

Impact of Dechlorination Processes on the Sediment-Water Exchange of PCDD/F in Passaic River Cores

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Introduction

The potential for natural dechlorination processes in sediments to impact the biogeochemical cycling of dioxins and furans has been proposed as a possible mechanism to explain the prevalence of lesser halogenated dioxins and furans at the air-water interface^{1,2}. The hypothesis was supported by multiple lines of evidence, but has not been directly demonstrated. Field evidence indicated dynamic air-water exchange of PCDD/Fs in the Raritan Bay/Hudson River Estuary, whereby lesser chlorinated (predominantly diCDD/F) were present in the particle and apparent dissolved phase³. Fugacity calculations indicated that the water column served as the source of these homologue groups. Laboratory evidence from Passaic River sediment cores and microbially-mediated dechlorination demonstrated that historic dioxins can undergo extensive dechlorination reactions, culminating in the formation of mono- and diCDD homologues (Figure 1)^{2,4,5}. Similar pathways have been observed with PCDF, resulting in the accumulation of triCDF⁶. The current paper reports on an investigation addressing the hypothesis of whether the lesser chlorinated PCDD/F observed at the air-water interface could be the result of selective dissolution of these congeners or homologues from sediments as they are produced during microbial dechlorination.

Materials and Methods

Inoculum. The sediment core was collected from the lower Passaic River (NJ) near the outfall of 24 Lister Ave., one of the presumed sources of the dioxin contamination in this estuary (Albrecht et al., 1999; Bopp et al., 1991). A 30-cm core section derived from approximately one meter below the riverbed was used to obtain the microbial fraction. Estuarine bottom water was collected at the same time from the same location. The salinity of the water column 1 m above the sediment ranged from 16-22 ‰.

Estuarine media. The estuarine media for the experiment included modified basal medium (in g/l) and was described in Barkovskii et al. (1998): Na₂CO₃, 3.0; Na₂HPO₄•7H₂O, 1.12; NH₄Cl, 0.5; cysteine-HCl•H₂O, 0.25; resazurine, 0.001. Trace element and vitamin solutions (1% each) were supplemented to the media. Estuarine medium with sulfate (E-Sulfate medium) contained (g/l): NaCl, 8.4; MgSO₄•7H₂O, 4.78; KCl, 0.27; CaCl₂•2H₂O, 0.05. The final sulfate concentration in the E medium was 19.4 mM. All of the components except for Na₂CO₃ and the vitamins were

subjected to a stream of N₂-CO₂ (75:25). The vitamin solution was filter-sterilized. The pH of the media was about 6.8. The salinity in the two estuarine media was 17‰.

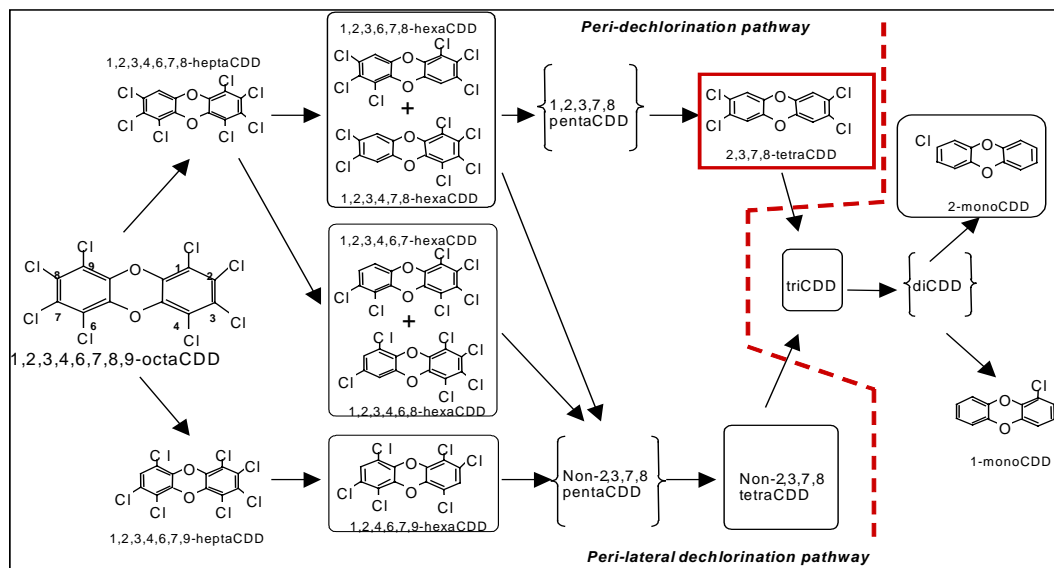


Figure 1. Peri- and Lateral Dioxin Dechlorination Pathways in Estuarine Sediments Resulting in the Accumulation of mono-triCDD⁷

Experimental Configuration. The sediments were incubated in a 4-L flat bottom flask outfitted with a mesh screen to separate the sediments from the bottom estuarine media aqueous phase (Figure 2). The sediments were overlain by estuarine media, and the gas phase was maintained under anaerobic (reducing) conditions using a CO₂/N₂ atmosphere. A low flow of a mixture of hydrogen/nitrogen gas was added through the sediments at 1 mL/min to maintain a dissolved hydrogen concentration in the 20-50 nM range, simulating reducing conditions in sediments and overlaying media.

