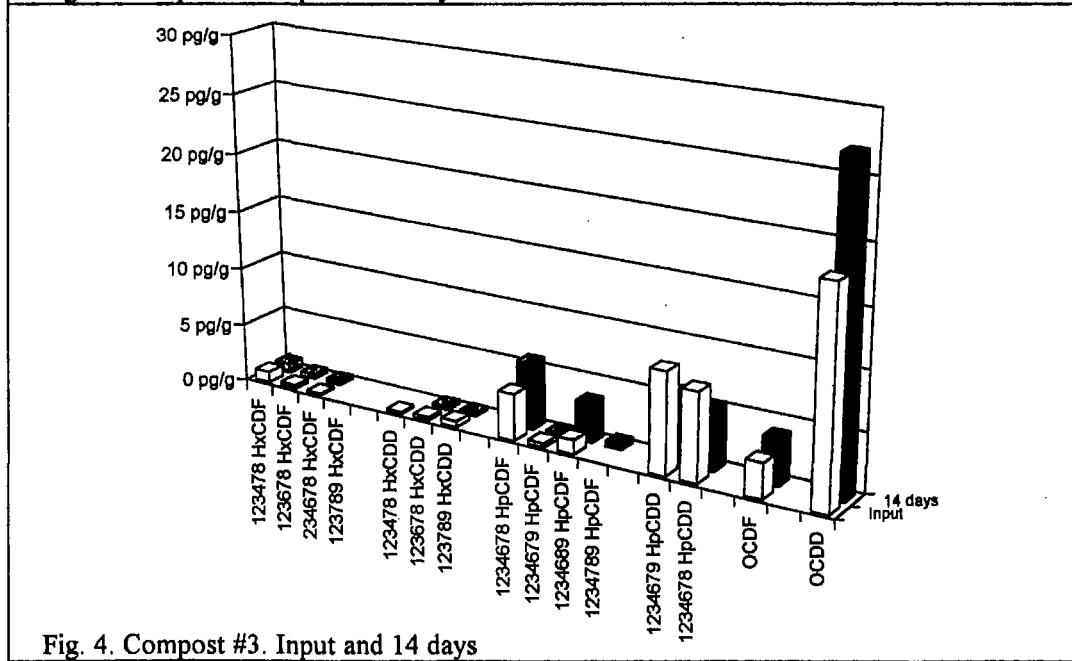


Fig. 4. Compost #3. Input and 14 days

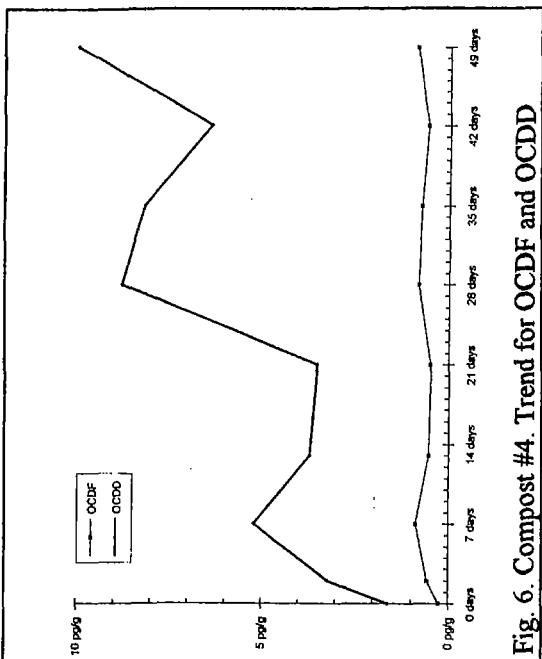


Fig. 6. Compost #4. Trend for OCDF and OCDD

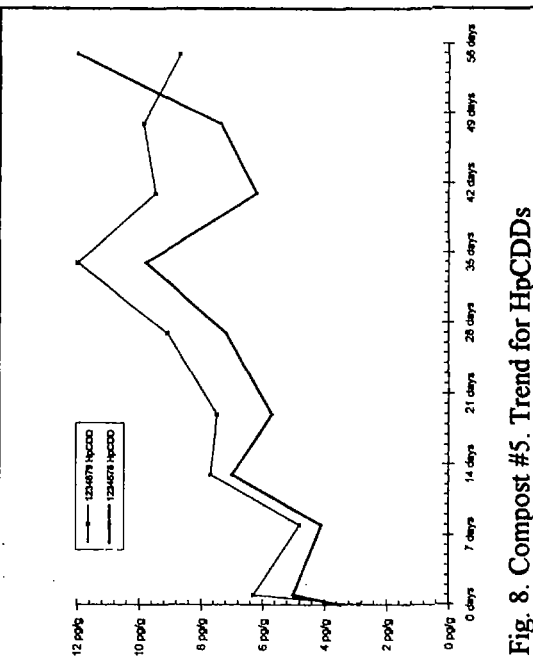


Fig. 8. Compost #5. Trend for HpCDDs

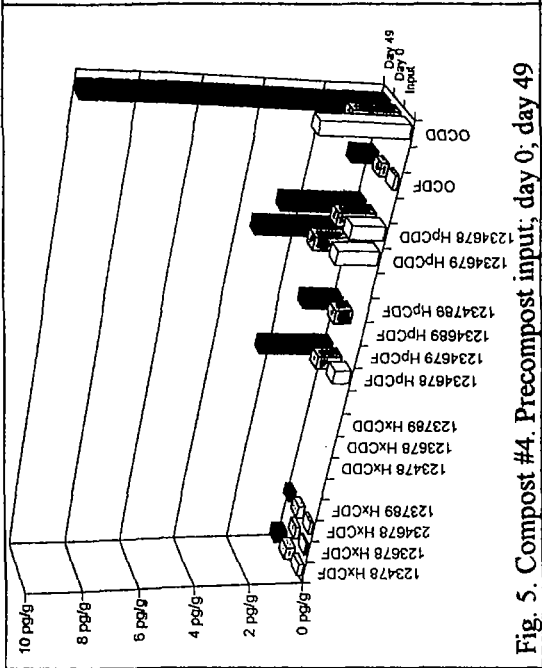


Fig. 5. Compost #4. Precompost input; day 0; day 49

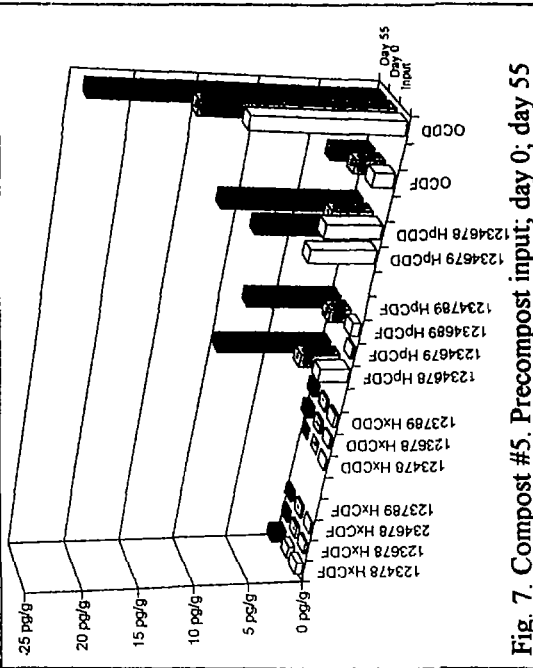


Fig. 7. Compost #5. Precompost input; day 0; day 55