Formation of Octa- and Heptachlorodibenzo-p-dioxins During Semi Anaerobic Digestion of Sewage Sludge

Schramm, K.-W., Klimm, C., Henkelmann, K., Kettrup, A.
GSF - Forschungszentrum für Umwelt und Gesundheit
Institut für Ökologische Chemie
Ingolstädter Landstr. 1, D - 85764 Oberschleißheim, Germany

Abstract

Octa- and heptachlorodibenzo-p-dioxins (OCDD and HpCDD) are formed during semi anaerobic digestion of sewage sludge at low temperature (20°C). A twofold increase of OCDD and HpCDD is found after a digestion period of 192 days even if concentrations are corrected by corresponding accumulation factors caused by the degradation of biomass. Other polychlorinated dibenzo-p-dioxins and furans (PCDD/F) are not increased. Under strictly anaerobic conditions, however, no OCDD and HpCDD are formed. Semi anaerobic formation of OCDD and HpCDD may explain the prevalence of higher chlorinated PCDD in the homologues pattern typical for sewage sludge.

Introduction

Microbial formation of PCDD/F in sewage sludge has recently become an important subject of investigation. Both aerobic and anaerobic processes have been of major scientific interest. Under aerobic conditions the enzymatic transformation of chlorophenols to PCDD/F by peroxidases has been demonstrated *in vitro*[1]. Furthermore it has been found that OCDD and HpCDD are formed in activated sludge in the presence of the precursor pentachlorophenol[2]. Obviously the anaerobic process is a more complicated one. Though some authors described an increase of PCDD/F concentration during anaerobic digestion[3] others could not confirm any significant biogenic formation of PCDD/F under strictly anaerobic conditions[4]. These results may be explained by differences in the exclusion of oxygen during anaerobic digestion. Traces of oxygen do not disturb digesting processes on the whole but may be responsible for partially aerobic metabolism. So the idea of this study was to compare anaerobic sludge digestion under strictly anaerobic with semi (not completely) anaerobic conditions. Semi anaerobic fermentation processes are of great environmental importance e.g. in anaerobic/aerobic surface layers of sediments. Conditions which are neither completely anaerobic nor aerobic may also occur in sewerage systems and open sludge digestion tanks of several sewage treatment plants.

Experimental

Sewage sludge was collected from a municipal sewage treatment plant in Sachsen-Anhalt, Germany. The digested sludge of this plant was known to be highly impacted with PCDD/F (500 ng I-TEQ/kg dwt). The plant's special feature was its anaerobic, psychrophilic digestion in open tanks. For the experiments raw and digested sludge samples were mixed at a ratio of 1:1. This high inoculate guaranteed the immediate initiation of psychrophilic fermentation.

The semi anaerobic fermentation was carried out in a 10 L wide mouth bottle which was covered with aluminium-foil to be pervious to air. For the digestion under strictly anaerobic conditions the bottle was sealed airtight with a bubble counter. In both experiments 7 L of sludge mixture were digested in the dark at 20°C without stirring. The first two samples of each experiment were taken fortnightly. The other sample intervals were approximately a month. Under strictly anaerobic conditions the formation of biogas finished after 96 days with the last sample taken after 100 days. Semi anaerobic fermentation was stopped after 192 days for the last sample.

Before taking samples at a volume of 1 L fermenter bottles were closed with a glass stopper and shaken rapidly for 5 minutes. The sludge samples were frozen and lyophilised at once and finally ground. Dried and homogenised samples were stored at room temperature in the dark. To minimise mean variation of measurements all samples of one experiment were worked up for quantification simultaneously in a single analytic series. The procedure of extraction, clean-up and analysis of PCDD/F was done by reported methods[5] and is briefly described in the following.