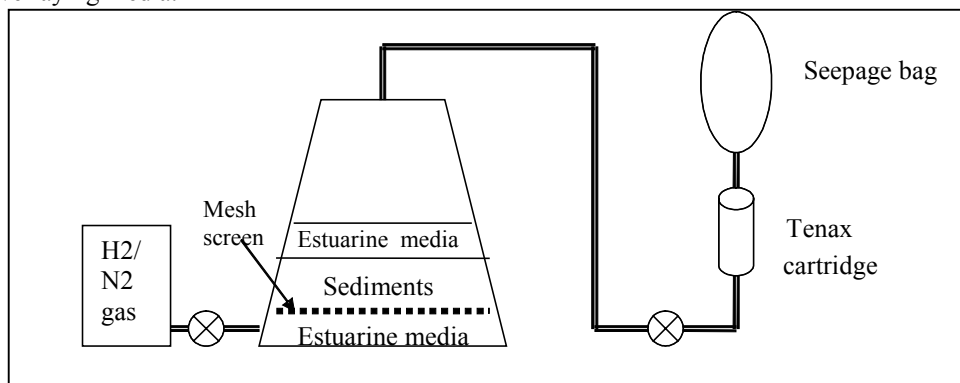


Figure 2. Experimental Configuration of the Multi-Media Dechlorination Experiment

The air/gas was extracted from the column through a Tenax column to sorb volatilized contaminants. At each time point (1, 3, 6, and 12 months), triplicate sediment samples were collected from the vessel, and the overlaying aqueous phase was replaced by fresh estuarine media. The collected aqueous phase was filtered through a Sephadex filter for sample concentration, and the Tenax column material was replaced and stored. The sediment samples were pooled and shipped on ice to the laboratories of Professor Kevin Jones at Lancaster University for PCDD/F analysis.

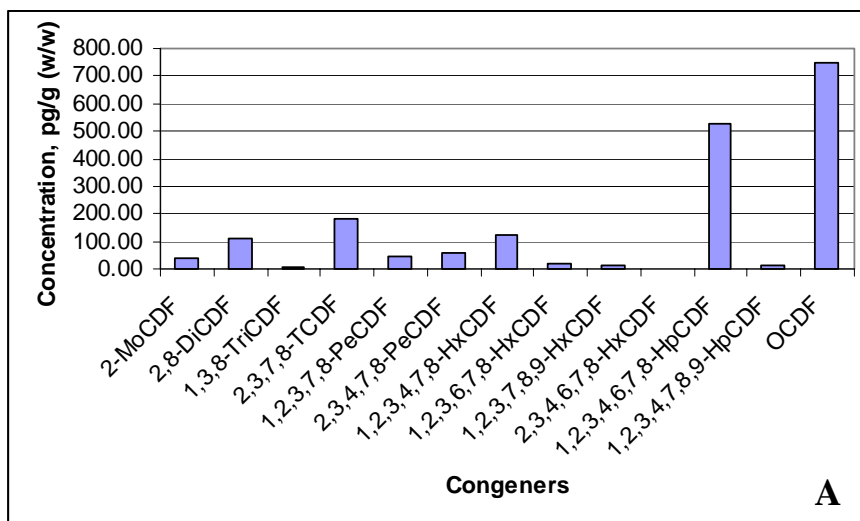
Analytical Methods. The sediment samples were analyzed for mono- to octaCDD/F as published³.

Results and Discussion

Due to analytical limitations and limited sample volume, only the sediment samples could be reliably analyzed to the levels of detection specified in the laboratory (< 1 pg/g w/w).

Baseline Passaic River Sediment Core Profile

The congener-specific PCDD/F profile for the Passaic River sediment core is dominated by OCDD/F and 1,2,3,4,6,7,8-HpCDF, with contributions of 2,3,7,8-TCDD/F in the 200-300 pg/g range (Figure 3). In addition to the Cl₄₋₈CDD, two triCDD (1,2,7- and 2,3,7-), one diCDD (2,3-), and monoCDD were observed, with the diCDD dominating (>100 pg/g). Similarly, 2,8-diCDF was predominant among the mono-triCDF. Mono-, di- (including 2,3-CDD) and tri- (including 2,3,7-CDD) have been demonstrated to accumulate from dechlorination reactions in sediments, but the origin of the lesser halogenated PCDD in these sediments is unknown. Albrecht et al. (1999) demonstrated a ten-fold increase of historic 2-MoCDD in Passaic River sediments following biotic dechlorination reactions over a three month timeframe⁵.



