

Radiolytic degradation of chlorinated contaminants in marine sediment with food-grade surfactants

Dianne Poster¹, Omer Kantoglu², Mahnaz Chaychian², Pedatsur Neta¹, Robert Huie¹, Joseph Silverman², Mohamad Al-Sheikhly²

¹Chemical Science and Technology Laboratory, National Institute of Standards and Technology

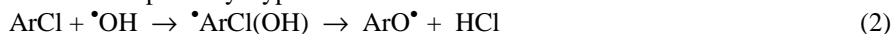
²Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA 20742

Introduction

Chlorinated compounds, such as polychlorinated biphenyls (PCBs), present in waste materials may be effectively degraded when treated with ionizing radiation. This treatment process makes use of a high energy source, such as a linear electron accelerator, to transform PCBs into less- or non-chlorinated species. Dechlorination occurs primarily through indirect effects, meaning the deposition of energy is not directed toward individual PCB molecules. Rather, it is dispersed in the matrix where the compounds reside and via this process the matrix becomes the source of the primary radiation-produced species that initiate the degradation reaction pathways. In aqueous media, where PCB congeners can be solubilized, the primary species formed are radicals, hydrated electrons, and stable compounds¹:



The hydroxyl radical ($\bullet\text{OH}$) is a powerful oxidizing species that reacts with PCBs via addition to the phenyl rings. The $\bullet\text{OH}$ radicals likely add to all of the carbons though a slight selectivity toward a ring that does not contain chlorine atoms may be expected due to steric and electronic effects. When addition occurs at a chlorine-laden carbon, rapid dechlorination is achieved. Various isomeric PCB adduct radicals are intermediate species that undergo rapid elimination of HCl to form phenoxy-type radicals:



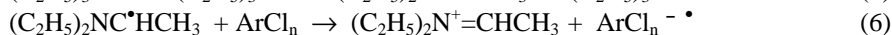
If the treated matrix contains additional organic compounds such as solvents, hydrocarbons, humic material, or inorganic ions such as metal and chloride ions, the $\bullet\text{OH}$ radicals will preferentially react with these materials and the degradation of PCBs by $\bullet\text{OH}$ radicals is not very efficient. This is particularly the case when PCBs are present at much lower concentrations relative to other organic compounds.

In contrast, the hydrated electron (e_{aq}^-) is a strong reducing agent whose reactivity depends on the availability of a suitable vacant orbital and its reactivity is enhanced by electron withdrawing atoms, such as chlorine. Hence, it is preferentially captured by PCB molecules and as a result the carbon-chlorine bond breaks very rapidly:

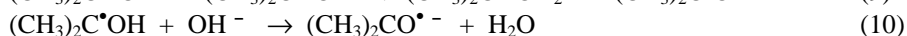
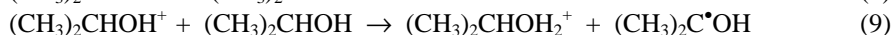
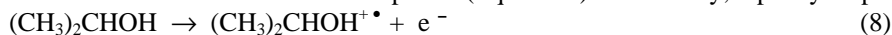


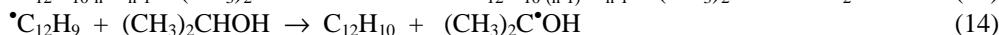
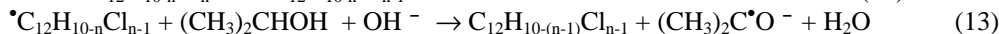
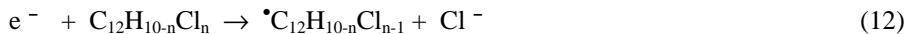
The reductive process (Eq. 3) tends to be the dominant pathway for PCB dechlorination via radiation treatment due to the more selective nature of e_{aq}^- . Hydrated electrons also react very rapidly with oxygen ($e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet-}$) and with the H_3O^+ formed in the radiolysis ($e_{\text{aq}}^- + \text{H}_3\text{O}^+ \rightarrow \text{H}^\bullet + \text{OH}^-$). These reactions will compete with the dechlorination process but are easily prevented by purging the system with nitrogen and by adding alkaline buffers. The addition of a buffer prevents the accumulation of H_3O^+ and also prevents the oxidation of Cl^- ions which would produce atomic chlorine. The latter has the capability to add to phenyl compounds in the irradiated matrix. This would produce PCBs in the material.

