Critical oxygen concentrations for biodegradation of PCBs

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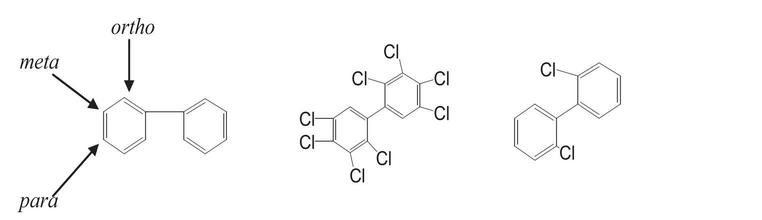
ABSTRACT
This work examines the concentration of oxygen necessary to *allow* aerobic mineralization of polychlorinated biphenyls (PCBs) and the concentration necessary to *inhibit* reductive dechlorination of PCBs. Microcosms were prepared by spiking a sediment sample from a region of the Grasse River in Massena, NY with a mixture of BZ4 (2,2'-dichlorobiphenyl), BZ29 (2,4,5-trichlorobiphenyl), and BZ70 (2,3',4',5-tetrachlorobiphenyl) as indicator PCBs. Aerobic biodegradation of BZ4 and BZ29 was observed at 8.1 ppm and 4 ppm dissolved oxygen (D.O.) within 4 weeks. No biodegradation was observed at 2.1 ppm D.O. or lower. Under anaerobic conditions (0 ppm DO) BZ29 and BZ70 were substantially dechlorinated to daughter congeners within a 12-week period. However, no dechlorination was observed at the lowest D.O. level (0.5 ppm).

These results clearly indicate that there is an interval of dissolved oxygen concentration over which neither aerobic nor anaerobic PCB biotransformation processes can occur.

Background and Motivation

Polychlroinated Biphenyls (PCBs)

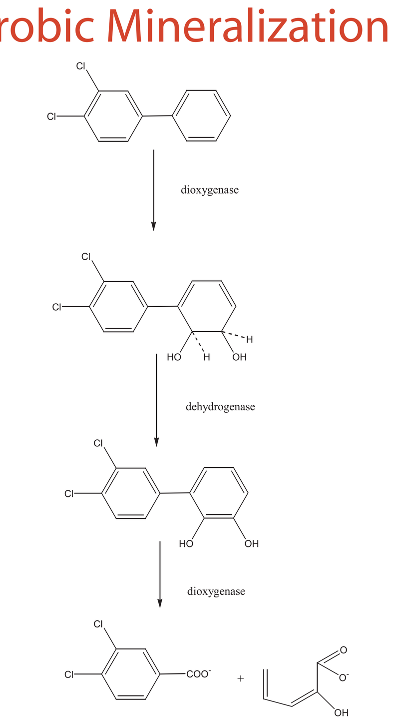
- Widely used
  - as insulating fluids in electrical equipment
  - as fire retardants in hydraulic and lubricating oils
- Chemically very stable
- Toxic and bioaccumulative
- Production banned in US in 1976
- 209 different congeners – with differing locations and numbers of chlorine
- 1975 estimate of 75,000 tons of PCBs mobile in the environment.



