

Reductive Dechlorination of Polychlorinated Dioxins by Humic Materials Under Reducing Conditions

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Introduction

Because of their high toxicity and suspected genotoxic potential, the fate and transformations of polychlorinated dioxins (PCDDs) in the environment are of great interest. It was shown previously that spiked PCDD could be dechlorinated when incubated with soils, sediments and sediment-derived microbial communities under reducing conditions (1-7). Abiotic reductive dechlorination of PCDDs with variety of reducing agents has also been demonstrated (8). Natural organic matter such as humic materials has been shown to facilitate electron transfer in reductive reactions (9). Hydroquinone/quinone type couples are hypothesized to dominate the redox properties of humic acid with hydroquinone groups as the reactive sites for electron transfer (10). For example, it has recently been shown that quinonic compounds such as catechol and resorcinol can effectively mediate dechlorination of PCDDs under reducing conditions (11). It is environmentally more relevant, however, to determine the effect of macromolecular humic materials on the dechlorination of PCDDs. In this study, we investigated the dechlorination of 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin (heptaCDD) with one humic acid and one model fulvic acid. The major goals of this research were (i) to investigate whether PCDDs can be reductively dechlorinated with humic acid materials under reducing conditions; and (ii) to correlate humic acid structure characteristics to the kinetics and product distribution of dechlorination of PCDDs.

Material and Methods

Chemicals and Stock Solutions. A commercial humic acid (AHA) (Aldrich Chemical Co., Milwaukee, WI), was purified according to a published procedure (12). Polymaleic acid (PMA) was synthesized according to a procedure described by Spittler and Schnitzer (13). Stock solutions were prepared by dissolving these materials in deionized water with 2 ml of 0.1 M NaOH solution under nitrogen atmosphere, adjusting the pH to 7 with 1 M HCl, and filtering the solutions through 0.45- μ m membrane filters (Gelman Science). The stock solutions were then purged with N₂ to remove oxygen from solution and headspace and used immediately. The chemical properties of the natural and synthetic organic macromolecules are included in Table 1 in the results and discussion section.

1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin (heptaCDD) was obtained from AccuStandard Inc. (New Haven, CT).

Tris buffer of 0.5 M was prepared according to the manufacture instructions (Sigma Chemical Co.). Titanium citrate stock solution of 0.1 M was prepared in an anaerobic chamber by dissolving sodium citrate in 0.5 M Tris buffer to make the concentration of 0.2 M sodium citrate and adding 15 ml 20% TiCl₃ solution (Fisher Scientific) to 200 ml of citrate-buffer solution. The titanium citrate stock solution was stored under dark in the

anaerobic chamber under room temperature. The anaerobic chamber was filled with a gas mix of hydrogen (5%), carbon dioxide (10%) and balanced with nitrogen.

Experimental Procedures. Experiments were conducted in 20-ml serum bottles. The bottles were capped with Teflon coated red rubber stoppers (The West Company, Lionville, PA) and sealed with aluminum crimps. The control solution was prepared to measure the disappearance of starting compound or the appearance of products in the absence of either AHA or PMA. A typical set up of a reaction vial contains anaerobic buffer medium (5 ml), heptaCDD (0.24 μ M), catalytic amount of either AHA or PMA, and bulk electron donor agent, titanium citrate (III) in excess. The experimental reaction vials were set up in the anaerobic chamber and agitated (270 rpm) under dark at room temperature. Triplicate of reaction vials were sacrificed for analysis of dioxin congeners after 0, 1, 2, 3 months of agitation.

Analytical Procedures. 100 μ l of 5 ppm 1,2,3,4,6,7,9-octachlorofuran was added to the reaction vials as the internal standard before extraction. Samples were then extracted with hexane (3x4 ml) and the extract was evaporated under a gentle stream of nitrogen gas. Toluene of 100 μ l was added and analyzed for mono- to heptaCDDs using a 5890-II Hewlett-Packard GC-MS equipped with a 5972A mass selective detector. Samples were analyzed with selective ion monitoring. The operating parameters and procedures were similar to one described by Barkovskii and Adriaens (5).

Results and Discussion

Reaction Kinetics. Reduction of 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin under reducing condition with the humic acid AHA and model fulvic acid PMA were observed with titanium citrate (III) as bulk electron donor. A $\ln(C/C_0)$ vs time plot indicated a pseudo-first-order rate of disappearance of heptaCDD. The rate of disappearance is nearly doubled with AHA, and increased by a factor of 1.7 with PMA, as compared to the rate in the presence of titanium citrate (III) alone. In this experiment, the rate constants should be directly correlated with the structural characteristics of AHA and PMA respectively. Since phenolic functionality is a structural moiety of hydroquinone, and the quinone-hydroquinone couple is believed to be the reactive site for electron transfer, the phenolic acidity, which is reflective of hydroquinone content of humic material, is hence expected to greatly affect the rate of the reductive dechlorination. Multilinear regression of the pseudo-first-order rate constants with various parameters characteristic of AHA and PMA was carried out to quantitatively correlate the rate constant with those parameters. The correlation results are quite in agreement with the hypothesis that the quinone-hydroquinone couple is responsible for facilitating electron transfer by humic materials from bulk electron donor to heptaCDD (Table 1).