Our main objective in the radiation-induced degradation of PCBs resides in increasing the efficiency of reducing methods. We have applied radiation processing to a number of matrices ranging from simple (water/alcohol) to complex (marine sediment) materials as part of a broader program focused on advancing the use of radiation technologies for the treatment of materials contaminated with chlorinated compounds. This work includes elucidating the mechanisms and kinetics of the dechlorination pathways. Effective dechlorination of PCBs in water/alcohol 3, aqueous micellar systems 4, 5, transformer oil 6, 7, and marine sediment 8 has been demonstrated. The majority of this work was conducted in the presence of organic solvents and bases. These additives were deemed necessary to effectively solubilize the PCBs or to enhance the radiolytic processes via their ability to provide radiation-produced radicals that contribute to the dechlorination pathways. For example, in used transformer oil with high concentrations of PCBs ($> 800,000 \mu\text{g/g}$) it was necessary to combine 2-propanol with triethylamine or KOH with the oil to obtain complete dechlorination through enhancement of the reduction processes 7. Upon irradiation of the oil with equal volumes of triethylamine, only partial dechlorination was achieved even at high doses (up to 9000 kGy). Dechlorination ceased around 5500 kGy because the mixture solidified due to formation of solid triethylammonium chloride. Upon irradiation of the triethylamine, solvated electrons are produced along with a triethylamine radical (Eq. 4) that leads to a carbon centered radical and a triethylammonium ion (Eq. 5). Upon the initial dechlorination of the PCBs (Eq. 6-7) the Cl^- eventually combines with the triethylammonium ion formed in Eq. 5 leading to the formation of solid triethylammonium chloride. When the mixture solidifies, reactions 6 and 7 cease 9.

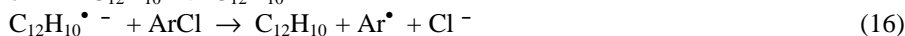


To achieve more complete dechlorination, the oil was diluted with 2-propanol and either triethylamine or KOH. Because the dielectric constant of the 2-propanol is much higher than the transformer oil, its addition to the system increases the solvated electron yield. The alcohol radical produced from radiolysis of 2-propanol (Eq. 8) undergoes a rapid ion-molecule reaction to produce a carbon-centered radical (Eq. 9), which ionizes at high pH (Eq. 10). This radical ion and the electron react with the chlorinated species (Eq. 11-12). Ultimately, biphenyl is produced (Eq. 14):





Additionally, oil contains hydrocarbons, such as biphenyl, that may also react with electrons to form radical anions. PCBs are degraded by attack from these anions, this would be the primary dechlorination pathway if there was not an additive in the oil:



In contrast to the radiation chemistry of aqueous solutions and oils, the radiation chemistry of PCBs in complex, organic-rich matrices, such as marine sediment, is in its infancy. We recently investigated the radiolytic dechlorination of PCBs in marine sediment⁸. The concentration sum of 29 PCB congeners decreased by 83 % at a dose of 500 kGy. Examination of gas chromatograms from an electron capture detector of an irradiated sediment also revealed the degradation of 4,4'-DDE (Figure 1). As an added benefit, it is likely that transition metal ions, including lead and mercury, were likely reduced to lower oxidation states that led to insoluble metals^{4, 10}. The complexity of sediments makes it difficult to elucidate the mechanisms and kinetics associated with the dechlorination processes in the same detail as that for water^{3, 5, 10} and oil^{7, 9, 11}. The sediment system is a non-homogeneous system. A portion of the PCBs will be associated with sediment particles (such as SiO₂) and a portion will be in the aqueous phase. Upon irradiation, aqueous electrons from the radiolysis of water are produced as well as Compton electrons from irradiated solid particles. Each type of electron may react with PCBs. The following equation describes the production and reactions of the aqueous electrons:

