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A comparative evaluation of anaerobic dechlorination of PCB-118 and Aroclor 1254 in sediment microcosms from three PCB-impacted environments

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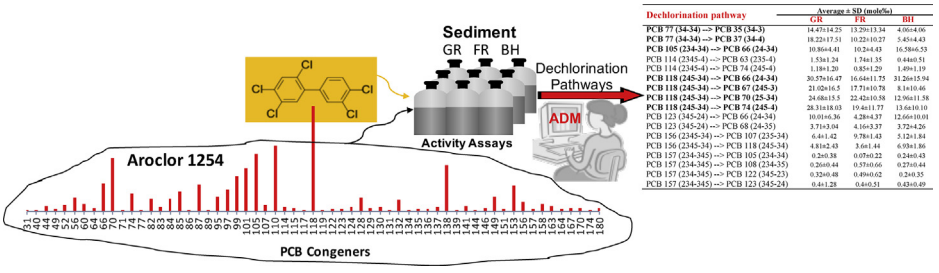
HIGHLIGHTS

- Anaerobic dechlorination model determined Aroclor 1254 dechlorination pathways.
- Major toxicity reducing pathways were determined in three sediment cultures.
- Dioxin-like toxicity was reduced by 53%, 45%, 21% in GR, FR, BH, respectively.
- Dechlorination end products were unflanked tri- & tetra-chlorinated biphenyls.

GRAPHICAL ABSTRACT



Dechlorination pathway	Average ± SD (mole%) GR	FR	BH
PCB 77 (34-34) --> PCB 35 (34-3)	14.47±14.25	13.29±13.34	4.00±4.06
PCB 77 (34-34) --> PCB 37 (34-4)	18.22±17.51	10.22±10.27	5.45±4.43
PCB 105 (234-34) --> PCB 66 (24-34)	10.86±4.41	10.2±4.43	16.58±6.53
PCB 114 (2345-4) --> PCB 63 (235-4)	1.53±1.24	1.74±1.35	0.44±0.51
PCB 114 (2345-4) --> PCB 74 (245-4)	1.18±1.20	0.85±1.29	1.49±1.19
PCB 118 (245-34) --> PCB 66 (24-34)	30.57±16.47	16.64±11.75	31.26±15.94
PCB 118 (245-34) --> PCB 67 (245-3)	21.02±16.5	17.71±10.78	8.1±10.46
PCB 118 (245-34) --> PCB 70 (25-34)	24.68±15.5	22.42±10.58	12.90±11.58
PCB 118 (245-34) --> PCB 74 (245-4)	28.31±18.03	19.4±11.77	13.6±10.10
PCB 123 (345-24) --> PCB 66 (24-34)	10.01±6.36	4.28±4.37	12.66±10.01
PCB 123 (345-24) --> PCB 68 (24-35)	3.71±3.04	4.16±3.37	3.72±4.26
PCB 156 (2345-34) --> PCB 107 (235-34)	6.4±1.42	9.78±1.43	5.12±1.84
PCB 156 (2345-34) --> PCB 118 (245-34)	4.81±2.43	3.6±1.44	6.93±1.86
PCB 157 (234-345) --> PCB 105 (234-34)	0.2±0.38	0.07±0.22	0.24±0.43
PCB 157 (234-345) --> PCB 108 (234-35)	0.26±0.44	0.57±0.66	0.27±0.44
PCB 157 (234-345) --> PCB 122 (345-23)	0.32±0.48	0.49±0.62	0.2±0.35
PCB 157 (234-345) --> PCB 123 (345-24)	0.4±1.28	0.4±0.51	0.43±0.49

