Degradation of Dioxins Under Aerobic and Anaerobic Conditions: State-of-the-Art and Implications for Bioremediation

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1. Introduction

Concerns over 2,3,7,8-substituted PCDD have prompted extensive characterization of freshwater, estuarine and marine sediments for both concentrations and patterns of 2,3,7,8-residues in these environments. Sink patterns were found to be dominated by either the higher chlorinated isomers, or by 2,3,7,8-substituted isomers in general (1,2). Attempts to link the 2,3,7,8-dioxin patterns found in sediments to known sources have not been very successful, in part due to the multitude of municipal and industrial sources, the unknown potential for natural biogenic dioxin production, and natural attenuation of PCDD due to sediment microbial activity or abiotic processes (3,4). This communication addresses the comparative impact of reduced and aerobic environments to the natural attenuation of PCDD.

2. Microbiology of Dioxin Transformation

Aerobic Processes. Well over two decades of research have indicated the existence of two main transformation pathways for aerobic oxidation of PCDD (Figure 1), using either complex environmental systems (soils, lake sediments) or pure cultures of bacteria or fungi obtained from a range of natural or engineered environments (e.g. soils, wastewater,..).

Biphenyl- and naphthalene-degrading bacteria (e.g. Beijerinckia, pseudomonads) were able to co-oxidize dibenzo-p-dioxin and some chlorinated derivatives, resulting in the production of cis-1,2- and 2,3-diols, which were further converted to either phenolic or catecholic end-products (5,6). Even though these reactions were inducible by either biphenyl or napthalene, co-oxidation occurred in the presence of succinate as well. Several other early studies (7) also reported the formation of 'polar metabolites', which were not further identified, in soil system incubations. Using a range of biaryl ether compounds as the growth substrates, several strains (e.g. pseudomonads, Brevibacterium, Sphingomonas sp.) were isolated on dibenzofuran and dibenzo-p-dioxin as sole carbon and energy sources (8,9). Degradation was initiated by an angular dioxygenase which inserts hydroxyl groups adjacent to the ether bond. Whereas this reaction was inducible by diphenylether, dibenzo-p-dioxin and dibenzofuran, latent activity was observed in the presence of acetate. No dioxygenase activity has been observed on 2,3,7,8-TCDD. The ability of peroxidase-harboring white rot fungi to mineralize and transform tetra-to octaCDD (including 2,3,7,8-TCDD)was investigated (10,11). Extensive co-oxidation was observed resulting in the production of di- and tetrachlorocatechols.

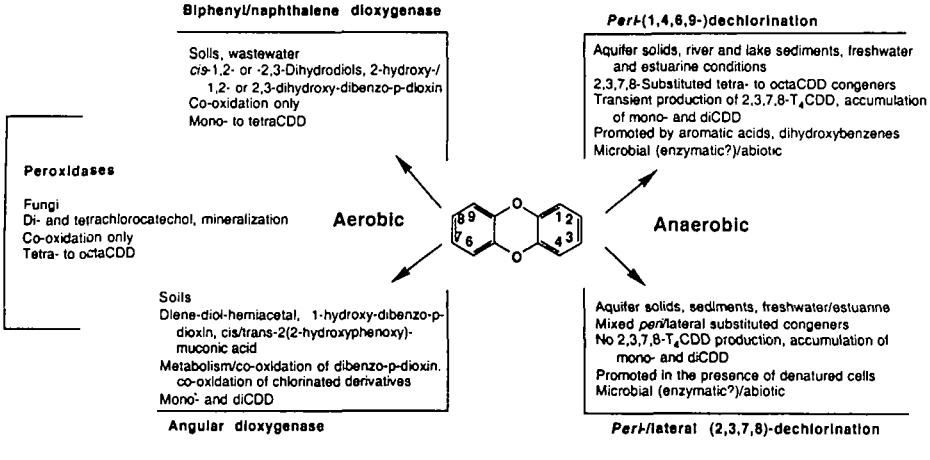

Fig. 1. Overview of aerobic and anaerobic microbial activity on PCDD

Anaerobic processes. No pure anaerobic cultures have been isolated which can grow at the expense of PCDD/PCDF, yet significant microbial dechlorination activity has been demonstrated using a wide range of environmental samples, and sediment-derived cells.

Isomer-specific analysis of the dechlorination pathway was achieved using sediment-derived mixed cultures which were either historically-contaminated with 2,3,7,8-T_4CDD, or spiked with octa- and 1,2,3,4-T4CDD (12-14). Estuarine Passaic River microorganisms exhibited two main dechlorination pathways (Fig. 1). The *peri*-dechlorination pathway (i.e. removal of 1,4,6,9 chlorines) was apparent for 2,3,7,8-substituted hepta- and hexachlorinated isomers, resulting in the transient production and further dechlorination of 2,3,7,8-T_4CDD. The alternate pathway resulted in the removal of both *peri* and lateral chlorines and was initiated starting with 1,2,3,4,6,7,9-H_7CDD. Anaerobic microorganisms enriched from Rhine river and Saale river sediments reductively dechlorinated freshly spiked 1,2,3,4-T_4CDD to 1,2,3- and 1,2,4-T_3CDD which were further dechlorinated to 1,3- and 2,3-D_2CDD and traces of 2-M_1CDD. Historical 2,3,7,8-T4CDD was stoichiometrically dechlorinated to 2-mono and several triCDD.

