FATE OF PCB (CLOPHEN A50) DURING ANAEROBIC TREATMENT OF ORGANIC HOUSEHOLD WASTE

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Introduction

In a previous study we have reported an apparent production of bioassay-measured dioxin-like compounds during anaerobic mesophilic or thermophilic degradation of source-separated organic household waste[1]. This may be due to de novo synthesis or to an increase in the dioxin-like potency of compounds in the material. One theory is that PCBs in the waste may be dechlorinated to more potent dioxin-like congeners during thermophilic and mesophilic anaerobic treatment. Degradation of halogenated aromatic compounds can occur through two different reactions, oxidative or reductive dehalogenation, depending on the environment[2]. Aerobic microorganisms can only dechlorinate biphenyls with less than five chlorines[2,3]. By biodegradation the PCB mixtures may be altered in the congeners composition which can result in change in the toxicity. The oxidative process involves loss of halogens during oxidation of the aromatic ring. The reductive process occurs only under anaerobic conditions and involves substitution of halogens by hydrogens. The reductive substitution is done by anaerobic microorganisms that are able to attack PCBs[4,5,6]. The process is based on the metabolic activities of anaerobic bacteria where they remove chlorines directly from biphenyl and replace them with hydrogens. This can also be performed on highly chlorinated biphenyls[4]. To test the dechlorination theory, we examined the changes in the composition of PCB congeners in samples of source-separated organic household waste spiked with Clophen A50 during anaerobic treatment.

Our hypothesis was that the numbers of substituted chlorines in the Clophen A50 mixture would decrease over time in the samples because of anaerobic microbial reductive dechlorination. Therefore more low chlorinated congeners would be found in the samples at the end of the incubation time. In addition, the higher microbial activity in the thermophilic process (higher temperature) would result in more effective degradation.

Material and methods

Biodegradation

Sub-samples of 12 tons source-separated organic household waste from Uppsala, Sweden, collected in spring 1995 were used in this study. The anaerobic degradation occurred in two semi-continuos digesters (45 L) who were operating at mesophilic (37 °C) and thermophilic (55 °C) temperatures. From the mesophilic reactor 48.8 g digested household waste was added to 2.4 g new substrate and from the thermophilic reactor 46 g digested household waste was added to 4 g new substrate. This is the same proportion as in the reactors where 700 ml household waste is added each day to the mesophilic reactor and 1300 ml is added to the thermophilic reactor. Samples of 50 ml were placed in serum bottles capped with butyl rubber stoppers. To each bottle Clophen A50 was added to a concentration of 1.2 mg/ml. The samples were incubated in 37 °C (mesophilic degradation) for up to 60

days and in 55 °C (thermophilic degradation) for up to 40 days. In order to obtain time-dependent information about the degradation, bottles were taken out and frozen during the incubation time.

Analysis

The samples were soxhlet extracted using toluene (24 hours). Dean-Stark water traps were used to remove water present in the samples. For clean-up, a multilayer silica column (1 mm i.d., 340 mm length) was used. Layers from top to bottom were 1 cm anhydrous Na_2SO_4 , 1cm neutral silica gel, 1.5 cm 20 % H_2SO_4 silica gel, 3 cm 40 % H_2SO_4 silica gel, 0.5 cm neutral silica gel, 3 cm KOH silica gel and some glass wool. To elute the spiked (^{13}C PCB 105/118) extracts, 80 ml hexane was used. All samples were further cleaned up by elution through mini silica gel columns packed with 1 cm KOH-impregnated silica gel and 1 cm 40 % H_2SO_4 -impregnated silica gel in Pasteur pipettes with n-hexane. Finally, a clean up with SPE (solid phase extraction) using aminosilica (Supelco LC-NH2 SPE Tubes, 3 ml) and n-hexane as mobile phase was done on the samples. Calculations from earlier experiments indicated that aliphatic compounds and monoaromatics would elute in fraction one (0- 0.2 ml), diaromatics (including PCBs) in fraction three to six (0.7- 2.7 ml). The calculations were tested on a sample with Clophen A50 (200 ml) and real sample. The impurities eluted in fractions one to three (0- 1.2 ml) so for GC/MS analysis a fraction 1.2- 4.2 ml was used. A standard with Clophen A50 (Dr. Ehrenstorfer, 10 ng/ml cyclohexane), IS and RS was analysed in GC/MS to identify the PCB congeners in the samples. As control samples four blanks with IS and RS and a non PCB spiked series (DMSO) with only IS and RS were used. The analysis was performed on an Agilent (HP 6890 Series) gas chromatograph equipped with a DB-5 fused-silica column (30 m*0.25 mm HP, 5 % phenyl methyl siloxane. The oven temperature program was 180 °C (2 min), 15 °C min-1 to 205 °C, 4 °C min-1 to 290 °C, isothermal for 2 minutes. When analysing the specific chromatograms of each congener group, the two most abundant masses of the chlorine cluster were monitored.