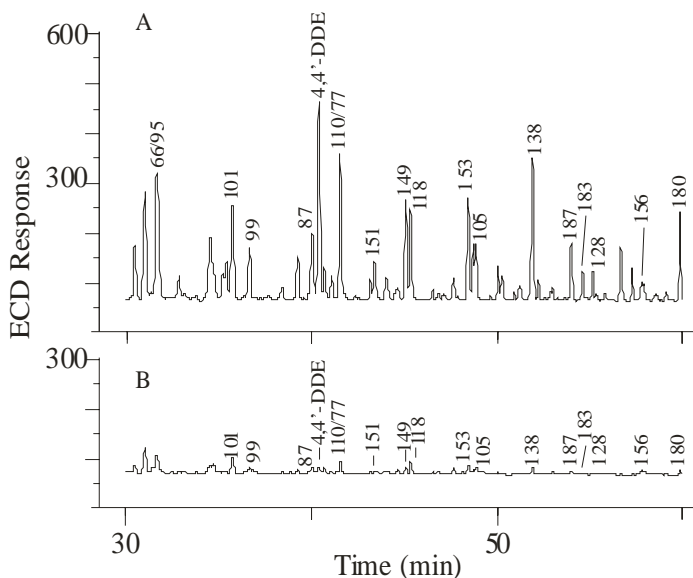


Figure 1. GC-ECD chromatograms of an (A) unirradiated and (B) irradiated (500 kGy) slurry of SRM 1944 (New York/New Jersey Waterway Sediment) with 2-propanol and aqueous buffer.

where: \dot{D} = dose rate, ρ = density, D = diffusion coefficient, ∇^2 = Laplacian operator, $[M^{n+}]$ = ions concentration (metal and other ions); $[P]$ = contaminant concentration, and $[S]$ = surfactant concentration. In the sediment/water/alcohol system, the degradation mechanisms are likely the

$$\frac{-\partial[e_{aq}^-]}{\partial t} = G(e_{aq}^-)\dot{D}\rho - D\nabla^2[e_{aq}^-] - k_1[e_{aq}^-][PCB_{aq}^s] - k_2[e_{aq}^-][PCB_{solid}^s] - k_3[e_{aq}^-][O_2] - k_4[e_{aq}^-][M^{n+}] - k_5[e_{aq}^-][P] - k_6[e_{aq}^-][S]$$

reductive processes described above whereas $\cdot\text{OH}$ is expected to be scavenged by the alcohol and other organic compounds in the sediment. PCBs that remain in association with or within (i.e., non-exchangeable with the aqueous phase) the sediment phase may undergo dechlorination by electrons that may be formed at particle sites or at the sediment-water interface. However, the yield of such electrons is expected to be low and, because of their limited mobility, they are only effective when produced in the vicinity of a PCB molecule. The deposition of ionizing energy directly onto a PCB molecule can also lead to dechlorination, though this process is also likely limited¹² since ionizing energy is indiscriminately absorbed by the entire medium. Despite the favorable results observed in our sediment study, the approach is likely limited in terms of a practical application. A combination of dredging and treatment with expensive and toxic additives, such as an alcohol, would be considered only in special cases. Some revisions may justify greater practical interest. The use of an environmentally friendly additive, such as a food-grade surfactant, could make radiation processing of sediments into a competitive technology. Surfactants have been used to extract PCB-laden oil from soil¹³⁻¹⁶, and to wash PCBs from soils for biodegradation¹⁷ or photolytic¹⁸ processing. We have demonstrated the use of a non-ionic surfactant for the complete dechlorination of selected PCBs in water via radiation processing⁵. We hypothesize that non-ionic surfactants may enhance the dechlorination of solubilized marine sediment chlorinated contaminants. Edible, food-grade surfactants (Figure 2) may be viable candidates. These increase the aqueous solubility of chlorinated solvents, such as tetrachloroethylene¹⁹ and may be effective for subsurface remediation of chlorinated compounds²⁰. Our recent radiation processing efforts are focused on the use of these food-grade surfactants as additives to marine sediment. We expect that the surfactants will enhance the solubility of chlorinated species in the liquid phase and may provide high yields of radiation-induced reactive species that will increase the efficiency of the dechlorination pathways. This work is on-going and is described below. The effect of sonication as part of the radiation processing train is also under investigation.

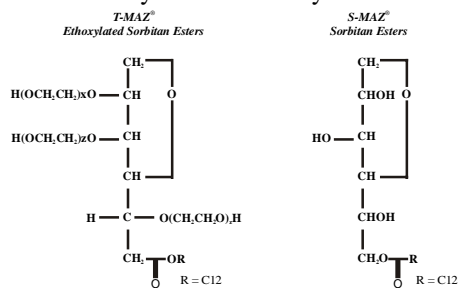


Figure 2. Food-grade surfactants.

