

Report for 2002MD13S: Advancement of Electron Beam Methodologies for Remediation of PCB Containments in Patuxent River and Chesapeake Bay Sediments

- Other Publications:
 - No publication
- Articles in Refereed Scientific Journals:
 - Dainne L. Poster, Mahanaz Chaychian, Pedatsur Neta, Robert E. Huie, Joseph Silverman and Mohamad Al-Shiekhly, 2003, Degradation of PCBs in a Marine Sediment Treated with Ionizing and UV Radiation, Journal of Environment Science and Technology, in press.
- unclassified:
 - No publication

Report Follows

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Electron beam radiolysis. PCB-laden sediment samples were mixed with an aqueous alcohol solution and irradiated with an electron beam under continuous stirring in the absence of oxygen. During this process, some PCB congeners are extracted into the liquid phase and undergo dechlorination within that phase; the rest remain within the sediment and undergo dechlorination either within the solid phase or at the interface. After the irradiation, solvent extracts of PCBs from both media were combined and analyzed. It is not possible to determine the increase in chloride ion concentration in the liquid phase because the sediment is rich in chloride and the fractional change in Cl⁻ concentration upon PCB dechlorination is negligible. Therefore, only the change in PCB concentration was determined. The results for individual PCB congeners indicate that the concentrations of PCBs in electron-irradiated sediment samples decrease as a function of dose (Figure 1). To estimate the initial radiolytic efficiency we calculated the decrease in concentration of each congener after irradiation with 10 kGy, the lowest dose. By assuming that each congener underwent a single dechlorination step, and taking the total dechlorination yield as if all the PCBs were in the liquid phase, we calculate a radiolytic yield (G-value) of $1.3 \times 10^{-11} \text{ mol J}^{-1}$. By comparison with the radiolytic yield of e_{aq}^- in aqueous alcohol solutions (Spinks and Woods, 1990), $2.7 \times 10^{-7} \text{ mol J}^{-1}$, our observed dechlorination yield is lower by four orders of magnitude. One reason is the fact that some of the PCBs remain within the solid phase and do not react with e_{aq}^- formed in the liquid phase. Reaction at the interface is likely not significant with the SRM 1944 sediment particles where the median diameter (dry) is on the order of 135 μm (Certificate of Analysis *SRM 1944*, 1999). Small amounts of water penetrate the channels within the particles and e_{aq}^- produced within these channels probably reacts with PCBs that may be present within the same channels. The lifetime of the e_{aq}^- in our system under electron beam irradiation is several microseconds or less. Therefore, if PCBs are not available in the immediate vicinity of hydrated electrons, the electrons decay by reacting with other compounds or other radicals, including self-reaction. Scavenging of e_{aq}^- by the protons formed upon radiolysis is prevented by the use of the carbonate buffer, which keeps the solution at $\text{pH} > 7$. Other compounds present in the sediment, which may react with e_{aq}^- , are metal ions. If we assume that all metal ions in the sediment, based on the concentration values reported for SRM 1944

(Certificate of Analysis *SRM 1944*, 1999), are extracted into the aqueous phase, we estimate the concentrations of the most abundant ions as follows: $[\text{Zn}^{2+}] = 1.5 \text{ mmol L}^{-1}$, $[\text{Pb}^{2+}] = 0.24 \text{ mmol L}^{-1}$, $[\text{Cr}^{3+}] = 0.77 \text{ mmol L}^{-1}$, and $[\text{Mn}^{2+}] = 1.4 \text{ mmol L}^{-1}$. Since all of these ions react with e_{aq}^- very rapidly (Buxton et al., 1988), and since their concentrations are much higher than the concentrations of PCBs, it is likely that most of the electrons are scavenged by the metal ions. The reduced metal ions formed by these reactions have lower reduction potentials than e_{aq}^- and are less likely to transfer an electron to PCB molecule.

