EFFECT OF COCONTAMINANTS AND CONCENTRATION ON THE ANAEROBIC BIOTRANSFORMATION OF PCDD/F IN METHANOGENIC RIVER SEDIMENTS

P. Adriaens and D. Grbic'-Galic'

Department of Civil Engineering, Stanford University, Stanford CA 94305-4020, USA

ABSTRACT

1,2,3,4,6,7,9-Heptachlorinated dioxin (144 µg/kg) was reductively dehalogenated to a hexachlorinated congener in methanogenic Hudson River sediments contaminated with 100 mg/kg of 'weathered' Aroclor® 1242. No lesser chlorinated products were identified from incubations with 144 µg/kg each of 1,2,4,6,8-pentaCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8-HxCDD, and 1,2,4,6,8,9/1,2,4,6,7,9-HxCDD,yet the methanogenic population exhibited dechlorinating activity on the endogenous Aroclor© 1242. The influence of concentration and bioavailability, as well as the presence of highly oxidized cocontaminants on methanogenic transformation of PCDD/F was studied.

INTRODUCTION

Methanogenic bacterial populations have been demonstrated to reductively dehalogenate mg/kg concentrations of polychlorinated biphenyls (PCBs), by using these compounds as alternative 'electron sinks' to CO_2 .[1-4] The source of the hydrogen atom which substitutes for the chlorine on the PCB is the proton from water instead of from the reduced substrate (Fig. 1).[5] Structural similarities between PCBs and PCDD/F invoke the potential for similar dehalogenation mechanisms to occur.

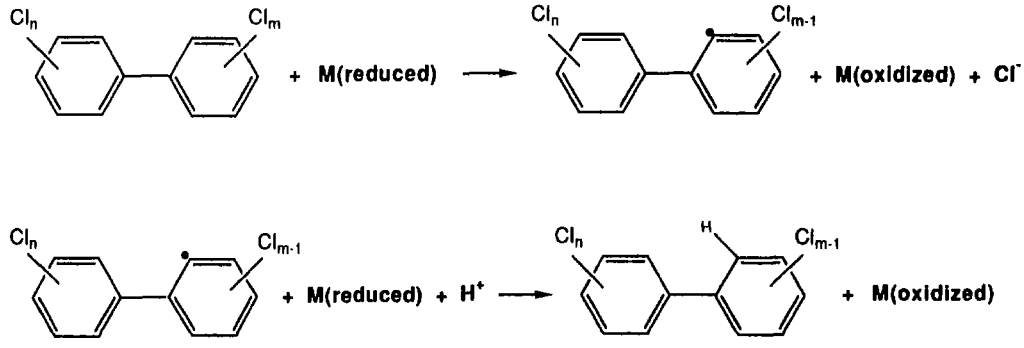

Figure 1: Proposed mechanism for reductive dehalogenation of PCBs: Two step (one electron each step) reduction by an unknown electron donor (M), with a PCB free redical transition state and proton abstraction from solution. Modified from Nies and Vogel. [5]

Substrate disappearance plots of H_xCDD-, H_pCDD- and PentaCDF-spiked Hudson River microcosms indicated that biotransformation at least contributed to the decreased substrate recovery in the active replicates (Figure 2, A-C). After 2 months, approximately 9 µg/kg of hexachlorinated dioxin evolved in the microcosms spiked with HeptaCDD. [6] The concentration of the intermediate decreased to 6 µg/kg after 9 months (Figure 1, D), and no lesser chlorinated congeners resulting from further dehalogenation were detected. [6]

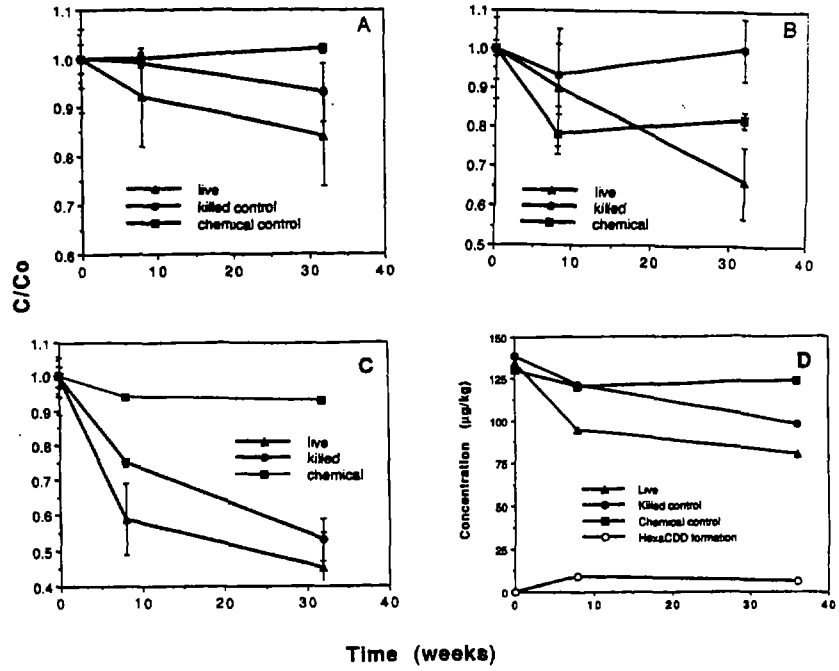

Figure 2: Fate of HxCDD (A), HxCDDI (B), and HpCDD (C) in Hudson River sediments, and product formation in HpCDD spiked microcosms (D). The values for the C/Co plots represent averages of three and two replicates for active microcosms and killed or chemical controls, respectively.