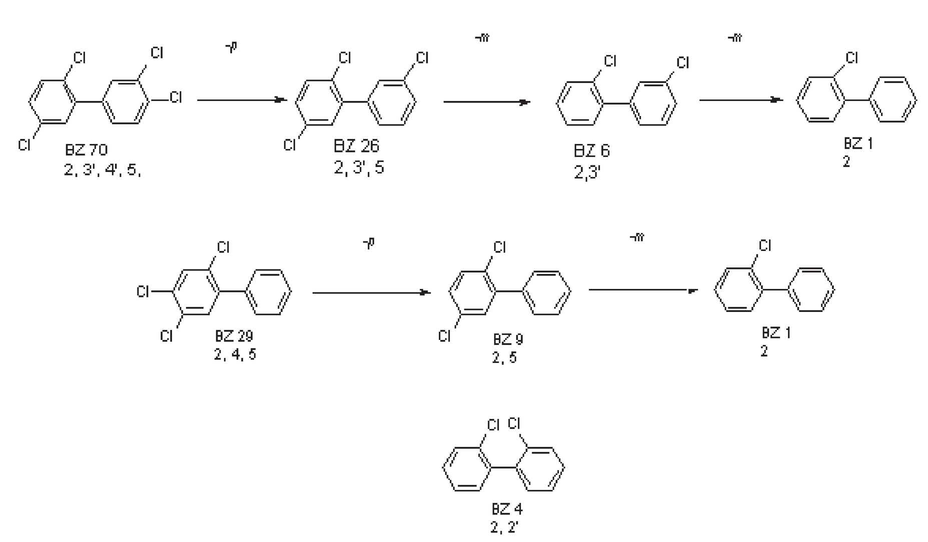
Biphenyl and polychlorinated biphenyl structures. *ortho*, *para* and *meta* positions are identified on the biphenyl.

Pathway of Biotransformation of PCBs

Aerobic Mineralization

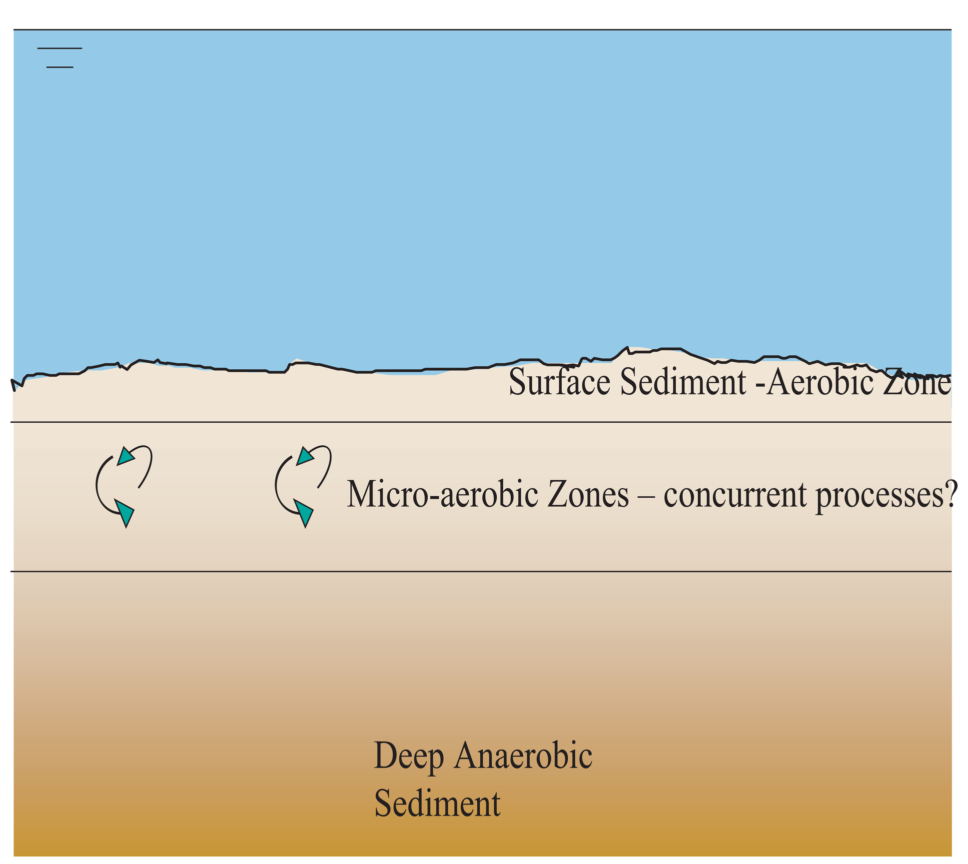


Reductive Dechlorination



Predominant pathways for dechlorination of BZ70, BZ29, BZ4, and their daughter products in Grasse River sediment anaerobic microcosms.