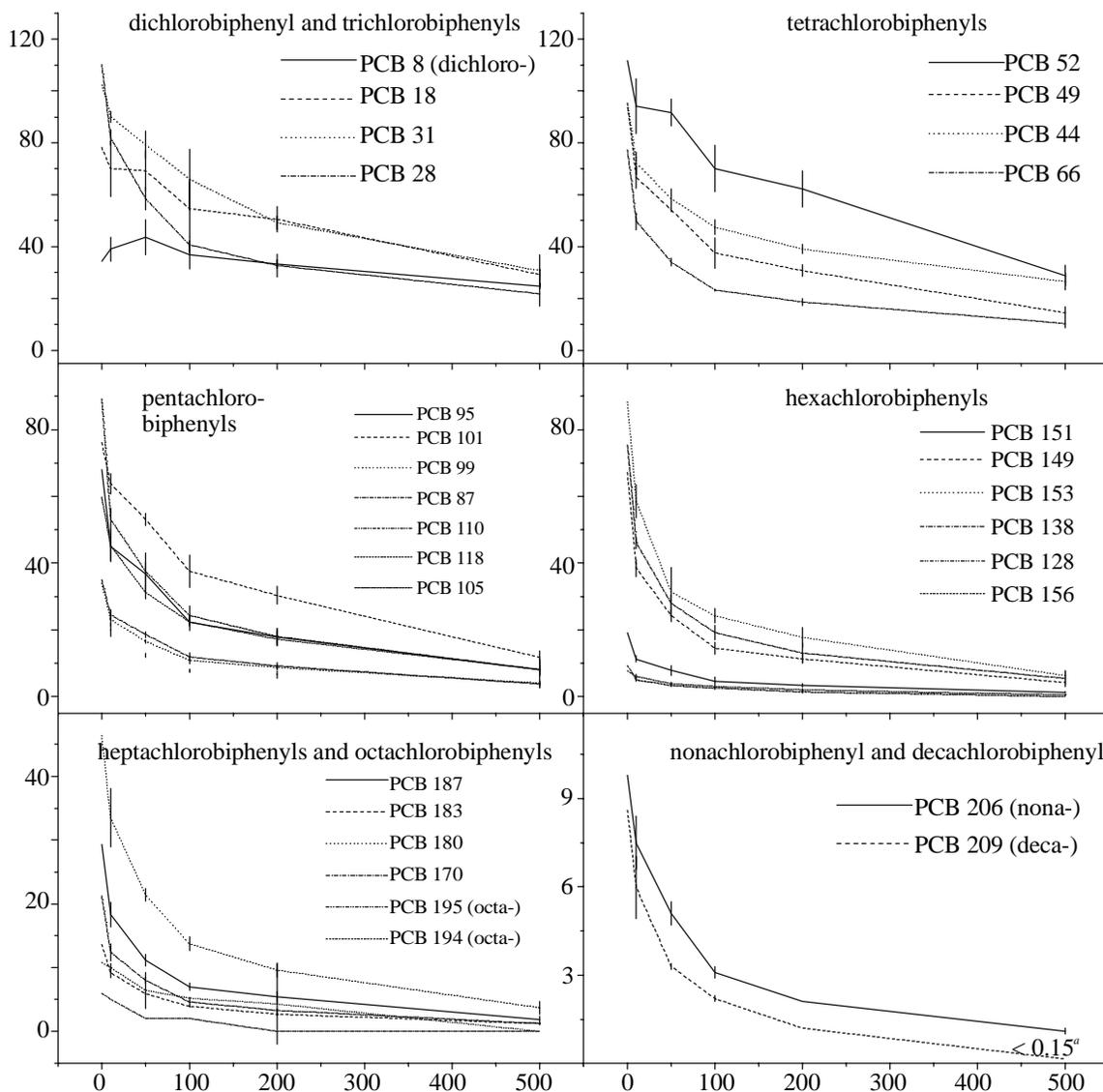


Figure 1. Concentrations (ng g⁻¹) of PCB congeners in electron beam irradiated slurries of SRM 1944 (New York/New Jersey Waterway Sediment) as a function of dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (n=3, represented by an error bar) was calculated. ^aValue is three times the standard deviation of the baseline noise.

Achievements

Our paper "Degradation of PCBs in a Marine Sediment Treated with Ionizing and UV Radiation" was accepted for publication in Environmental Science and Technology on May 21, 03.