EFFECTS OF SEDIMENT BIOGEOCHEMISTRY ON DIOXIN DECHLORINATION PATTERNS: THE NEW YORK-NEW JERSEY ESTUARY

Adriaens, Peter, Shiang Fu, Iris D. Albrecht, and Andrei L. Barkovskii

Environmental and Water Resources Engineering, The University of Michigan, Ann Arbor MI 48109-2125

Introduction

The fate and disposition of dioxins in general, and 2378-TCDD in particular, in sediments has been at the fore of public concern on account of their ecosystem toxicity. Moreover, their presence in sediments such as the New York-New Jersey estuary presents significant impediments to remedial and navigational dredging efforts (NRC, 1997). Research during the last ten years has advanced our knowledge on the reactivity of dioxins in freshwater (Adriaens et al., 1995; Barkovskii and Adriaens, 1996; 1998) and estuarine (Albrecht et al., 1999; Fu et al., 1999) environments. Microbial, mineral, and humic catalysts were found to extensively dechlorinate spiked and historical dioxins, resulting in the formation and further dechlorination of 2378-TCDD (reviewed in Adriaens et al., 1998). This paper describes how sediment biogeochemistry characteristics such as salinity and sulfate concentration are likely to affect the dechlorination patterns on account of differences in natural microbial activity which affect fatty acid turnover and equilibrium hydrogen concentrations.

Materials

Microbial enrichments were obtained after elution of microorganisms from contaminated lower Passaic River estuarine sediments (Fig. 1) and amended with organic acids (Barkovskii and Adriaens, 1996) either in the presence (20 mM) or absence of sulfate in estuarine medium (27 ‰ salinity). After centrifugation, 20 ml aliquots were dispensed in serum bottles, and spiked with 200 ppb of either 1234678-HpCDD or 1234679-HpCDD. Biological end points (H_2, CH_4, SO_4^{2-}, protein, organic acids) were measured as described in Lendvay et al. (1998), and analysis of dioxins for disappearance of starting HpCDDs and appearance of lesser chlorinated products was conducted as per Adriaens and Barkovskii (1996).

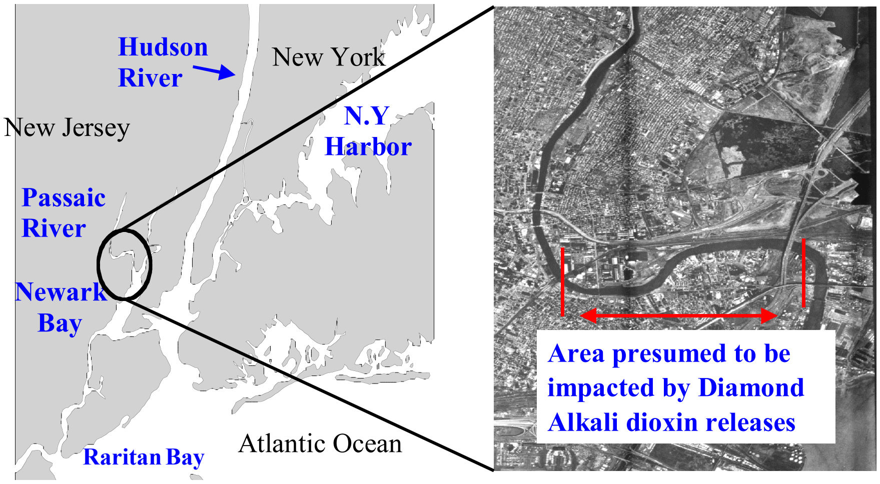

Fig. 1. The New York-New Jersey Estuary

Results and discussion

Microbial respiratory activity

Endpoints indicative of dominant respiratory activity (terminal electron accepting process, TEAP) in estuarine systems are presented in Table 1, and are compared to literature values for freshwater and marine systems. It is clear that the salinity gradient (3-35 ‰) and increasing sulfate concentrations in the transition from freshwater to marine environments affect the predominant respiratory activities (shaded areas pertain to the current study). The methane data indicate that, whereas sulfate-depleted estuarine systems generate methane in excess of the sulfate-rich systems, it represents <10% of that generated in a similar timeframe (7 months) in freshwater systems. Whereas this phenomenon has been attributed to incomplete substrate oxidation at salt concentrations above 15‰ in marine systems (Skyring, 1987), incomplete substrate oxidation under anaerobic conditions results in the accumulation of acetate and hydrogen gas from fermentative processes. However, our results indicate that not only was fatty acid turnover complete but residual hydrogen concentrations were much lower than those observed in the absence of salt. Based on the methane and sulfate stoichiometry, the sulfate-depleted system produced 20% of theoretical methane (vs. 1% for the sulfate-rich system), and the sulfate-rich incubation depleted 55% of the available sulfate (Table 1).