A $^{13}C_{12}$-labelled internal standard mixture of sixteen 2,3,7,8-substituted PCDD/F was added to 10 g of dried and homogenised sample. After Soxhlet extraction of sample with toluene for 24 hours the raw extract was treated with multi column chromatography method. This clean-up combines a set of 4 established chromatographic steps in series, first chromatography on silica, secondly activated alumina, thirdly sulphuric acid coated silica gel and at last deactivated florisil™. Before quantification by high-resolution GC/MS the sample was spiked with a recovery standard. After splitless injection the sample was separated on a Rt_x-2330 GC column (60m x 0.25mm x 0.25µm) and quantified by Finnigan MAT 95 mass spectrometer at resolution 10000.

Results

Percentual change in concentrations of PCDD/F and ignition residues during semi anaerobic digestion of sewage sludge at 20°C is represented in Fig. 1. There was a great increase of OCDD and HpCDD after a lag period of 30 days. Both 1,2,3,4,6,7,8-and 1,2,3,4,6,7,9-HpCDD were formed in equivalent

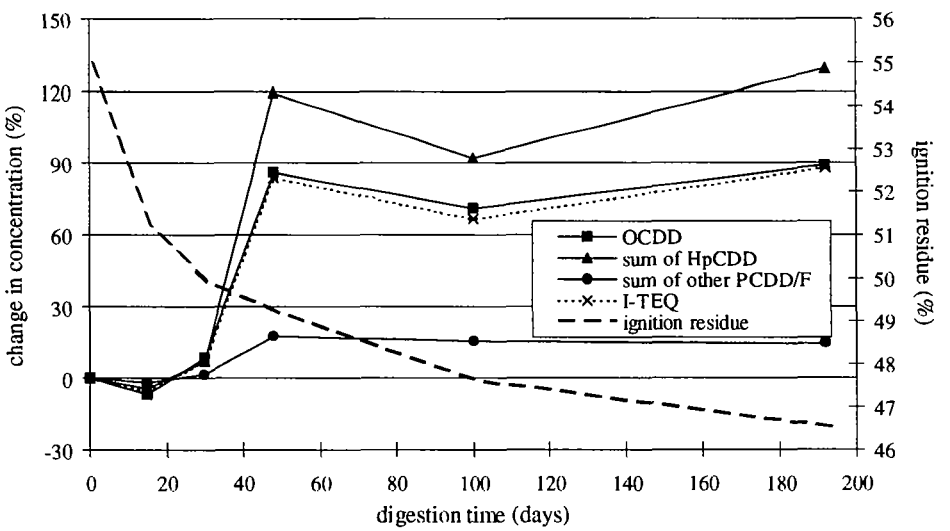

Fig. 1: Percentual change in concentrations of PCDD/F and ignition residues during semi anaerobic sludge digestion over 192 days at 20°C.

amounts. Simultaneously the degradation of biomass was highest. After 192 days of digestion the degree of mineralisation reached a total of 15%. Taking into account the accumulation factor caused by the degradation of biomass there was an approximately twofold increase of OCDD (75%) and HpCDD (105%). Besides this the sum of the other PCDD/F, however, did not seem to change. I-TEQ increased correspondingly to the formation of HpCDD and OCDD.

In Fig. 2 the strictly anaerobic digestion is shown. Compared with the semi anaerobic experiment there was no significant change of neither OCDD nor HpCDD nor the sum of other PCDD/F after a digestion period of 96 days. After this period the degree of mineralisation reached a total of 12%. It can be expected that after 200 days the degree of mineralisation would have reached a similar value as for the semi anaerobic experiment.