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ABSTRACT

Aroclor 1254 (A1254) is the most toxic commercial PCB mixture produced, primarily due to its relatively high concentrations of dioxin-like congeners. This study demonstrates a comparative evaluation of dechlorination of A1254 and PCB-118 by indigenous organohalide respiring bacteria enriched from three PCB impacted sites: Grasse River (GR), NY; Fox River (FR), WI; and Baltimore Harbor (BH), MD. PCB-118 dechlorination rates in GR, BH, and FR was 0.0308, 0.015, and 0.0006 Cl^-/biphenyl/day, respectively. A1254 dechlorination rates in GR, FR, and BH were 0.0153, 0.0144, and 0.0048 Cl^-/biphenyl/day, respectively. A1254 dechlorination was achieved through the removal of doubly-/singly-flanked chlorines in *meta* and *para* positions of mostly penta- followed by hexa- and hepta-chlorinated congeners by 88%, 69%, and 51% in GR, and 88%, 87%, and 83% in FR, respectively, while in BH mostly hepta- (70%) followed by hexa-chlorinated congeners (66%) were dechlorinated. A previously developed Anaerobic Dechlorination Model (ADM) quantified a total of 17 toxicity-related dechlorination pathways in all three sediment microcosms. The toxic equivalency of A1254 based on seven dioxin-like congeners decreased by about 53%, 45% and 21%, in GR, FR and BH microcosms, respectively. The dechlorination products were generally tetra- and tri-chlorinated congeners with unflanked chlorines, all of which is susceptible to further degradation by aerobic bacteria. Concerning the toxic congeners, ADM can be useful to initiate further research focusing on the stimulation of the toxicity reducing pathways for risk assessment and effective remediation strategies.

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1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants which are persistent, lipophilic and strongly hydrophobic with a high potential for bioaccumulation in living organisms. Environmental PCB exposure is a major health concern due to the toxic, carcinogenic, and endocrine disruptive effects of PCBs [1]. Among the commercial PCB mixtures manufactured in the USA, A1254 had one of the widest applications ranging from coolants for transformer and capacitor oils, ink solvents, pesticide extenders, plasticizers to a variety of adhesives [2]. A1254 is the most toxic of the commercial mixtures with a greater proportion of non- and mono-*ortho* chlorinated congeners with dioxin-like properties since the total weight percent of toxic compounds in A1254 is between 11.99% (Lot G4 production) and 23.8% by weight (Lot A4 production or Late production). A1254 is 8–16 times more toxic than Aroclor 1248, and about 3–6 times more toxic when compared to Aroclor 1242 and 1260 [3]. Among the PCB congeners of A1254, PCB-118 is the most abundant dioxin-like congener accounting for an average 7% to 13.5% by weight depending on the production lot [3]. Sales record of world biggest PCB producer, the Monsanto U.S., between 1957 and 1974 pointed out that Aroclor 1254 was the second most produced/sold Aroclor mixtures after Aroclor 1242 [4].

One potential mechanism for reducing the risks associated with A1254 is through microbial degradation (bioremediation) since anaerobic and aerobic microorganisms were shown to transform PCBs under a variety of laboratory and environmental conditions [5–8]. Several microorganisms were previously isolated that can degrade PCBs aerobically [9–12], although the aerobic degradation of PCBs is only effective for lightly chlorinated congeners limiting aerobic degradation of A1254 [9,13]. Typically, only the top few millimeters of sediments are aerobic and the largest reservoirs of PCBs in rivers and lakes are in the anaerobic zones of sediments. Complete degradation of heavily chlorinated PCBs such as A1254 can therefore only occur after anaerobic dechlorination by organohalide respiring bacteria [14]. There are a limited number of studies on dechlorination of A1254 [9,13,15,16] where the impact of use of various inoculum on transformation of this mixture is investigated. In this study, we compared the dechlorination and detoxification of A1254 by using inoculum from sites e.g. GR, FR, and BH with three different PCB contamination histories. An in-depth analysis of biotransformation pathways is essential to better compare and understand the fate of these compounds in the three sets. Individual quantification of anaerobic dechlorination pathways was revealed through a previously developed model ADM [17], which enabled the investigation of toxicity change in microcosms representing each site. Rates and pathways of PCB dechlorination can vary greatly between PCB-impacted sites due to the different populations of indigenous organohalide respiring bacteria [15]. In addition to the dechlorination potential of A1254 and PCB-118 by the indigenous microorganisms, changes in the dechlorinating communities were evaluated by denaturing high pressure liquid chromatography (DHPLC).