Methods and Materials

Samples of SRM 1944 (Figure 1), a marine sediment reference material that is well-characterized for PCBs and pesticides, were mixed (about 6 g) with 60 mL of 10 mM (1 g/L) Na_2CO_3 and surfactant (single or in combination). The following surfactants were used: T-Maz 20, T-Maz 60, S-Maz 20, and S-Maz 90. Samples contained 0.3 g or 3 g of either T-Maz 20 or T-Maz 60. Additional samples contained 0.3 g of each of two surfactants: T-Maz 20/S-Maz 20, T-Maz 20/S-Maz 90, T-Maz 60/S-Maz 20, and T-Maz 60/S-Maz 90. Selected slurries were sonicated for 3 h prior to radiation treatment to possibly enhance dissolution of PCBs in the liquid phase. A linear electron accelerator was the source of ionizing radiation for some or all of the following doses: 0 (no dose), 50, 100, 250, 500, and 750 kGy. For the determination of the concentrations of PCBs, the liquid portion of each sediment sample was filtered using clean glass fiber filters (sonicated in methylene chloride and dried [100 ° C]). The filtrate of each sample was prepared for gas chromatography and either mass spectrometry (MS) or electron capture detection (ECD) by liquid-liquid partitioning with hexane and acetone. The polar layer was washed three times with hexane, combined, and concentrated (about 0.5 mL) using an automatic N_2 evaporation system. The

extracts were passed through silica SPE cartridges with 15 mL of 10% methylene chloride in hexane (v/v), concentrated, and transferred to GC vials. The sediment portion of each sample was dried (mortar and pestle) with clean Na_2SO_4 and then pressurized fluid extracted with methylene chloride. The extracts were concentrated, passed through silica SPE cartridges, concentrated, and transferred to GC vials. After examination of initial samples by GC/MS, it was deemed necessary to further clean-up the samples due to residual, more-volatile compounds remaining in the solvent extracts. Samples were fractionated on a semi-preparative amino-propyl liquid chromatographic column. This process isolates PCBs and lower polarity pesticides from the more polar pesticides. Eluants were concentrated and transferred to GC vials. Prior to

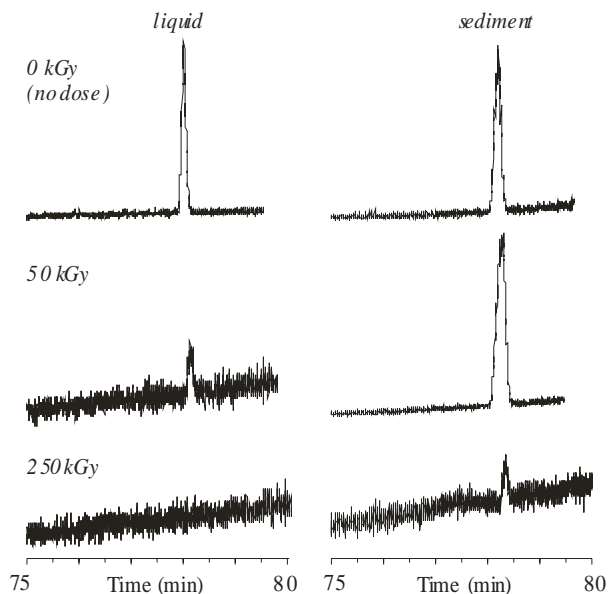


Figure 3. GC/MS ion traces of decachlorobiphenyl in slurries of SRM 1944 with 0.3 g surfactant and aqueous buffer.

processing, a weighed aliquot of a gravimetrically prepared internal standard solution of a mixture of octachloronaphthalene, 4,4-DDT- d_8 and biphenyl- d_{10} or ^{13}C -labeled PCBs and pesticides and biphenyl- d_{10} was added to each sample. Activated copper removed sulfur. Liquid-liquid partitioning control samples consisted of aliquots of SRM 1493 (a PCB solution). Sediment control samples consisted of SRM 1944 as received. Gravimetrically prepared solutions of SRMs 2261, 2262, 2274, 2275, and biphenyl were used for quantification purposes. GC/MS (electron impact, select ion mode) and GC-ECD analyses made use of a retention gap coupled to a relatively non-polar capillary column (DB-XLB) that was configured in the cool on-column injection mode.

