

REDUCTIVE DECHLORINATION OF PCDD/F BY ANAEROBIC CULTURES AND SEDIMENTS

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INTRODUCTION

Whereas the widespread distribution of PCDD/F in the different environmental compartments has been recognized, little is known about their fate in the ultimate environmental sinks, soils and sediments. In particular, the susceptibility of PCDD/F to biological oxidation and reduction reactions has only recently received (limited) attention.

Reductive dehalogenation of organohalogen compounds is mainly a cometabolic process whereby a fraction of the electrons generated during oxidation of the microbial growth substrate fortuitously reduce the highly oxidized (i.e. chlorinated) compounds, resulting in a sequential dechlorination reaction. This mechanism has been shown to be dependent on concentration and bioavailability of the organohalogen, and can be stimulated by amendment with simple organic growth substrates. Thus, reductive dehalogenation of PCBs has been demonstrated to occur in previously contaminated Hudson River sediments, and in methanogenic microcosms containing pristine or adapted sediments, spiked with either Aroclor mixtures or individual PCB congeners¹⁻³. The PCB-molecule is preferentially dechlorinated at the *meta*- or *para*- position.

APPROACH

Because of the structural similarity between dioxins or furans and PCBs, the potential for susceptibility of the PCDD/F to reductive dehalogenation processes was investigated. Previously, it was demonstrated that 1,2,3,4,6,7,8-HeptaCDD was dechlorinated to two hexachlorinated isomers in microcosms inoculated with aquifer material, 1,2,3,4,7,8- and 1,2,3,6,7,8-HexaCDD, respectively⁴. The extensive removal of the peri-chlorines of the HeptaCDD congener, resulting in an enrichment in 2,3,7,8-chlorinated congeners is similar to what was found during photolysis (6). Moreover, it was found that higher concentrations of co-contaminants such as PCBs may compete for electrons generated during growth⁵.

The fate of selected highly chlorinated dibenzo-*p*-dioxins and dibenzofurans was studied in PCB-contaminated Hudson River sediments, dioxin-contaminated aquifer samples (Pensacola, FL), and dichlorophenol-enriched suspended cultures. All samples were incubated anaerobically at 35 °C

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under reduced conditions which promote the growth of methanogenic populations and which have been shown to be conducive for reductive dechlorination to occur. The samples were spiked with $144 \pm 14 \mu\text{g/kg}$ of 1,2,3,4,7,8-HexaCDD; 1,2,4,6,8,9/1,2,4,6,7,9-HexaCDD; 1,2,3,4,6,7,8-HeptaCDD; 1,2,4,6,8-PentaCDF; and 1,2,3,4,6,7,8-HeptaCDF.

RESULTS AND DISCUSSION

The fate of the spiked PCDD/F (except for 1,2,4,6,8,9/1,2,4,6,7,9-H_xCDD) in anaerobic sediments and soils (expressed as C/C_0) is shown in Figure 1. All time samples for the active microcosms represent an average of three replicates, whereas those for chemical (no inoculum) and autoclaved controls represent two replicates. In all cases are the losses over time in the chemical controls negligible compared to the other treatments. However, the disappearance of PCDD/F in the autoclaved controls is in most cases nearly as extensive as that in the active microcosms, indicating the importance of sorption processes during the incubation period. The total decrease of PCDD/F appears to be slightly less in the low organic carbon (0.02%) aquifer samples, when compared to the 7-8% organic carbon Hudson River sediment samples.

The first-order rate constants for disappearance, calculated from $\log(C/C_0)$ plots, are given in Table 1. The net rates calculated indicate that the biological component increased the rate of PCDD/F disappearance by 15 to 35%, dependent on the PCDD/F isomer spiked and the inoculum used.