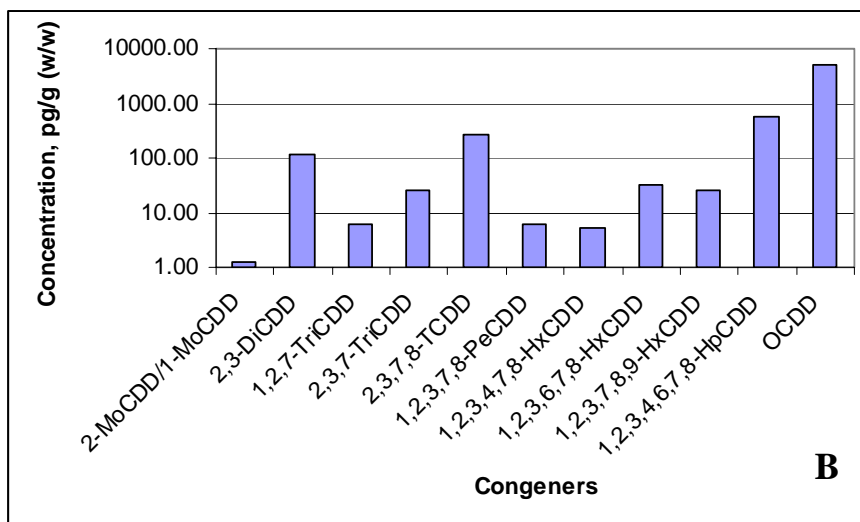


Figure 3. PCDF (A) and PCDD (B) Concentration Profiles in Passaic River Core

Impact of Sediment Incubations on Congener Profiles

The results of a one-year incubation experiment are presented in Table 1 and Figure 4 for the homologue groups. There is considerable variation in the actual concentrations of the five time samples, which is probably to some extent attributable to sediment heterogeneity, despite extensive homogenization of the sediments prior to incubation. Despite the heterogeneity, the following trends can be observed: (i) the 12-month time point exhibits substantial shift in PCDD/F congener profile, yet as a percent of total only the PCDF shifts are significant; (ii) a temporal increase in hexa-octaCDF/D; (iii) gradual decreases in the di- and triCDFs and a concomitant increase in absolute, but not relative, monoCDF contributions.

The interpretation of the homologue shifts in light of potential reactivity (i.e. dechlorination, figure 1) and fugacity processes should be based on a comparison of isomer-specific and homologue data. Preliminary data analysis of the lesser chlorinated PCDD/F indicates a temporal increase (3-5 mo.) of 2-MoCDF, 2,8-DiCDF, 2,3-DiCDD and 2,3,7,8-TCDD/F. After 3 months, the concentrations of 2,3,7,8-TCDF and 2,3-DiCDD decrease by 55%, and 80%, respectively (Figure 4). On a relative basis (as a fraction of Σ PCDD/F, the concentrations to di- and triCDF decrease as well (data not shown), indicating that the lesser chlorinated PCDF (but not PCDD) may be selectively partitioning to the aqueous phase.

Overall, this experiment indicates that dechlorination is not a significant contributor to the multimedia partitioning of PCDD/F in estuarine systems as the reaction rates associated with microbial processes are likely much lower than those governing phase distribution. The main trends observed for the homologues are explained rather by sediment heterogeneity and homologue partitioning, rather than reactivity.

Table 1. Homologue-specific distribution of PCDD/F during the one-year experiment

Homologues	1 Mo. pg/g	2 Mo pg/g	3 Mo. pg/g	6 Mo. pg/g	12 Mo. pg/g
Total Mono-F	104.30	85.28	116.77	107.58	121.00
Total Di-F	842.56	233.07	258.38	223.48	479.30
Total Tri-F	1140.23	992.63	844.65	791.58	293.28
Total Tetra-F	663.27	574.16	694.65	628.37	235.26
Total Penta-F	527.77	636.10	636.26	603.06	250.45
Total Hexa-F	399.60	550.23	516.70	500.74	447.79
Total Hepta-F	649.32	930.16	945.87	749.04	1472.31
OCDF	745.10	1025.50	1006.40	933.68	2129.80
Total Mono-D	7.22	6.14		6.70	15.78
Total Di-D	515.81	677.42	748.99	596.06	686.08
Total Tri-D	78.43	153.24	120.16	114.36	103.89
Total Tetra-D	338.89	381.72	426.04	353.36	369.33
Total Penta-D	82.26	89.73	116.02	99.11	49.31
Total Hexa-D	290.28	386.07	379.07	393.23	294.38
Total Hepta-D	962.36	1180.04	1544.35	1315.02	1322.34
OCDD	5062.41	6490.41	6216.43	5357.29	6423.30
Σ P(4-8)CDD/F	9402.64	12199.26	12481.78	10932.91	12994.27
Σ WHO-TEQ	189.33	441.82	480.84	428.16	445.71
Σ PCDD/F	11790.45	14347.05	13489.54	11713.71	14693.60
Σ Isomers	7401.64	9923.48	9688.89	8458.78	11544.82