2. Materials and methods

2.1. Chemicals

All PCBs (99–100% purity) were purchased from AccuStandard. PCE was purchased from Sigma-Aldrich. All other chemicals were reagent grade.

2.2. Sediment sampling

Sediments collected with a Ponar grab sampler were stored anaerobically in glass jars sealed with Teflon lined tops at 4 °C in the dark prior to use. GR sediment was collected during Spring 2008 from the lower GR in the Village of Massena, NY, US, as described previously [18]. GR was contaminated primarily with A1248 from aluminum production since the 1930s [19]. FR sediment was collected from the Lower Fox River site located in central and northeastern Wisconsin, US, during dredging in Fall 2008 as described previously [20]. FR was contaminated primarily with A1242 from a number of carbonless paper plants along the river [21]. BH sediment was collected in late Spring 2009 from the Northwest Branch of BH a coastal embayment located in a highly urbanized watershed of the Chesapeake Bay, US, as described previously [22]. BH was primarily contaminated with A1260 with smaller amounts of A1254 [22]. Sediments were black in color and had a sulfide odor indicative of reduced anoxic conditions.

2.3. Sediment microcosm

Low-sulfate (<0.3 mM) estuarine medium [23] prepared without Na_2S was anaerobically dispensed as 50-mL aliquots into 160-mL serum bottles and autoclaved at 121 °C for 20 min. The final pH of the medium was 6.8. All subsequent additions were performed in an anaerobic glove box (Coy Laboratory Products, Ann Arbor, Michigan, USA) containing N_2:CO_2:H_2 (75:20:5). Microcosms were prepared as described previously [24] by adding 10 mL of sediments (GR, FR, and BH) and a fatty acid mixture (acetate, propionate, and butyrate) at a final concentration of 2.5 mM. PCB-118 or A1254 solubilized in acetone were added (0.2%, v/v) to the microcosms at a final concentration of 100 ppm, or 50 ppm, respectively. Microcosms were sealed with 20-mm Teflon-coated butyl stoppers (West Pharmaceutical, Inc.) secured with aluminum crimp seals and incubated statically at 30 °C in the dark and sampled immediately after inoculation and subsequently every 30 days.

2.4. PCB extractions and analytical procedures

Microcosms were sampled every 30 days. Triplicate samples for PCBs (AccuStandard, Inc., New Haven, CT) were analyzed by the extraction of 1 mL culture with 5 mL of hexane (Fisher Scientific, PA) on a wrist action shaker (Burrell Corp., PA) overnight according to previously explained method [24]. PCBs 30 and 204 were added as internal standards. Recovery of PCB-166 added as a surrogate was 88 ± 2%. No surrogate recovery correction was performed. Calibration table consisted of 132 congener groups with co-elution, and a total of 172 individual congeners prepared and analyzed as explained before [24]. The PCB concentrations were measured as μg PCB/mL of microcosm slurry and converted to mol%. Total chlorines per biphenyl was calculated as the product of the average number of chlorines and molar concentration of each congener divided by the sum of the total molar concentration of all congeners [24]. The dechlorination rate was calculated within the linear slope of the dechlorination curve by dividing total chlorine removed per biphenyl with the time elapsed in days [11]. Reduction in the total toxic equivalent (TEQ) was calculated based on the toxic equivalent factor for each dioxin-like congener relative to 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin as defined by the World Health Organization [25]. The TCDD (2,3,7,8-Tetrachlorodibenzo-*p*-dioxin) equivalency, i.e. dioxin-like toxicity of each sediment microcosm for time 0 and time final was calculated by multiplying the concentrations of toxic congeners by the TEF (Toxicity Equivalency Factors) values [25].

2.5. DNA extraction and enumeration of PCB dehalorespiring bacteria by qPCR

Triplicate DNA samples was extracted from 0.25 mL of sediment slurry with a 96-well bead-beating plate (MOBIO Laboratories, Inc.) according to the manufacturer's directions. DNA was eluted in