Table 1. Effects of sediment geochemistry on respiratory activity and carbon metabolism

Environmental system	**Methane, µM (% of theor.)**	***Resid. Sulfate[3], mM*** (%)	**H_2, nM**	**Fatty acid turnover**	**Dominant TEAP**
Freshwater[1]	46.7 (80)	na	>20	Incomplete	Methanogenesis
Estuarine/Sulfate-depleted	3.2 (20)	na	7	Complete	Methanogenesis
Estuarine/Sulfate-rich	0.2 (0.9)	8.2 (45)	8	Complete	Sulfate-reduction
Marine/Sulfate-depleted[2]	na	na	>20	Complete	Methanogenesis
Marine/Sulfate-rich[2]	nd	nd	<20	Complete	Sulfate-reduction

[1] Barkovskii and Adriaens (1996); [2] Lovley and Klug (1982); [3] Sulfate added: 18mM. Legend: na, not applicable; nd, not determined.

Amendments of the various geochemical systems with 200 ppb of HpCDD resulted in TEAP- and isomer-dependent effects (Table 2). First, methanogenesis in freshwater systems decreased, and under estuarine conditions increased, in the presence of dioxins. This observation may be attributed to a shift from predominantly hydrogenotrophic (freshwater) to acetoclastic (estuarine) methane production, the latter being less sensitive to possible uncoupling of electron flow by dioxins. Second, the 2378-substituted isomer effects lower residual hydrogen concentrations than the 2379-HpCDD, both in sulfate-free and sulfate-rich incubations. These differences are significant, in that they may be related to isomer-specific toxicity to the cells. Indeed, the fatty acid turnover in the presence of this isomer is incomplete.

Table 2. Effects of dioxin spike on respiratory activity and carbon metabolism

Conditions	***Dioxin spiked***	***Methane, µM (% of theoretical)***	***H_2, nM***	***Resid. Sulfate[3], mM (%)***	***Fatty acid turnover***
Estuarine/ Sulfate-free	1**23**46**78**-HpCDD	5.25 (32)	3	na	Incomplete
Ibid.	1234679-HpCDD	5.57 (34)	2	na	Complete
Estuarine/ Sulfate-rich	1**23**46**78**-HpCDD	0.15 (0.9)	4	2 (1)	Incomplete
Ibid.	1234679-HpCDD	0.14 (0.8)	3	2 (1)	Complete
Freshwater[1]	OCDD	1.3 (25)	nd	na	Incomplete

[1] Barkovskii and Adriaens (1996); [3] Sulfate added: 18 mM. Legend: na, not applicable; nd, not determined.

Microbial dechlorination activity

The effects of differences in dominant TEAPs under both incubation conditions and with both dioxin isomers spiked are summarized in Table 3, along with literature information on dechlorination of octaCDD in freshwater incubations with cells derived from the same sediments.

The following trends can be discerned: (i) Sulfate-depleted and sulfate-rich estuarine conditions promote both *peri*- and mixed *peri*-lateral dechlorination pathways, but the latter is dominant under sulfate-rich conditions; (ii) Whereas *peri*-dechlorination is dominant for the 2378-HpCDD isomer, neither pathway dominates during 2379-HpCDD dechlorination; (iii) MonoCDD accumulated under all conditions, even though the relative molar fractions and ratios were dependent on the electron acceptor and dioxin spiked (not quantified yet); (iv) The ratio of 2378- vs. non-2378-TCDD is strongly dependent on the incubation conditions, ranging from 0.2 (freshwater) to 2 (estuarine sulfate-rich). The results on production and dechlorination of 2378-TCDD during dioxin dechlorination under estuarine conditions concur with the predominance of a peri-dechlorination pathway in dioxin-contaminated estuarine sediments (Albrecht et al., 1999). It should be noted that there is no direct correlation between 2-monoCDD production and the 2378:non-2378 tetraCDD ratio, as the monoCDD can be produced from both spiked heptaCDD spiked.

Table 3. Dioxin dechlorination patterns

Conditions	***Dioxin spiked***	***Patterns Observed***
Estuarine/ Sulfate-free	1**23**46**78**-HpCDD	Peri > lateral 2378:non-2378 = 3:2 2-MCDD > 1-MCDD
Ibid.	1234679-HpCDD	Peri≈lateral
Estuarine/ Sulfate-rich	1**23**46**78**-HpCDD	Peri > lateral 2378:non-2378 = 2:1 2-MCDD > 1-MCDD
Ibid.	1234679-HpCDD	Peri≈lateral
Freshwater[1]	OctaCDD	Peri < lateral 2378:non-2378 = 1:5 2-MCDD >> 1-MCDD

[1] Barkovskii and Adriaens (1996).