Results and discussion

In both the thermophilic and the mesophilic processes the total concentration of the tetra- to hexa CBs decreased over time. The thermophilic samples changed PCB concentrations from day 0 to day 40; tetra CBs from 170 to 122 ng/ml, penta CBs from 313 to 217 ng/ml and hexa CBs from 63 to 51 ng/ml (figure 1). No reduction was observed in the concentration of hepta CBs (7 ng/ml). The changes in PCB concentration in the thermophilic reaction correspond to a reduction of 28 % for tetra CBs, 31 % for penta CBs and 21 % for hexa CBs. In the mesophilic reaction concentration decreased from day 7 to day 60. The tetra CBs decreased from 118 to 116 ng/ml, penta CBs from 330 to 203 ng/ml of, hexa CBs from 79 to 43 and hepta from 14 to 5 ng/ml (figure 2). The mesophilic reduction was 3% for tetra CBs, 39 % for penta CBs, 46 % for hexa CBs and 64 % for hepta CBs.

Table 1. PCB congeners of which peak areas were used to calculate the total amounts of PCB congener groups.

PCB groups	PCB congeners
Tetra CBs	52, 44, 72/71/41/64, 76/70 and 60/56
Penta CBs	88/95, 101, 99, 110, 118 and 105/127
Hexa CBs	151, 149, 153, 138, 158, 128, 156 and 157
Hepta CBs	179, 182/187, 183, 170/190 and 189

Totally the thermophilic samples reduced 28% of the initial PCB concentration over 40 days (from day 0 to day 40) which corresponds to 0.7 % reduction a day. The mesophilic samples reduced 33 % over 53 days (from day 7 to day 60) which corresponds to 0.6 % a day. No large difference in dechlorination rates between thermophilic and mesophilic dechlorination could thus be observed. These results indicate that if dechlorination occurs it is not dependent on incubation temperature.

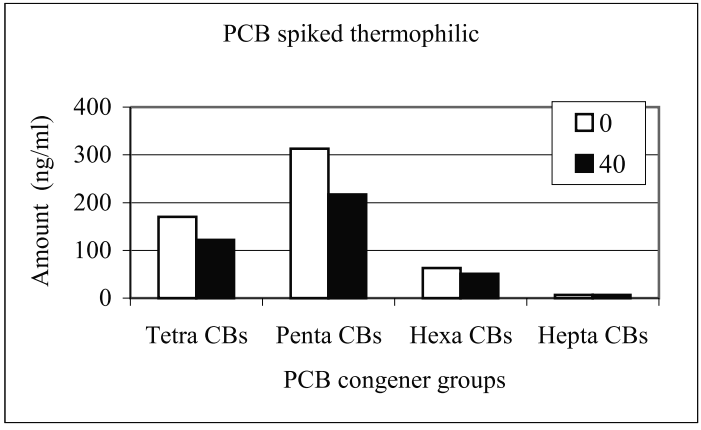

Figure 1. Amounts of different PCB congener groups in the thermophilic samples on day 0 and day 40.

PCB concentrations did not decrease in autoclaved samples incubated in mesophilic and thermophilic temperatures, respectively (data not shown). This strengthens the theory that anaerobic micro-organisms were responsible for the reduction in the mesophilic and thermophilic reactions. The lack of observations in concentration changes of low chlorinated congeners was due to methodological problems, and this makes it impossible to investigate any accumulations of low chlorinated biphenyls. The anaerobic microorganisms in the household waste seemed to have the ability to dechlorinate some of the PCB congeners, though in limited extent. The microorganisms might dechlorinate more effectively after a longer adaptation period.

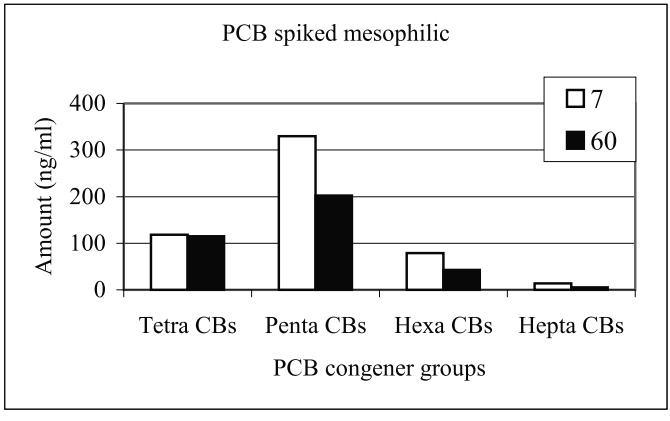

Figure 2. Amounts of different PCB congener groups in the mesophilic samples. Comparison between day 7 and day 60.

Another conclusion of this study is that SPE may be a useful method as a clean-up procedure when analysing complex matrixes such as organic household waste. This method is easy and fast to perform and requires small volumes of organic solvent. Studies are also under way to elucidate if any accumulation of dioxin-like PCB congeners occurs as a result of reductive dechlorination of Clophen A50 in the anaerobic systems described in this abstract. This will be examined using a chick embryo hepatocyte bioassay for dioxin-like compounds.

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