Acknowledgements

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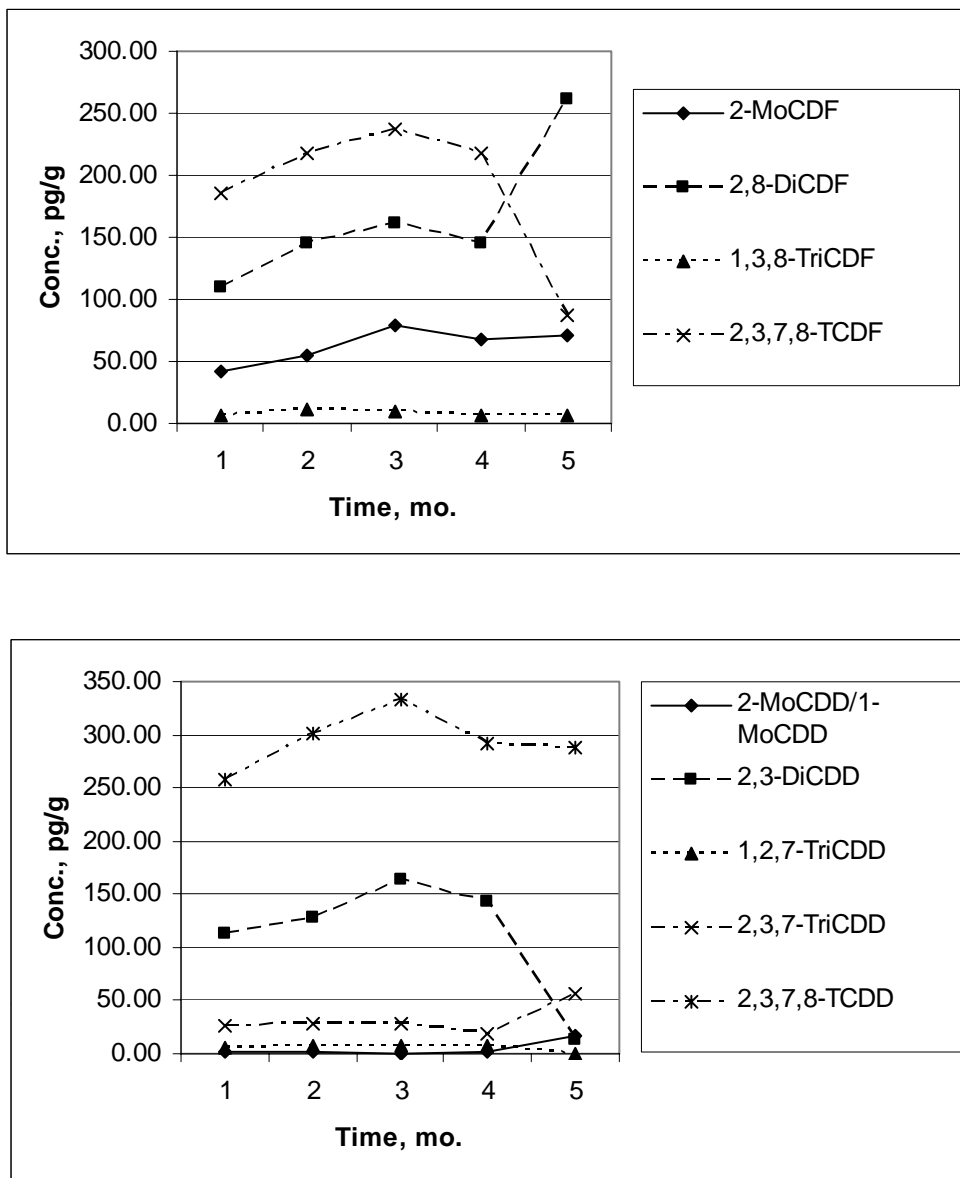


Figure 4. Isomer-specific trends of Mono-TetraCDF/D in sediment incubations (Legend: times 1,2,3,4 and 5 refer to 1,2,3,6, and 12 month data points)