Concurrent aerobic-anaerobic processes in micro-environments?



Reductive dechlorination takes place in anaerobic sediments.

Mineralization takes place in aerobic sediments.

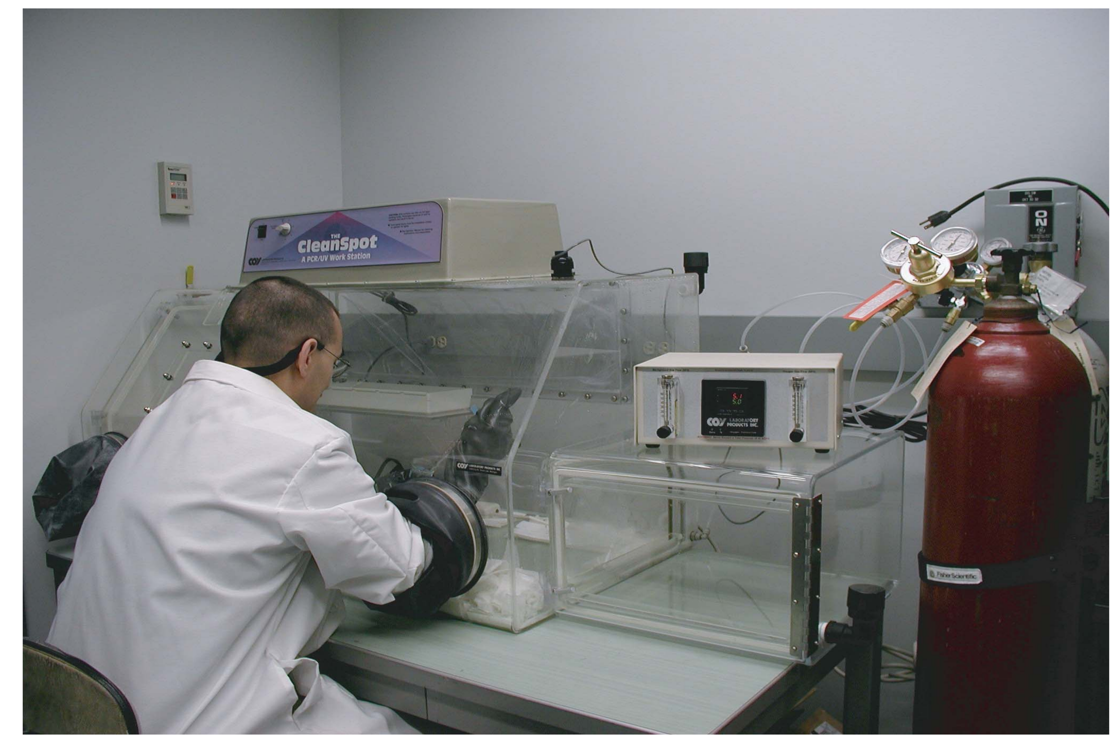
Is there a zone where oxidative and reductive processes can take place concurrently?

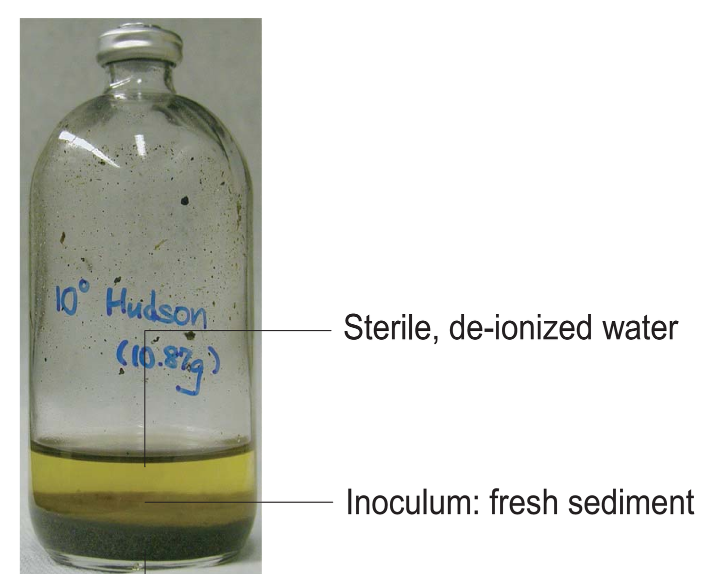
Could aerobic processes take place under low oxygen conditions in micro-environments?