The prevalence and apparent ubiquitous capability of sediment microbial communities derived from soil cores and incubated under conditions simulating estuarine and freshwater environments to effect dioxin dechlorination, not only may help explain differences between sink patterns in areas impacted by one dominant source (point or non-point) based on natural bioattenuation processes, also aid in the development of remedial technologies. The current study complements our earlier work on dechlorination under freshwater (methanogenic) conditions (Barkovskii and Adriaens, 1996; 1998), and corroborates evidence for predominant peri-dechlorination in estuarine environments (Albrecht et al., 1999).

A conceptual model which incorporates these findings as they might pertain to the Passaic River, which encompasses the salinity and sulfate gradient described earlier, and which may serve as a model for the entire estuary, is provided in Figure 2. Based on this model it is argued that the likelihood of 2378-TCDD formation increases with increasing salinity/sulfate concentrations and in sediments exhibiting estuarine and marine characteristics. Under the latter conditions, sulfate reduction becomes the dominant respiratory process, resulting in increasingly complete fatty acid turnover and decreasing accumulation of hydrogen. However, since all conditions support further dechlorination to monoCDD, the relative kinetics of 2378-TCDD formation through *peri*-dechlorination of higher chlorinated PCDD *vs.* its dechlorination become important. Albrecht et al. (1999) argued, based on calculated rates of 2378-TCDD and 2-monoCDD formation in solid free (freshwater) and sediment (estuarine) systems, that the TCDD isomer is not likely to accumulate under organic (fatty acid) and inorganic (hydrogen) electron donor surplus conditions. No kinetic analysis has been performed yet on the current incubations.

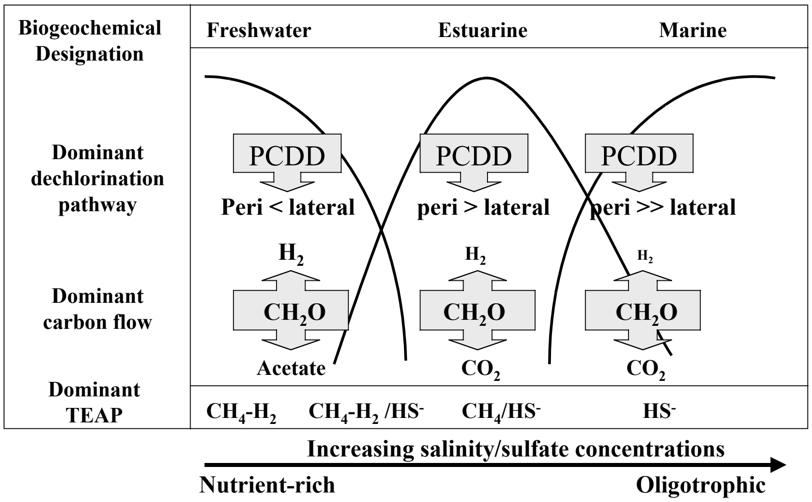

Fig. 2. Conceptual carbon and dioxin turnover model for the Passaic River estuary(CH_4-H_2: hydrogenotrophic methanogenesis; CH_4: acetoclastic methanogenesis)

A central question which remains is how fast these reactions can be expected to occur under natural conditions. Considering the trace concentrations of dioxins in the environment, the low estimated energy fluxes associated with a single dechlorination step (e.g. 4.7×10^{-9} Jmg dry cell weight^{-1} h^{-1}; Harms, 1988), and the concurrence of methanogenic and sulfate-reducing processes, it could be argued that dioxin dechlorination may be attributed (at least in part) to cometabolic reactions. Based on a mass balance ratio for methane production (46.7 μM) to 2378-TCDD dechlorination (18.7 nM) under freshwater conditions, 4×10^{-4} μmole of of 2378-TCDD is dechlorinated to predominantly tri- and monoCDD for every μmole of methane generated. Taking into account mean freshwater sediment respiration rates of organic matter on the order of 1-10 μmole CH_2O L^{-1} d^{-1} (Murphy and Schramke, 1998), the estimated dechlorination rates for 2378-TCDD range from 10^{-3}-10^{-4} μmole L^{-1} d^{-1}, or 0.4-0.04 μmole L^{-1} yr^{-1}.

Applying these rates to TCDD concentrations in Passaic River sediment cores (6.3 µmole kg^{-1} or , Albrecht et al., 1999), the mean residence time is on the order of 15-150 years. These calculations assume a first order kinetic reaction, bioavailability of all sediment-associated dioxin, and the absence of higher chlorinated dioxins which may generate 2378-TCDD. Considering that the dechlorination rates increase with increasing chlorine level (up to ten-fold), and that *peri*-dechlorination becomes dominant with increasing sulfate and salinity levels, it would be expected that natural dechlorination reactions in freshwater sediments result in a steady decrease and those in estuarine/marine sediments in an increase in 2378-TCDD. Within this context, bioremediation strategies aimed at increasing reaction rates and minimizing 2378-TCDD accumulation should emphasize increasing carbon or electron fluxes, as has been demonstrated recently (Albrecht et al., 1999).

Acknowledgements

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