Table 1. First-order Disappearance Rates of PCDD/F in Hudson River Sediment and Aquifer Material Inoculated Microcosms

PCDD/F Congener	Inoculum	Rate* ($\times 10^{-2} \text{ wk}^{-1}$)		
		Active	Autoclaved	Net Rate (%)
HpCDD	HR	2.81 ± 0.07	2.38 ± 0.14	0.43 ± 0.14 (15)
	PS	3.44 ± 0.10	2.19 ± 0.02	1.25 ± 0.10 (36)
HxCDD	HR	4.56 ± 0.30	3.19 ± 0.09	1.37 ± 0.30 (30)
	PS	2.48 ± 0.13	1.85 ± 0.16	0.63 ± 0.16 (25)
HxCDDi	HR	4.00 ± 0.16	4.13 ± 0.14	(-0.13 ± 0.16)
	PS	ND	ND	ND
HpCDF	HR	4.13 ± 0.10	3.56 ± 0.05	0.57 ± 0.10 (14)
	PS	4.88 ± 0.06	3.13 ± 0.01	1.75 ± 0.06 (36)
PentaCDF	HR**	2.69 ± 0.40	1.06 ± 0.02	1.63 ± 0.40 (60)
	PS	1.54 ± 0.10	1.23 ± 0.02	0.31 ± 0.10 (20)

* $n = 6-12$

** Not in 95% Confidence interval.

No disappearance data over time are available for the chlorophenol-enriched suspended cultures. Analysis of microcosms incubated with 1,2,4,6,8-pentaCDF after a 6 month incubation period, showed the appearance of several tetrachlorinated isomers (Figure 2).