Several lines of evidence suggest possible enzymatic mediation of dechlorination activity. First, vitamin B12, a cofactor ubiquitous in methanogenic bacteria which thrive under the incubation conditions used for the dechlorination studies, was shown to be able to mediate dioxin dechlorination (15). Second, 1,2,3,4-T_4CDD dechlorination occurred only in sediments, and not in soil systems, indicating the presence of specific cofactors or populations (12). Third, preacclimation of river sediments with hexachlorobenzene resulted in dechlorination activity only against 1,2,3,4-T4CDD; no dechlorination of higher chlorinated congeners was observed (J. Parsons, Personal Communication). Fourth, the peri-dechlorination pathway was lost upon cell denaturation (13). Fifth, dioxin dechlorination in historically-contaminated sediments can be stimulated using either electron donor cocktails, structurally analogous compounds (e.g. tribromodibenzo-p-dioxin), or hydrogen (16).

3. Abiotic Contributions to Dioxin Attenuation

Abiotic sediment components were shown to attenuate PCDDs in reduced environments and have an impact on 2,3,7,8-substituted PCDD patterns (17-19). Elemental zinc stoichiometrically

dechlorinated octaCDD; up to 40% of octaCDD was converted to mainly pentaCDD, with lower concentrations of hepta- and hexaCDD accounting for 30% of the products observed. Vitamin B_{12} catalyzed dechlorination of octaCDD to tetraCDD, and 1,2,3,7,8-pentaCDD to at least two tetraCDD, including 2,3,7,8-tetraCDD. Dechlorination was not stoichiometric, and the lesser chlorinated products account for up to 10% of the disappeared octaCDD.

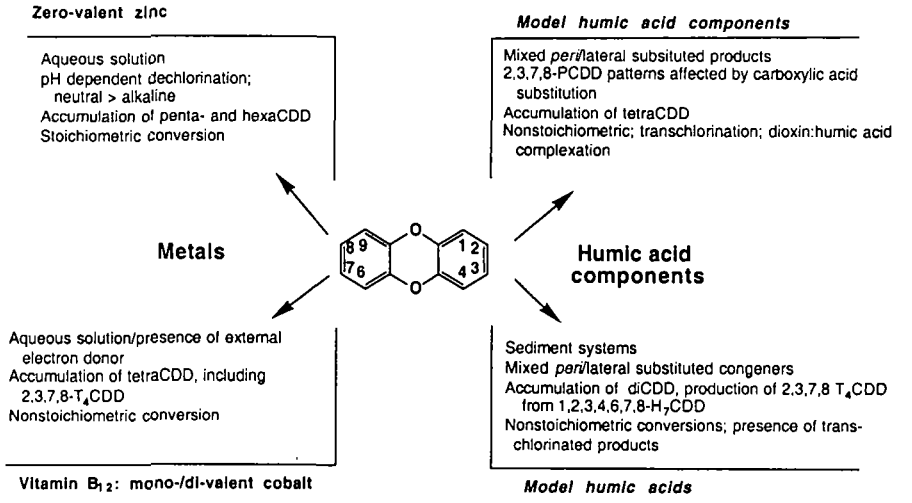

Fig. 2. Abiotic dechlorination of highly chlorinated dioxins under reduced conditions

Model humic constituents (MHC, catechol; 3,4-dihydroxybenzoic acid; resorcinol) and model humic acids (polymaleic acid, Aldrich humic acid) either directly or indirectly dechlorinate PCDDs to tetraCDD and diCDD, respectively (18-19). Direct dechlorination ensues from the redox chemistry of phenolic compounds which allows them to act as direct electron donors; indirect dechlorination results from the ability of phenolic and carboxylic compounds to act as electron transfer mediators for external electron donors. In contrast to humic constituents, humic acids did not promote the *peri*-dechlorination pathway, and 2,3,7,8-tetraCDD was observed in these incubations at much lower concentrations.

Aside from dechlorination reactions to lesser chlorinated PCDD, compounds were detected in the extract which reflected evidence of transchlorination, complexation , and rearrangements. Humic-acid and MHC-mediated reactions were non-stoichiometric, with the lesser chlorinated congeners accounting for up to 25% of the parent compound (octaCDD or heptaCDD) removed. Important to note is that when microorganisms and MHC were incubated together, the patterns exhibited by MHC dominated the upper part of the pathway (octa- to tetraCDD), and microbial activity was responsible for the lower part of the pathway (tetra- to monoCDD).

4. Conclusions

Bioemediation of dioxin-contaminated environments will require the participation of both anaerobic reductive and aerobic oxidative processes, and an analytically-challenging monitoring program, considering the multitude of transformation products involved. If detoxification of dioxin-impacted environments is the main goal, resulting in the decrease of 2,3,7,8-tetraCDD residues, it is likely that only reductive processes may be sufficient. It has been demonstrated that 2,3,7,8-tetraCDD is both produced from highly chlorinated PCDD, and can be further

dechlorinated to 2-monoCDD, and is thus dynamic in anaerobic environments. Whereas this process is exceedingly slow under natural conditions, it can be effectively stimulated using various enhancers, resulting in an orders of magnitude increase in detoxification rates. Even though the aerobic destruction of lesser chlorinated PCDD has not been demonstrated to occur in sediments, evidence for similar natural processes acting on PCBs (20) may lend support to this possibility.

Another implication of these findings is that dioxin patterns observed in environmental sinks may indeed have been impacted by abiotic and biotic transformation processes which may help explain the link between source and sink patterns. Recent evidence that 2-monoCDD has accumulated to up to 50% of the 2,3,7,8-tetraCDD present in Passaic River sediments (21) gives credence to a natural attenuation pattern.

Acknowledgements

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