Could anaerobic processes take place in the presence of small concentrations of oxygen?

Materials and Methods

- Hypoxic chamber (Coy Laboratories) fitted with an oxygen sensor-controller
- Replicate microcosms with graded series of controlled dissolved oxygen concentrations (0 to 8 ppm)
- DO maintained by adjusting the oxygen percentage in the headspace gas
- Intermittent shaking was used (30 minutes of shaking at 12-hour intervals) to avoid significant volatilization while still maintaining equilibrium.





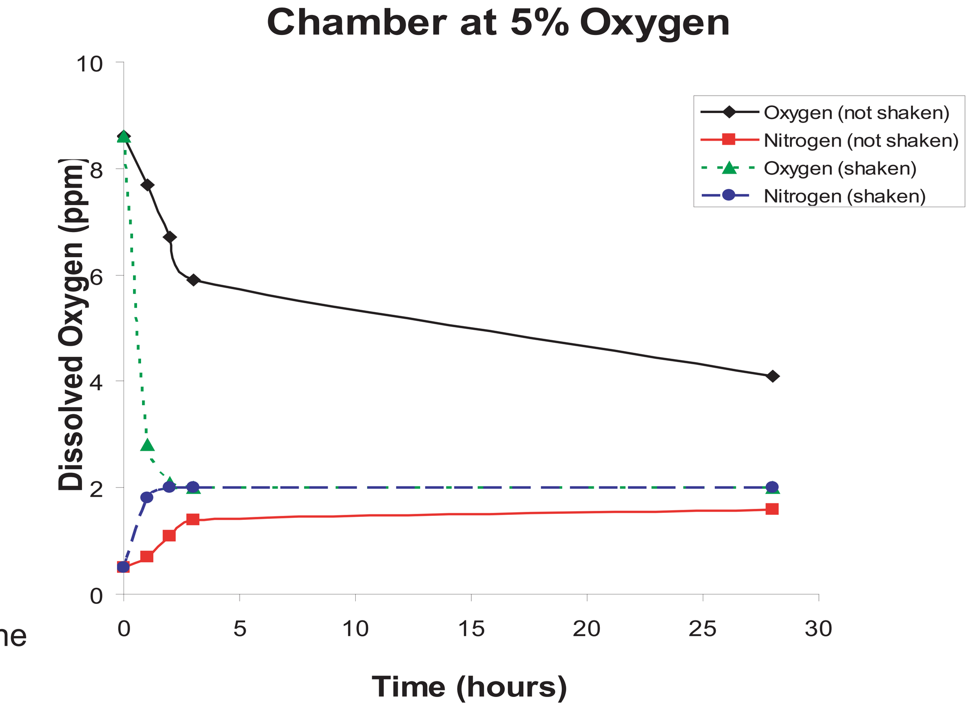
- Microcosms were prepared in 150 mL serum bottles.
- Sediment sample from Grasse River in Massena, NY
- < 5 ppm PCBs in sediment
- Each bottle contained
  - 50-g of a 15% sediment-water slurry (sediment dry weight basis).
  - Sediment portion consisted of
    - 80% wet sediment as viable inoculum
    - 20% sediment dried and then spiked with defined PCB congeners consisting of a mixture of BZ4 (2,2'-dichlorobiphenyl), BZ29 (2,4,5-trichlorobiphenyl), and BZ70 (2,3',4',5-tetrachlorobiphenyl) as indicator PCBs (final concentration of 12 ppm each in the microcosm).
- Congeners were chosen
  - based on our prior experience in using them in sediment microcosms
  - the fact that BZ4 and BZ29 can be aerobically biodegraded, whereas BZ70 cannot
  - the fact that BZ29 and BZ70 can be anaerobically dechlorinated, whereas BZ4 cannot.