Results and Discussion

The radiolytic decay of PCBs in marine sediment in the presence of surfactants is evident in the initial samples examined. Figure 3 provides GC/MS ion chromatograms for decachlorobiphenyl in the liquid and sediment phase from a mixture of SRM 1944 with T-Maz 20. The GC/MS response is diminished in both phases at 250 kGy relative to the mixture that was not irradiated (0 kGy). The compound is completely eliminated in the liquid phase. Similar results were observed with 3 g T-Maz 20. Examination of additional PCBs is underway along with the determination of the concentrations of PCBs in sediment with surfactant mixtures. Also, due to the complexity of these systems, we are endeavouring to establish the bounds of reproducibility.

Acknowledgements

The authors thank Anna Kalema for assistance in the laboratory and Allen Davis, Department of Civil and Environmental Engineering, University of Maryland, for valuable discussions. Support from the International Atomic Energy Agency for Omer Kantoglu through project RER/0/021, Education and Training in Nuclear Sciences and Technology, and from the Maryland Water

Resources Center and the National Science Foundation is appreciated. Certain commercial equipment or materials are identified to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References

- 1 Spinks, J.W.T. and Woods, R.J. (1990) *An Introduction to Radiation Chemistry*, 3rd ed., John Wiley and Sons, New York.
- 2 Buxton, G.V., Greenstock, C.L., Helman, W.P., and Ross, A.B. (1988) *J. Phys. Chem. Ref. Data* 17, 513.
- 3 Al-Sheikhly, M., Silverman, J., Neta, P., and Karam, L. (1997) *Environ. Sci. Technol.* 31, 2477.
- 4 Schmelling, D., Poster, D., Chaychian, M., Neta, P., McLaughlin, W., Silverman, J., and Al-Sheikhly, M. (1998) *Radiat. Phys. Chem.* 52, 371.
- 5 Schmelling, D.C., Poster, D.L., Chaychian, M., Neta, P., Silverman, J., and Al-Sheikhly, M. (1998) *Environ. Sci. Technol.* 32, 270.
- 6 Chaychian, M., Silverman, J., Al-Sheikhly, M., Poster, D.L., and Neta, P. (1999) *Environ. Sci. Technol.* 33, 2461.
- 7 Jones, C.G., Silverman, J., Al-Sheikhly, M., Neta, P., and Poster, D.L. (2003) *Environ. Sci. Technol.* 37, 5773.
- 8 Poster, D.L., Chaychian, M., Neta, P., Huie, R.E., Silverman, J., and Al-Sheikhly, M. (2003) *Environ. Sci. Technol.* 37, 3808.
- 9 Jones, C.G. (2001) Ph.D. Thesis, Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD.
- 10 Chaychian, M., Al-Sheikhly, M., Silverman, J., and McLaughlin, W.L. (1998) *Radiat. Phys. Chem.* 53, 145.
- 11 Chaychian, M., Jones, C.G., Poster, D.L., Silverman, J., Neta, P., Huie, R., and Al-Sheikhly, M. (2002) *Radiat. Phys. Chem.* 65, 473.
- 12 Gray, K.A. and Hilarides, R.J. (1995) *Radiat. Phys. Chem.* 46, 1081.
- 13 Abdul, A.S. and Ang, C.C. (1994) *Ground Water* 32, 727.
- 14 Abdul, A.S., Gibson, T.L., Ang, C.C., Smith, J.C., and Sobczynski, R.E. (1992) *Ground Water* 30, 219.
- 15 Abdul, A.S. and Gibson, T.L. (1991) *Environ. Sci. Technol.* 25, 665.
- 16 Scholz, R. and Milanowski, J. (1984) *J. Hazard. Mater.* 9, 241.
- 17 Billingsley, K.A., Backus, S.M., Wilson, S., Singh, A., and Ward, O.P. (2002) *Biotechnology Letters* 24, 1827.
- 18 Chu, W., Jafvert, C.T., Diehl, C.A., Marley, K., and Larson, R.A. (1998) *Environ. Sci. Technol.* 32, 1989.
- 19 Shiau, B.J., Sabatini, D.A., and Harwell, J.H. (1994) *Ground Water* 32, 561.
- 20 Shiau, B.J., Sabatini, D.A., and Harwell, J.H. (1995) *Environ. Sci. Technol.* 29, 2929.