C/Co

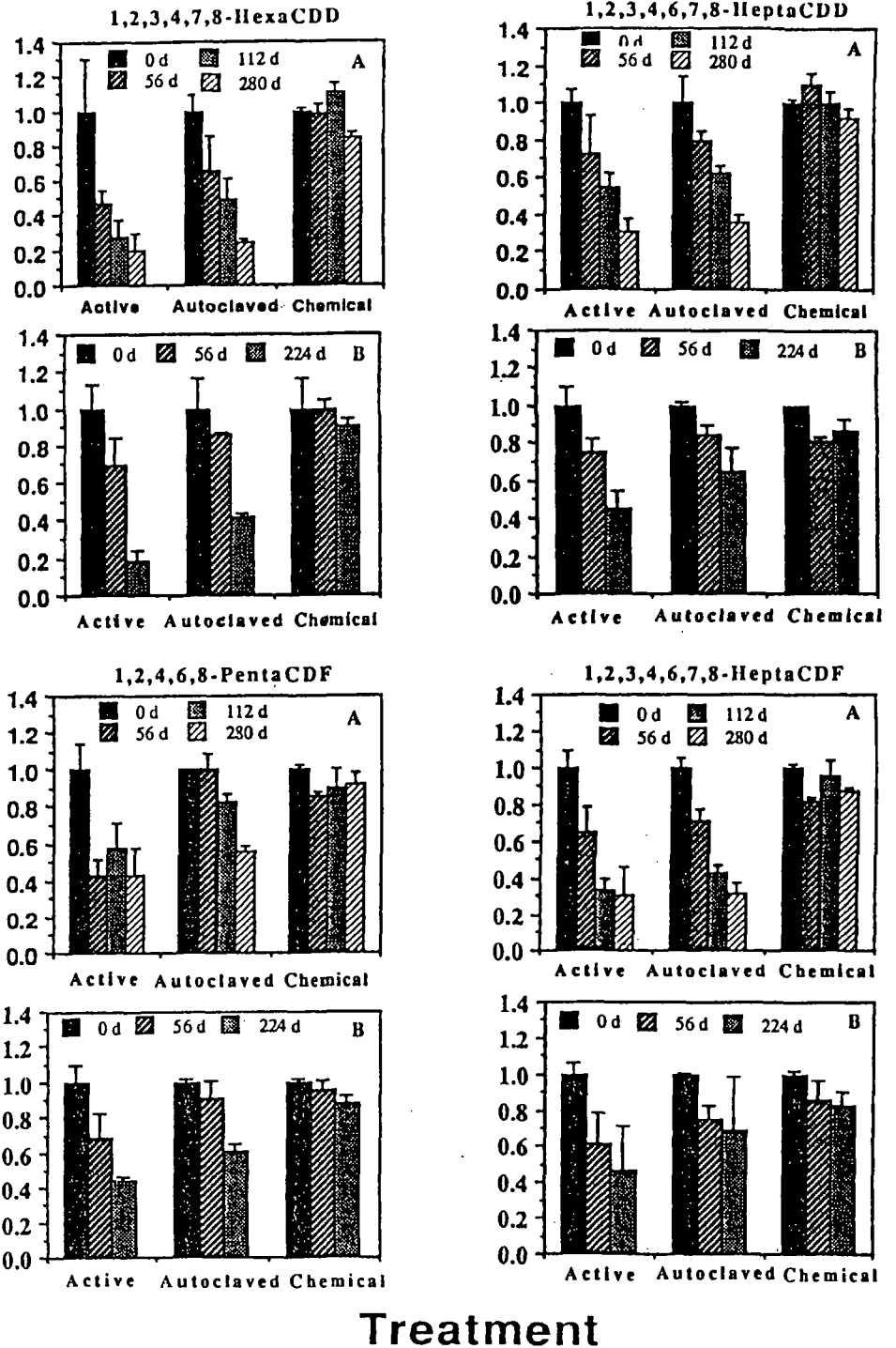
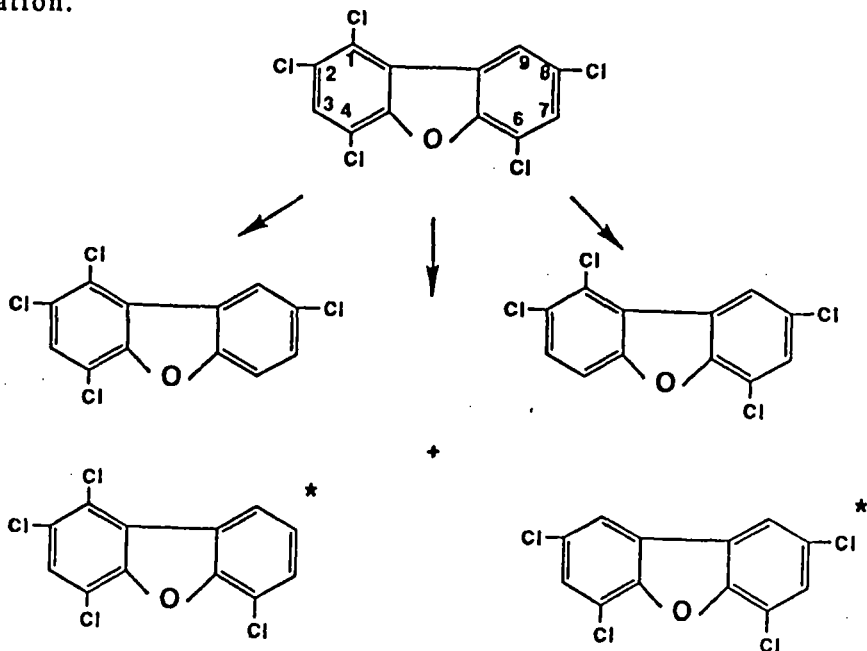


Figure 1: Fate of Selected PCDD and PCDF in Hudson River Sediments (A) and Pensacola Aquifer material (B)

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Tentative identification of the products indicate that peri-dechlorination was the preferential route of reduction, as has been observed with heptaCDD in aquifer microcosms. This observation is contrary to photolysis of PCDF, which results in preferential removal of the lateral chlorines.

Whether this is due to the type of dechlorination mechanism, or the choice of the pentachlorinated isomer chosen in this study obviates further investigation.



* Note: Marked congeners coelute

Figure 2. Proposed Dechlorination of 1,2,4,6,8-PentaCDF by Suspended Dichlorophenol-Enriched Cultures.

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