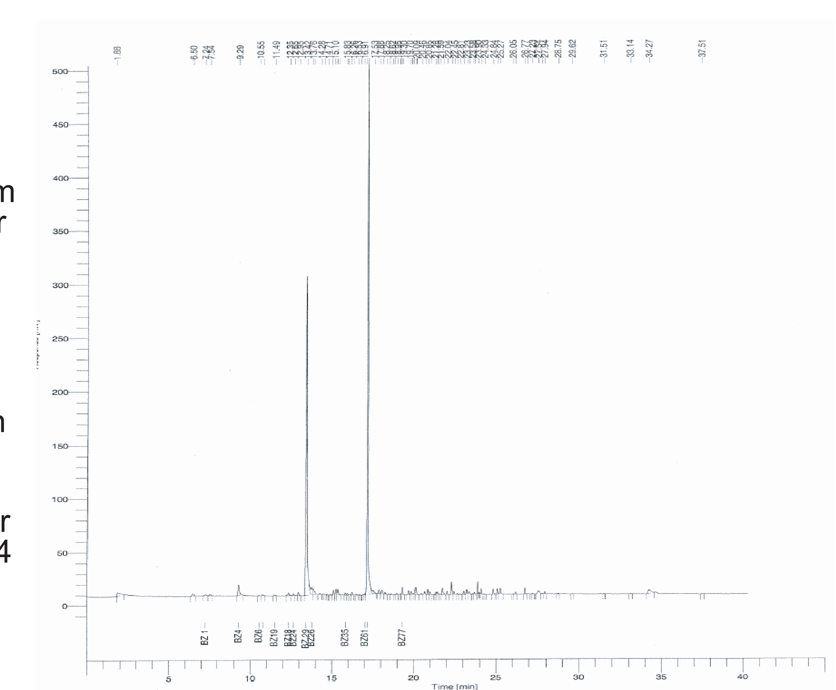
Anaerobic Microcosms
- crimp sealed with Teflon®-lined butyl rubber stoppers
- purged with nitrogen
- incubated with continuous shaking
- Headspace gas analysis by gas chromatography with a thermal conductivity detector

Aerobic Microcosms
- uncrimped rubber stoppers removed periodically to permit re-equilibration with atmospheric oxygen.

Procedures
- Multiple replicates of microcosms for each condition tested were incubated at ambient laboratory temperature for the duration of the experiment.
- PCB analyses were carried out by extracting wet, centrifuged sediment with hexane-acetone (1:1), followed by florisil and sulfur clean-up.
- Quantitative PCB deteminations were made on a Perkin-Elmer Autosystem gas chromatograph with a DB-5 capillary column and ECD detector.
- A positive result for anaerobic PCB dechlorination was inferred from a decrease in the levels of BZ70 and BZ29, the appearance of their dechlorination products, and no change in the amount of BZ4.
- A positive result for aerobic degradation was inferred from a decrease in the levels of BZ4 and BZ29 and no change in the amount of BZ70.
- Because there were small losses of BZ4 and BZ29 due to volatilization from the uncapped microcosms that were incubated in the hypoxic chamber, all changes in PCB levels were assessed relative to sterile control microcosms.
- Micocosms were analyzed for aerobic biodegradation of PCBs after 1, 2 and 4 weeks of incubation, and for dechlorination after 12 or 24 weeks of incubation.