Methanogenic dechlorinating activity in dioxin-contaminated (up to 20 µg/kg 2,3,7,8-TCDD) Passaic River sediments was indicated by the detection of p,p'-DDD, a metabolite formed after reduction of DDT, which was present as a cocontaminant in the sediment.[7]

METHODS

Microcosms containing (34 ± 2) g Hudson River (New York) sediments were established in 125 ml serum bottles, spiked with 144 ± 14 µg/kg of all congeners, except for 1,2,3,4,6,8,9/1,2,3,4,6,7,9-HxCDDI (14.4 ± 1 µg/kg) and incubated at 35°C. Replicate incubations were established as indicated in Fig.2. All microcosms were sampled at regular time intervals, extracted and analyzed for PCDD/F. After 16 months, a total extract of the microcosms was analyzed both for Aroclor© 1242 and PCDD/F. The analytical method was according to Kleopfer et al. [8], except for that octachloronaphthalene was used as an internal standard. Passaic River (New Jersey) samples (4-5 g) were incubated anaerobically with either defined reduced anaerobic medium (20 ml) or reduced river water. Spiked with 10 mg/kg of HpCDD and HpCDF, each time sample analyzed represented a total extract of the microcosm.

RESULTS AND CONCLUSIONS

The analyses of Hudson River extracts spiked with PCDD/F was impeded by interferences in the PCDD/F window (tetra and penta) by the higher chlorinated PCB congeners of Aroclor© 1242. Although most of the interferences could be eliminated by GC-MS analyses of isotopic ratios in the molecular ion cluster, no products were conclusively identified, due to the low signal-to-noise ratios. The recovery of PCDD/F (normalized with respect to octachloronaphthalene), as exemplified for the dioxins, is given in Figure 3. The low extraction efficiencies obtained for all PCDD/F after extended incubation in a relatively high organic carbon inoculum (1.5%) may indicate that the (higher) chlorinated congeners are strongly sorbed and rendered biologically unavailable. None of the PCDD/F congeners other than HpCDD showed accumulation of lesser chlorinated isomers, although all decreased over time relative to the killed controls.

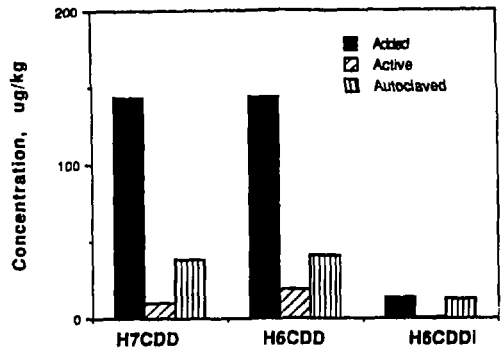

Figure 3: PCDD added to and recovered from final Hudson River extracts after a 16 month incubation period.

This may be explained by the presence of 'weathered' Aroclor© 1242 as an alternative electron acceptor. Since a mixture of fatty acids was added to the microcosms to augment the indigenous methanogenic populations, the already dechlorinated Aroclor© 1242 (B) was further dehalogenated, resulting in the accumulation of di- and trichlorobiphenyls at the expense of tetra- and pentachlorinated congeners (C). The distribution of PCB homologs in an Aroclor© 1242 standard, in the 'weathered' Aroclor© 1242 present in Hudson River sediments (time 0), and in the active microcosms after 16 months, is shown in Figure 4. Assuming the same populations are responsible for dechlorinating activity on PCDD/F and PCBs, a threshold value might be invoked below which no dehalogenation occurs. To test this hypothesis, Passaic River microcosms were spiked with 10 mg/kg of HpCDD and HpCDF, but data were not available at the time of this abstract.

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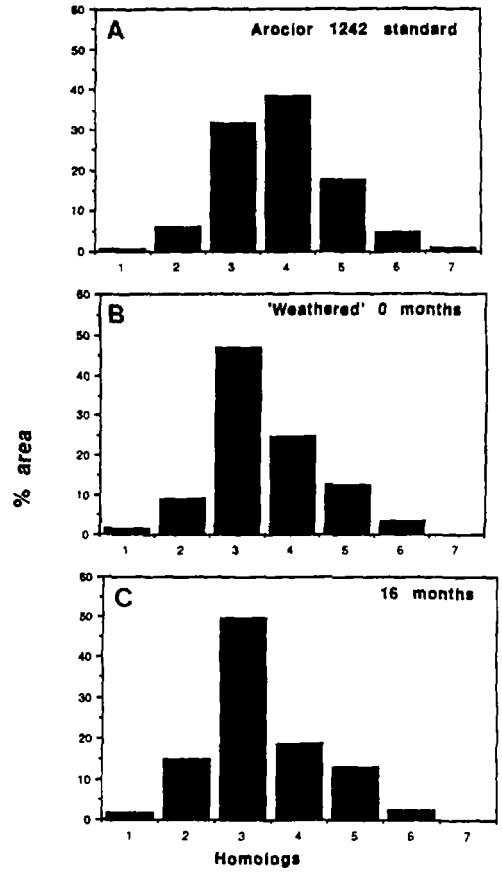

Figure 4: PCB homolog profile of an Aroclor© 1242 standard (A), and Hudson River sediment inoculated microcosms at time 0 (B), and after 16 months (C).