As expected, phenolic acidity has the highest positive correlation coefficient, meaning highest contribution to the pseudo-first-order rate constant. This also explains the larger rate constant in reactions with AHA than that with PMA. The contribution from carboxylic acidity is also very positive, but the implications are less clear. We speculate that this positive correlation might be due to structural interactions involving carboxyl group between heptaCDD and AHA or PMA, and such interactions facilitate the electron transfer. While a smaller positive correlation from aromaticity of AHA and PMA can be attributed to the fact that quinone or hydroquinone is directly associated with the aromatic ring structure, a negative correlation from carbon content of AHA and PMA indicates that a higher carbon content may very well decrease the amount of reactive functionalities such as quinone or

hydroquinone, and consequently decrease the effectiveness of the electron transfer by humic materials.

Table 1. Correlation of the pseudo-first-order rate constants of heptaCDD disappearance with structural characteristics of AHA and PMA.

	% C	Aromaticity	Phenolic acidity (meg/gDOC)	Carboxylic Acidity (meg/gDOC)	<i>k</i> _{obs} (1/day)
AHA	50.7	57.7	3.6	7.9	0.0266
PMA	49.6	23.0	3.2	13.0	0.0237
Correlation Coefficient	-0.031	0.010	0.091	0.070	

Lesser Chlorinated Products. Lesser chlorinated products were observed after one month of reaction. Hexa-, penta-, tetra-, tri-, dichlorodibenzo-*p*-dioxin congeners were identified as dechlorination products in reactions of heptaCDD with AHA, PMA as well as in control experiment containing titanium citrate (III) (Figure 1). Monochlorinated products were not observed in this study. While five chlorine atoms were removed in all treatments, the individual congeners produced within each isomer group in each treatment were different. The major dechlorination products formed under the experimental conditions are hexa- and pentachlorinated congeners in both AHA and PMA treatments, accounting for more than 90% of all the lesser chlorinated products formed.

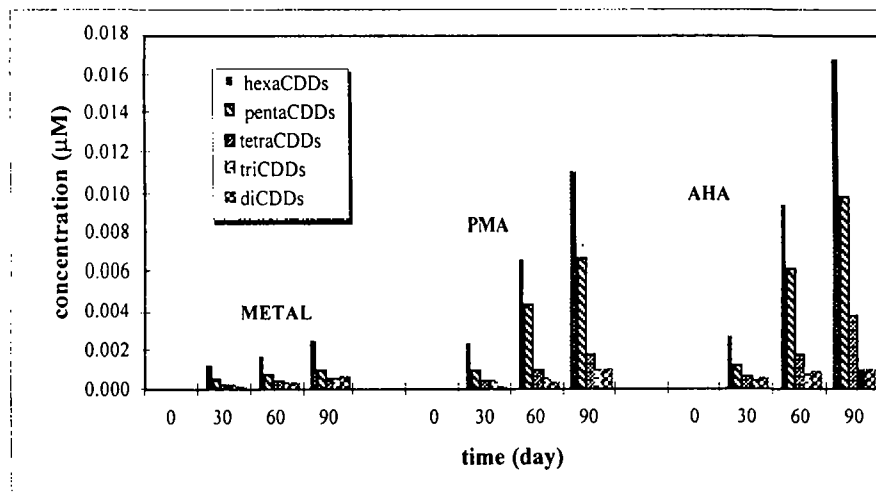


Figure 2. Lesser chlorinated products profiles with AHA and PMA compared with control

The bottle neck appears to be dechlorination of pentaCDD to tetraCDD which is in contrast to microbial dechlorination where the bottle neck rests at tetraCDDs. After three months, the total amount of products formed accounts for 18% and 12% of the loss of

heptaCDD in reactions with AHA and PMA respectively. The higher amount of lesser chlorinated products formed with AHA than those with PMA is consistent with the larger pseudo-first-order rate constant observed with AHA and possibly for the same reason, its higher phenolic acidity content.

The results of this investigation with humic materials contribute to our knowledge on the fate and transformations of PCDDs in the environment, especially for dioxin contaminated sediments where the environment is abundant with humic materials and highly reduced (14). The abiotic processes involving humic materials may greatly affect the rate as well as the reaction pathways of transformations, in particular reductive dechlorination of highly chlorinated dioxins.

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