Equilibration of Water in Hypoxic Chamber at 5% Oxygen





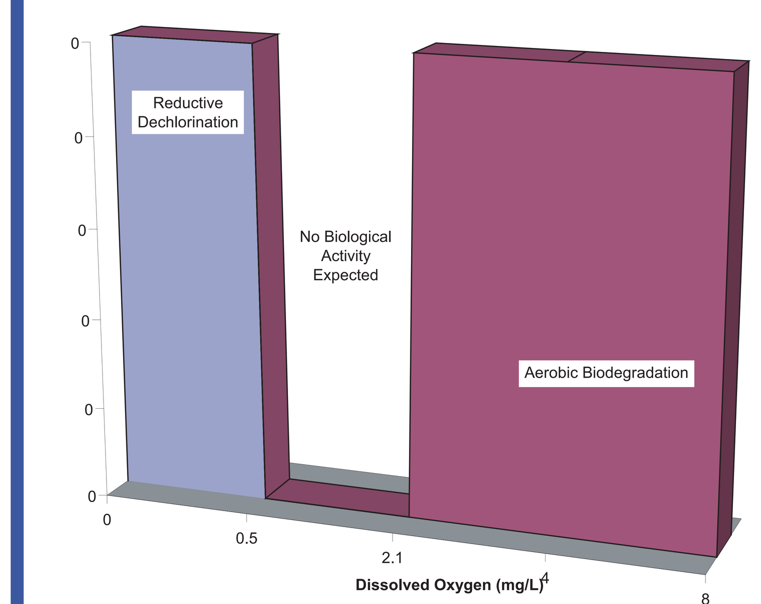
Results and Discussion

- Under fully aerobic conditions (8.1 ppm D.O.) the spiked BZ4 and BZ29 were both substantially biodegraded within a 4-week period whereas there was no BZ70 removal after either 12 or 24 weeks of incubation.
- In the corresponding fully anaerobic microcosms (0 ppm D.O.), after an initial lag period of approximately 6 weeks, the spiked BZ29 and BZ70 were both substantially dechlorinated to daughter congeners within a 12-week period whereas there was no dechlorination of BZ4 after either 12 or 24 weeks of incubation.

D.O., ppm	PCB Degradation (t = 4 weeks)	PCB Dechlorination (t = 12 weeks)
8.1	+	-
4	+	NT
2.1	-	NT
0.5	-	-
0	-	+

- Biodegradation of the PCB congeners BZ4 and BZ29 was observed at 4 ppm D.O. (10% oxygen in the headspace gas of the hypoxic chamber) but not at 2.1 ppm D.O. (5% headspace oxygen) or lower.
- Anaerobic dechlorination did not take place even at the lowest D.O. level that we could maintain with the hypoxic chamber (*i.e.*, 0.5 ppm D.O. at 1.25% headspace oxygen).

Conclusions



- The dependence of aerobic PCB biodegradation on dissolved oxygen concentration(> 4 ppm required) is similar to that for other oxygenase-mediated processes.
- The inhibition of reductive dechlorination of PCBs at relatively low dissolved oxygen concentration (> 0.5 ppm) suggests that this process will take place only in sediment systems that are fully anaerobic.
- The combination of these two observations indicates that there is an interval of dissolved oxygen concentration over which **neither** aerobic nor anaerobic PCB transformation processes can occur.

Acknowledgment

This work was supported by a grant from the Packard Foundation as part of the Interdisciplinary Science Program. The project, "Effects of Sediment Biogeochemistry on the Environmental Fate and Persistence of Polychlorinated Biphenyls," was conducted by an interdisciplinary team at Carnegie Mellon University. The authors thank the members of the team: David Dzombak, Sandra Karcher, Gregory Lowry, Kathleen McDonough, Paul Murphy, Jay Rao, Mitchell Small, and Christine Wang for their contributions to this research.