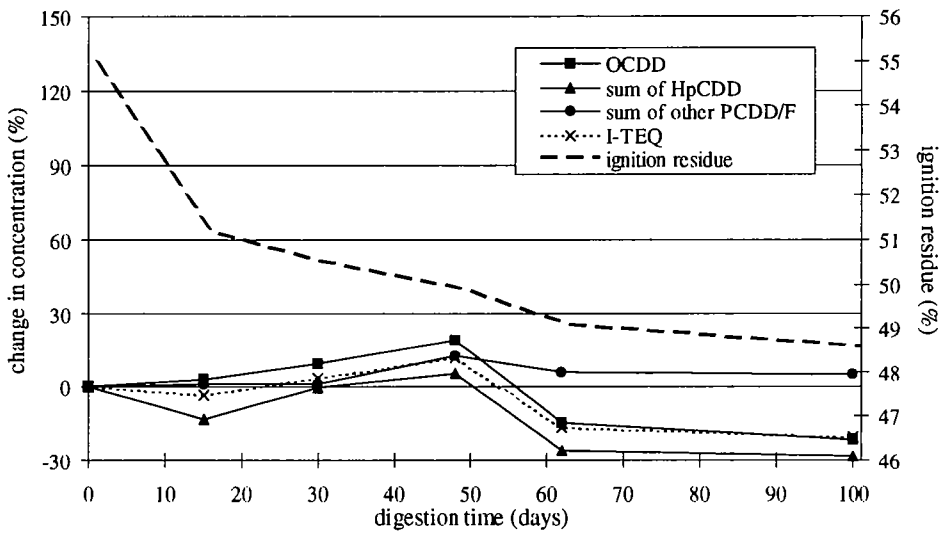

Fig. 2: Percentual change in concentrations of PCDD/F and ignition residues during strictly anaerobic sludge digestion over 100 days at 20°C.

Conclusions

The origin of PCDD/F in sewage sludge is up to now not completely understood. Degradation and formation of PCDD/F especially by micro-organisms are therefore of broad scientific interest. Öberg et al.[2] for example demonstrated aerobic formation of OCDD and HpCDD in activated sludge with the precursor pentachlorophenol. It was discussed that this transformation is likely to be caused by biologic activity although abiotic factors could not definitely be ruled out.

In the present paper it is also shown that dominantly OCDD and HpCDD are formed during semi anaerobic digestion of sewage sludge. Although no precursors were added to the experiments it is most likely that the digested sludge contained chlorinated organic compounds. We suppose that the reasons for formation of OCDD and HpCDD under semi anaerobic conditions are similar to those discussed for aerobic conditions, i.e. aerobic microbial activity. Moreover this is consistent with our findings that no OCDD and HpCDD are formed under strictly anaerobic conditions.

Biogenic formation processes which were found in both aerobic and semi anaerobic experiments may explain the prevalence of OCDD and HpCDD in the homologues pattern typical for sewage sludge.

Further investigation on this subject will lead to a profound understanding of the microbial processes and even to a minimisation of PCDD/F in sewage sludge.

References

1) Öberg, L.G., C. Rappe (1992): *Biochemical formation of PCDD/Fs from chlorophenols.* Chemosphere 25, 49–52.

2) Öberg, L.G., R. Andersson, C. Rappe (1992): *De novo formation of hepta- and octachlorodibenzo-p-dioxins from pentachlorophenol in municipal sewage sludge.* in: Organohalogen Compounds, Vol 9, Dioxin '92, Tampere, ISBN 951-801-933-9, 351–354.

3) Hengstmann, R., R. Hamann, H. Weber, A. Kettrup (1990): *Impact of sewage sludge and sewer slimes by polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans.* in: Organohalogen Compounds, Vol 4, Dioxin '90, Bayreuth, 407–409.

4) Weber, H., G. Disse, R. Hamann, H.-J. Haupt, (1995): *Influence of the aerobic and anaerobic digestion on the levels of chlorinated dibenzofurans and dibenzodioxins in sewage sludge.* in: Organohalogen Compounds, Vol 24, Dioxin '95, Edmonton, ISBN 3-928379-44-5, 81–85.

5) Schramm, K.-W., M. Merk, B. Henkelmann, A. Kettrup (1995): *Leaching of PCDD/F from fly ash and soil with fire-extinguishing water.* Chemosphere 30, 2249–2257.